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THE RADIOCARBON INTRACAVITY OPTOGALVANIC SPECTROSCOPY SETUP AT UPPSALA

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ABSTRACT. Accelerator Mass Spectrometry (AMS) is by far the predominant technology deployed for radiocarbon tracer studies. Applications are widespread from archaeology to biological, environmental, and pharmaceutical sciences. In spite of its excellent performance AMS is expensive and complicated to operate. Consequently, alternative detection techniques for radiocarbon are of great interest, with the vision of a compact, user-friendly and inexpensive analytical method. Here we report on the use of intra-cavity optogalvanic spectroscopy (ICOGS) for measurements of the $^{14}\text{C}/^{12}\text{C}$ ratio. This new detection technique was developed by Murnick and co-workers (Murnick et al. 2008). In the infra-red (IR) region, CO_2 molecules have strong absorption coefficients. The IR-absorption lines are narrow in linewidth and shifted for different carbon isotopes. These properties can potentially be exploited to detect $^{14}\text{CO}_2$, $^{13}\text{CO}_2$ or $^{12}\text{CO}_2$ molecules unambiguously. In ICOGS, the sample is introduced as CO_2 gas, eliminating the graphitization step which is required in most AMS labs. In this paper, the status of the ICOGS setup in Uppsala is presented. The system is operational but not yet fully developed. Data are presented for initial results which illustrate the dependence of the optogalvanic signal on various parameters, such as background and plasma induced changes in the sample gas composition.

INTRODUCTION

Isotope-ratio measurements provide valuable information in a number of pure and applied disciplines of science. Due to the extremely low abundance of ^{14}C in most samples, Accelerator Mass Spectrometry (AMS) has been the main choice for such measurements, replacing the traditional decay counting techniques. AMS has been used to perform precise isotope ratio measurements with sensitivities in the $10^{15}:1$ range for carbon, resulting in a number of applications in diverse disciplines such as archaeology and environmental sciences. A growing segment in AMS is in the biomedical field where ^{14}C labeled molecules are used as

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a biological marker in, for example, pharmaceutical drugs. The biological applications have pushed the sensitivity limit of quantification down to 120 zmol ($1 \text{ zmol} = 10^{-21} \text{ mol}$) in absolute sample amount (Salehpour et al. 2008). A noteworthy application of AMS in the pharmaceutical research and development sector is Microdosing (Lappin and Garner 2003), which is based on administering very small doses of drugs below 100 μg directly to humans. The increased interest in such new applications for AMS has prompted development of alternative techniques, partly because AMS has some major limitations, e.g., the high capital and running costs as well as the complexity of operating a particle accelerator. Furthermore, AMS suffers from limitations in the minimum sample size, which has implications for a number of applications with limited sample amounts. Any new technique must be able to provide a comparable sensitivity and sample size to that which is possible with AMS, in order to become an alternative in these new fields. Furthermore, a less destructive method than AMS is of greater interest.

New developments in this direction are based on laser spectroscopy technology and have the potential to provide a low-cost and easy-to-operate table-top experimental setup. In recent years, two new laser based techniques have been reported; Intracavity Optogalvanic Spectroscopy (ICOGS) (Murnick et al. 2008) and Cavity Ring Down (CRD) spectroscopy (Galli et al. 2011). Both these techniques are based on high resolution, ultrasensitive infrared absorption spectroscopy. The sample is oxidized to CO_2 and the isotopic species of the gas can be distinguished from the shift in the infrared absorption spectra due to the difference in the mass of the carbon atoms (Labrie and Reid 1981). These techniques require the use of highly stable, single frequency lasers. Unlike AMS, the laser-based measurement techniques do not destroy the CO_2 sample, so that it can be stored and used in repetitive measurements.

ICOGS is based on the optogalvanic (OG) effect. The interaction of the incident laser with atoms or molecules present in a glow discharge (plasma) induces changes in the electrical properties (impedance) of the plasma which can be measured electrically. The measured impedance change is proportional to the number of interacting molecules but also will depend on the plasma parameters, e.g., pressure, as well as the laser intensity and gas composition in the discharge (Ilkmen 2009).

In ICOGS, the plasma cell containing the sample, here referred to as the sample cell, is placed inside the laser cavity (Murnick et al. 2008), rather than outside the laser as it is in the conventional absorption method (Murnick and Peer, 1994). In the intracavity experiment, two stabilized, single frequency lasers, with the active lasing media being $^{12}\text{CO}_2$ and $^{14}\text{CO}_2$, respectively, were used to excite the plasma in the sample cell. High sensitivity was reported down to isotope ratios in the 10^{-13} range. However, the technique suffers from problems with calibration over a wide $^{14}\text{CO}_2$ concentration range (Ilkmen 2009) as well as a large background.

Galli et al. have recently reported another technique in which saturated-absorption CRD spectroscopy is used to measure the $^{14}\text{C}/^{12}\text{C}$ ratio (Galli et al. 2011). In CRD, the gas sample

cell is placed between two highly reflective mirrors which form a Fabry-Perot cavity. The infrared light from a laser, tuned to a specific ro-vibrational transition of CO₂, enters the cavity and will undergo multiple reflections between the cavity mirrors. The high reflectivity of the mirrors ensures that photons can make many round trips resulting in a long effective path, and consequently an ultrasensitive absorption measurement. The authors report a linear response in concentration down to 43 parts per quadrillion, i.e., 43:10¹⁵ (Galli et al. 2011). However, this method requires a rather complicated laser system to obtain stable single frequency operation at 4.5 μm. Furthermore, a relatively large sample size of about 70 mg is required, which may limit its applications.

In this article, we report on the progress made in the development of an ultrasensitive ¹⁴C:¹²C detection system using ICOGS at Uppsala University. Details of the experimental setup are presented including methods of detection and control. We discuss the potentials and limitations of this technique and possible sources of the background in the experiment and propose methods of improvement.

METHODS

The experimental setup

A schematic description of the experimental setup can be seen in figure 1. The foundation of the setup is the three CO₂ lasers, with lasing frequencies stemming from the ro-vibrational transitions of ¹²C¹⁶O₂, ¹³C¹⁶O₂, and ¹⁴C¹⁶O₂. Here, the ¹²C¹⁶O₂ laser was a model Merit-SL, and the ¹³C¹⁶O₂ laser was a model L20-SZ, both single longitudinal mode lasers from Access Laser Co (Everett, WA, USA). The beams from the three lasers were power modulated using three optical choppers with orthogonal chopping frequencies (Figure 1 (a)). This enabled separation of the OG signal, induced by the different lasers, in the frequency domain. The ¹⁴C¹⁶O₂ laser was a single longitudinal mode laser, custom made by LTG Lasertech Group Inc. (Concord, ON, Canada). The laser cavity of the ¹⁴CO₂ laser contained a grating on one end and an output coupler with piezo position control on the other end. The piezo positioning controlled the length of cavity and consequently the laser wavelength (Figure 1 (a)), with a maximum stroke of ΔL=7 μm. The laser had a maximum output power of about 11 W at 11.8 μm. The length of the laser cavity was extended to 1.7 m to accommodate the intracavity sample cell and an internal optical chopper. The output power was reduced by about 20% by the introduction of the sample cell, mostly due to losses in the Brewster windows, and by 55% by the chopper, due to the power modulation of the laser beam.

The laser outputs were monitored in both a CO₂ Laser Spectrum Analyzer from Macken Instruments Inc. (Santa Rosa, CA, USA), and in two power meters – either a conventional thermopile Vega Laser Power and Energy Meter from Ophir Optronics Solutions Ltd. (Jerusalem, Israel) or a discrete pyroelectric sensor Model QS-I-Test from GenTech-EO (Quebec, QC, Canada). Here, the Ophir power meter was used for measuring the laser output power *in situ*, whereas the GenTech power meter with a faster reaction time was used for, e.g., timing signals.

Figure 1 Schematic description of the optics (a) and electronics (b) of the experimental setup. M denotes a steering mirror, O/C output coupler, PM power meter, B/S beam splitter, C chopper, S/A spectrum analyzer, DAQ data acquisition unit, and D/A differential amplifier.

The setup contained two plasma cells; 1) a reference cell containing 0.5% ¹⁴CO₂, 4.5% ¹²CO₂ and 95% air at a total pressure of 467 Pa, and 2) a sample cell, which could be filled with an arbitrary gas mix at pressures down to tens of Pa (Figure 1 (a)). In the reference cell, air was used as a buffer gas to reduce the dissociation of CO₂ into CO in the plasma. The sample cell had a cross beam geometry (Figure 2), allowing for the ¹²CO₂ and the ¹³CO₂ laser beams to be passed through the cell transversely to the ¹⁴CO₂ beam (Figure 1 (a)). In the direction of the ¹⁴CO₂ beam, the cell was equipped with Brewster angle ZnSe windows to minimize the power loss in the laser. Plasma in each cell was excited by RF power coupled capacitively into the cell from an RF oscillator operating at 10 MHz or 40 MHz and ~5 W (Figure 2). In accordance with the design by Murnick et al., the RF oscillators consisted of a tunable oscillating circuit and a transistor (May and May, 1986). The OG signal manifested itself as a change in the plasma impedance and could be quantified by measuring the amplitude of the RF wave in the oscillator. The OG signal was amplified by a custom made differential amplifier, with a variable gain of 40 dB, and sampled by a 4-channel BNC-2110 data acquisition (DAQ) unit from National Instruments Corp. (Austin, TX, USA). Apart from the OG signals from the sample and reference cells, the output of the GenTech power meter was recorded by the DAQ, whereas the thermopile power meter was connected to the computer directly via a USB interface.

Figure 2 Photograph of the sample cell with an ignited plasma. The direction of the laser beams are indicated in the picture. Copper tape forms the electrodes for the capacitive coupled plasma.

The piezoelectric tuning of the cavity length of the $^{14}\text{CO}_2$ laser was controlled by the computer via a RS-232 interface. This control was based on the feedback from either one of the power meters or the reference cell OG signal. The $^{14}\text{CO}_2$ laser could be either scanned through its gain profile or locked at the maximum intensity of a particular laser line.

The inputs from the DAQ and the output to the piezo control were processed and controlled by tailor made software written in Lab View 2010 (10.0, National Instruments Inc., Austin, TX, USA). The DAQ had a sample rate of 1 kHz, and the software transformed series of 1000 time sample (Figure 3 (a)), into the frequency domain using Fourier transformation, .i.e. each transformation consisted of 1000 samples over a total of 1 s. The OG signal was defined as the integral of the peak corresponding to the particular chopping frequency, in an interval given by a variable base parameter, typically set to about 10% of the peak amplitude (Figure 3 (b)). Consequently, the sample rate of the OG signal was 1 Hz. In the initial stages of the project, these parameters were varied to find the optimum settings. It was found that changing the sample and transformation rates did not have a strong influence on the signal to noise ratio, and neither did the base parameter, as long as it clearly exceeded the noise floor. The data in figure 3 was measured with the sample cell and the $^{12}\text{CO}_2$ laser.

Figure 3 Typical time profile of the OG response of the plasma (a), with the upper curve showing the OG time response and the lower curve showing the power of the $^{12}\text{CO}_2$ laser. To the right is the Fourier transform of the OG time sequence (b), where the cross-hatched area under the peak indicates the integral corresponding to the OG signal.

Measurement modes

There are two alternative approaches to the CO₂ sample handling in ICOGS:

- 1) The static mode (Batch mode) where the gas is confined to a well defined volume. The advantage of this method is twofold: a) The sample can be recovered after use and b) The amount of sample needed is small, facilitating analysis of μg samples.
- 2) The dynamic mode (Flow mode), where the sample is continuously exchanged and renewed. The advantages of this method include continuity in plasma operation for better signal stability, and consequently better signal reproducibility.

In the study presented here we have worked solely with the static mode as the perceived advantages were deemed important for our application, namely small biological samples in the microgram carbon range. Furthermore, the water content in the analyzed gases was removed in a -80°C cold trap as this has a detrimental effect on the reproducibility of the OG signal (Murnick, private communications).

Measurements

In the standard measurement procedure a laser transition was firstly chosen by tuning of the grating using micrometer screws. Secondly the lasing frequency was locked by tuning of the cavity length to the center of the transition. This was done by using the piezo controller with feedback from the fast power meter or the reference cell. The cavity length was then stable over time scales up to one hour. The OG response of the sample and reference cells could be monitored and the OG signal measured.

Alternatively, the piezo controlled output coupler was used to vary the lasing frequency around the center of a laser transition, to study the spectral shape of the laser gain profile, and/or the OG response of the CO₂ molecules in the reference and sample cells. The frequency was typically varied about ± 54 MHz, corresponding to a wavelength shift of around ± 25 pm around the peak. The maximum scan width of the output coupler corresponded to a variation of the laser cavity of about ± 33 pm (± 72 MHz). A measurement series consisted of a number of sweeps going from maximum to minimum frequency in steps of 0.9 MHz. At each step the amplified signal from the RF oscillator was sampled by the DAQ for 1 s. The sampled time sequence was then transformed into the frequency domain and the OG signal was calculated as described above. To improve the signal to noise ratio, the final result was taken as the mean of multiple sweeps. In this paper, only results using the ¹²CO₂ and ¹⁴CO₂ lasers are presented.

Residual gas analysis

Apart from the OG measurements, a residual gas analyser (RGA) – a Model XT100 from Extorr Inc. (New Kensington, PA, USA) – was used for analysing the gas chemistry of the CO₂ plasma. The RGA was a compact quadrupole mass spectrometer with integrated Pirani and ion gauges. It consisted of a probe (173 mm long and 35 mm in diameter) that was inserted into the vacuum system. Attached to the probe was a communications and control unit (CCU) which contained the electronics for the probe control and computer communications. The device came with its own software for mass spectrum analysis and had a resolution of less than 1 amu. The RGA experiments were performed offline in a separate setup. Here, a second sample cell, identical to the one used in the ICOGS measurements, was connected to the vacuum system where the RGA probe was inserted. In order to connect the sample cell, which operated around 100 Pa, to the RGA, which operated at pressures below 10⁻⁴ Pa, a fused silica capillary column from Supleco Inc. (Bellefonte, PA, USA), intended for use in gas chromatography, was used. The capillary column provided a continuous and very small gas flow between the two parts of the system. The inner diameter of the column was 0.32 mm and the length of the column was 40 cm. The RGA was pumped by a turbo pump (65 l/s), backed by a membrane vacuum pump, where the latter also was used to evacuate the sample cell. The time-scale of the gas transfer from the sample cell to the RGA was less than 1 s.

Simulations

An important concept in order to understand the response of a CO₂ plasma to resonant irradiation is the spectral line shape of the transitions between different ro-vibrational states in general, and the broadening of the line profile, due to, e.g., collisions in the gas, in particular. ICOGS of CO₂ utilizes the transition between rotational quantum levels in the first excited vibrational level of the asymmetric stretch, denoted (00⁰1), and corresponding rotational quantum levels in the first excited vibrational level of the symmetric stretch mode, denoted (10⁰0), in the molecules, i.e., the same transitions that are utilized in an CO₂ laser. For these transitions the selection rule $\Delta J = \pm 1$ applies. Here, J is the rotational quantum number. The transitions can be divided into two branches – the R and P branch – where a transition from level J to $J+1$ corresponds to the P branch and a transition from J to $J-1$ corresponds to the R branch..

In an ideal case, the spectral lines are distinct and well separated, but in reality, two effects in particular will cause broadening of the lines; namely collision and Doppler broadening (Silfvast 1996). Collision broadening is caused by the reduction of the lifetime of the excited states due to collisions between the molecules. The collision broadening of the spectral line, S_c , at frequency f , is homogeneous around the center frequency f_0 , and can be described by a Lorentzian distribution (Demtröder, 1981):

$$S_C(f) = \frac{\alpha_L}{\pi} \cdot \frac{1}{(f-f_0)^2 + \alpha_L^2} \quad (1)$$

where α_L is the half width at half maximum of the broadening and is proportional to the collision rate. Assuming ideal gas conditions for a plasma consisting of pure CO₂, α_L is given by (Silfvast 1996):

$$\alpha_L = \frac{p\sigma}{2\pi k_B T} \sqrt{\frac{8k_B T}{\pi m}} \quad (2)$$

where p is the pressure, T is the temperature, m is the mass of the CO₂ molecule, k_B is Boltzmann's constant, and σ is the collision cross section between two CO₂ molecules. Here, the temperature was estimated to $T=340$ K from measurements on a similar plasma (Deju et al. 1968) and the collision cross section to $\sigma=1.57 \cdot 10^{-18}$ m² (Meyer et al. 1993). For a plasma with several species, inter-species collisions have to be accounted for, making the equations somewhat more complicated (Ilkmen 2009).

The Doppler broadening stems from the distribution of velocities of the molecules in the inertial system of the system (Silfvast 1996). For each velocity, this will cause a Doppler shift, in turn causing an inhomogeneous broadening of the spectral line peak around f_0 which can be described by $S_D(f)$, a Gaussian distribution (Ilkmen 2009):

$$S_D(f) = \frac{1}{\alpha_G} \cdot \sqrt{\frac{4\ln(2)}{\pi}} \cdot \exp \left[-4\ln(2) \cdot \frac{(f-f_0)^2}{\alpha_G^2} \right] \quad (3)$$

where α_G is the full width at half maximum of the broadening given by:

$$\alpha_G = \frac{2f_0}{c} \sqrt{\frac{2\ln(2)k_B T}{m}} \quad (4)$$

and c is the speed of light. The actual line profile will be given by a combination of the two effects known as the Voigt profile. Mathematically, the Voigt profile, S_V , is given by the convolution of the Gaussian and Lorentzian distributions which is given by the integral (Huang and Yung 2004):

$$S_V(f - f_0) = \int_{-\infty}^{\infty} S_D(f' - f_0) S_C(f - f') df' \quad (5)$$

which can be evaluated as the real part of the complex error function $w(z)$ given by:

$$S_V(f) = \frac{1}{\alpha_G} \cdot \sqrt{\frac{4\ln(2)}{\pi}} \cdot \text{Re} \left[w \left(\frac{\sqrt{4\ln(2)}}{\alpha_G} \cdot [(f - f_0) + i\alpha_L] \right) \right] \quad (6)$$

A major concern in ICOGS is distinguishing the ¹⁴CO₂ signal from the background which is primarily stemming from the tail of the collision broadened peaks of nearby ¹²CO₂ and ¹³CO₂

lines. It has been claimed that when estimating the background, it is sufficient to include only a few peaks in the closest vicinity of the $^{14}\text{CO}_2$ line that is being studied (Murnick et al. 2008, Ilkmen 2009). In order to investigate this further, a Matlab (R2010a) script simulating the spectrum of all the peaks of the transitions P(2)-P(100) and R(0)-R(58) for $^{12}\text{C}^{16}\text{O}_2$, $^{13}\text{C}^{16}\text{O}_2$, and $^{14}\text{C}^{16}\text{O}_2$ between 10-13 μm was constructed. In order to do so, the peaks had to be scaled, firstly due to the population densities at different energy levels, and secondly due to the relative abundance of ^{12}C , ^{13}C , and ^{14}C . The population density of the different rotational levels, N , was assumed to follow a Boltzmann distribution:

$$N(J) \propto (2J + 1) \exp \left[-\frac{hcBJ(J+1)}{k_B T} \right] \quad (7)$$

where h is Planck's constant, and $B=39 \text{ m}^{-1}$ is the rotational constant of CO_2 (Chedin 1975). Tabulated data (Bradley et al. 1986) was used in order to translate the ro-vibration transitions P(2)-P(60) and R(0)-R(58) into wavelengths. For the transitions P(62)-P(100) there were only tabulated data for a few lines (Ilkmen 2009). Instead, the positions of P(62)-P(100) were extrapolated from the data for P(2)-P(60) using a quadratic polynomial fit. This approach caused a shift of the higher P-lines of about 2 nm. However, this shift was deemed insignificant for the investigations of this study, since the tail of the Lorentzian is not wavelength sensitive.

The relative abundance of the different carbon isotopes, along with the pressure and temperature, could be set arbitrarily in the script, making it a powerful tool in investigating the background over the whole spectrum or at specific P-lines, for different samples, and pressures.

RESULTS AND DISCUSSION

One of the key features of the ICOGS method is the unambiguous detection of ^{14}C , ^{13}C and ^{12}C . As the sensitivity range for $^{14}\text{C}/^{12}\text{C}$ ratios is expected to be as low as 10^{-15} and extend orders of magnitude to higher isotopic ratios, a number of issues become important. These include various sources of noise and background, the linearity and dynamic range of the OG signal as well as reproducibility. Here, we present the data obtained so far, focusing on some of these issues.

Spectral absorption

In order to achieve the extreme sensitivity required for unambiguous detection of ^{14}C , it is crucial to optimize the signal to background ratio of the OG signal – the background stemming from other carbon isotopes as well as other chemical species in the plasma. This can only be accomplished by a spectroscopic system with a maximum selectivity in terms of which ro-vibrational transitions that are utilized in the detection, since different transitions will have different signal to background ratios depending on their position in the spectrum (Ilkmen, 2009). Ideally, only the transition with the best signal to background ratio should be studied,

using a laser with a linewidth comparable to the absorption width of the transition. Consequently it is imperative firstly, to use a single frequency laser with $\Delta\lambda/\lambda$ below 10^{-5} , and secondly, that the detected species should have spectral distribution corresponding to that of the laser line. The first study aimed at demonstrating these issues. Figures 4 (a) and (b) show the laser power and OG signal measured as a function of the piezoelectric actuator's applied voltage (proportional to change in wavelength) for $^{12}\text{CO}_2$ and $^{14}\text{CO}_2$, respectively. The total scan range corresponds to 165 MHz (63 pm) at $\lambda=10.6\text{ }\mu\text{m}$ for $^{12}\text{CO}_2$ and 108 MHz (50 pm) at $\lambda=11.8\text{ }\mu\text{m}$ for $^{14}\text{CO}_2$. The data shows that the OG signal has a maximum that coincides with the laser power maximum for both isotopes. Since the laser power varies during the wavelength scan, the OG signal needs to be normalized (scaled) in order to get the correct absorption intensity, by dividing the OG signal with the measured laser power from one of the power meters or from the reference cell. This is shown for $^{14}\text{CO}_2$ in figure 4 (b). As will be presented in the Simulations section, background sources have non-symmetric or flat spectral shapes, depending on the source of the background. In contrast, an OG signal closely resembling the laser line profile is a strong evidence for a true ^{14}C signal. Equivalent measurements to figure 4 (a) and (b), with the sample cell filled with pure nitrogen, shows a flat OG signal that is independent of wavelength.

Figure 4 Spectral shape of the P(20) line of $^{12}\text{C}^{16}\text{O}_2$ (a) measured in the sample cell at $p=80\text{ Pa}$ with a mix of 10% CO_2 in 90% N_2 . The OG signal (solid line) was measured during a single piezo scan. The laser power (dashed line) is shown as a reference. Similarly, the spectral shape of the P(20) line of $^{14}\text{C}^{16}\text{O}_2$ (b) was measured in the reference cell at $p=467\text{ Pa}$ with a mix of 5% CO_2 in 95% air and a $^{14}\text{C}/^{12}\text{C}$ ratio of $\sim 10\%$. Here, the curves represent an average over 57 piezo scans. The dash-dotted line shows the OG signal scaled by the laser power.

In order to unambiguously verify an OG signal at the transitions of interest (in this study P(20) and P(22)), it can be assumed that the spectral shape of the OG signal should relate to the expected width and shape of the transition at a given pressure and temperature, i.e., the OG signal should reflect the absorption properties of CO_2 in the sample cell. The homogeneous broadening caused by collisions and inhomogeneous broadening due to Doppler shift have been calculated with the resultant Voigt distribution (equation (6)). Figure 5 shows the calculated Voigt profile and the measured OG signal as a function of the wavelength for P(20)

of $^{14}\text{CO}_2$ in the reference cell. As can be seen, the OG signal follows the expected Voigt profile with a coefficient of determination of $R^2=0.982$. The small deviation at the longer wavelengths is suspected to stem from background from broadened nearby peaks.

Figure 5 Simulated Voigt profile of the P(20) line of $^{14}\text{C}^{16}\text{O}_2$ in the reference cell (dashed line) compared to the OG measurements (filled squares). The coefficient of determination of the fit was $R^2=0.982$.

The full width at half maximum (FWHM) of the Voigt profile was 67 MHz corresponding to $\Delta\lambda/\lambda=2.7\cdot 10^{-6}$. This could be compared to the FWHM of the laser at P(20), which was specified to 144 MHz or $\Delta\lambda/\lambda=5.7\cdot 10^{-6}$. The main reason for the laser profile being broader than the OG response is the higher pressure in the laser tube (2.7 kPa), which caused increased collisional broadening.

It should be noted that the data in figure 5 were measured with the reference cell filled with a ^{14}C -enriched gas corresponding to a $^{14}\text{CO}_2 / ^{12}\text{CO}_2$ ratio of 10% (ca. $8.5\cdot 10^{10}$ Modern). In order to study the sensitivity of the ICOGS setup and the effect of the intracavity enhancement factor, the OG response of the sample cell, filled with 5% of either 0.2 Modern or 20 Modern CO_2 in 95% N_2 , was investigated. Here, 100 Pa CO_2 was mixed with 1900 Pa N_2 after any residual water had been removed in a -80°C cold trap. The gas mix was then pumped to 100 Pa before the plasma was ignited and the measurement started. The standard measurement procedure was employed, where the $^{14}\text{CO}_2$ laser was tuned and locked to the center of the P(20) transition using feedback from the reference cell. The measurement was repeated 12 times where two measurements with 20 Modern CO_2 were followed by two measurements with 0.2 Modern CO_2 and so forth. This was to be able to distinguish any memory effects or long time drift in the setup. Between the measurements, the system was pumped to around 1 Pa after being purged with pure N_2 . The OG signal varied up to $\pm 10\%$ between measurements on samples with the same ^{14}C content but, more importantly, the signal differed

insignificantly between samples with different ^{14}C content. In fact, the mean difference between the 0.2 Modern and the 20 Modern samples was only about half the standard deviation in the measurements meaning that no clear dependence of the OG signal on the ^{14}C content could be distinguished.

Similar measurements to those of figure 5 were performed with the sample cell at slightly lower pressure and with much lower $^{14}\text{CO}_2/^{12}\text{CO}_2$ ratios. Here, non-symmetric distributions were observed (Figure 6). As can be seen, the spectral shape of the laser power and the OG signal did not coincide, in this case for a sample with an activity of 20 Modern. The two distributions had dissimilar shapes and centroids indicating a significant background contribution from non- $^{14}\text{CO}_2$ sources. This can also be seen from the shape of the scaled OG signal (Figure 6), which had a continuously increasing dependence on the piezo voltage, and consequently on the wavelength. Such a dependence can be interpreted as background from a nearby $^{13}\text{CO}_2$ or $^{14}\text{CO}_2$ line, in this case probably the P(68) line of $^{13}\text{C}^{16}\text{O}_2$. Alternatively a superposition of different distributions may give rise to similar observations. Consequently an understanding of the background contribution from non- $^{14}\text{CO}_2$ sources is crucial.

Figure 6 Spectral shape of the P(20) line of $^{14}\text{C}^{16}\text{O}_2$ measured in the sample cell at $p=40$ Pa with a mix of 5% CO_2 in 95% N_2 . The 20 Modern OG signal (black solid line) was calculated from the mean of 166 piezo scans. The laser power (dashed line) and the scaled OG signal (dash-dotted line) are shown as a reference.

Simulations

The background contributions from $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ are of particular interest as they have transitions in the same spectral region as $^{14}\text{CO}_2$. In a first approximation, we ignore other oxygen isotopes than ^{16}O due to lower abundance (0.2% for ^{18}O). Figure 7 shows the calculated spectral distributions from the transitions P(20), P(40), P(60), P(80) and P(100) for $^{12}\text{C}^{16}\text{O}_2$ at 100 Pa over a broad spectrum. The P(20) line for $^{14}\text{CO}_2$, which is one of the lines of

interest to this study, is shown for comparison. Here, the peaks are represented by the Lorentzian distribution (Equation (1)), since the integral defining the complex error function, which is used to calculate the Voigt profile (Equation (6)), cannot be evaluated in closed form. Instead, the integral is evaluated from its Taylor series making it valid only relatively close to the peak. However, the Voigt profile approaches a Lorentzian function as $(f-f_0)$ increases wherefore the latter can be regarded as a fair approximation far away from the peak (Huang and Yung 204), as is the case for the background in the spectrum relevant for ^{14}C ICOGS. Still, this approximation should only be regarded as a minimum transition probability far away from resonance, since, e.g., transitions from non-electric dipole transitions will cause additional broadening, and thus higher background. As can be seen, the background contribution from other $^{12}\text{CO}_2$ lines are significant, overshadowing the $^{14}\text{CO}_2$ P(20) line. This contradicts the claim that only the background of the $^{12}\text{CO}_2$ lines closest to the $^{14}\text{CO}_2$ line measured has to be considered (Murnick et al. 2008, Ilkmen 2009), which is true only if the lines almost coincide. However, for the peaks investigated in this study, such a coincidence was only found for the P(2) line of $^{14}\text{C}^{16}\text{O}_2$ which was situated merely 40 pm away from the P(92) line of $^{12}\text{C}^{16}\text{O}_2$. In the case of the $^{14}\text{C}^{16}\text{O}_2$ P(20) line, which is separated from the nearest $^{12}\text{CO}_2$ or $^{13}\text{CO}_2$ peak by more than 500 linewidths (Murnick et al. 2008), the contribution from the densely populated $^{12}\text{CO}_2$ levels around 10.6 μm , and not the nearby P(100) peak, will dominate the background. This can be explained by the fact that the population density of the states with higher J decays much faster than the tail of the Lorentzian. This can be seen from the dependency of the Lorentzian on the frequency shift away from f_0 which is $S_C \sim (f - f_0)^{-2} \sim (\lambda - \lambda_0)^{-2}$ (Equation (1)), whereas for the Boltzmann distribution $N \sim J \exp(-J^2)$ which could be interpreted as $N \sim (\lambda - \lambda_0) \exp(-(\lambda - \lambda_0)^2)$ (Equation (7)). Hence, it is important to sum up the contribution of many $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ peaks in order to estimate the background in radiocarbon ICOGS, and not merely the ones closest to the $^{14}\text{CO}_2$ line that is being investigated. In this study, only the contribution from P(2)-P(100) and R(0)-R(58) for the (00⁰1)-(10⁰0) band in $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$ were included, but in a more thorough investigation, the contribution of different oxygen isotopes (Bradley et al. 1986), e.g. $^{12}\text{C}^{18}\text{O}_2$, as well as the (01¹1)-(11¹0) band with transitions around 11.0 μm for $^{12}\text{C}^{16}\text{O}_2$ (Hartmann and Kleman, 1966), should be included. Moreover, transitions of other chemical species in the plasma such as CO, O₂ and N₂ should be investigated.

Nevertheless, the calculations provide a reliable minimum possible background. Furthermore, the method is accurate enough to make the conclusion that for pure CO₂ samples with isotopic ratio around 1 Modern, the signal is expected to be dominated by the background from $^{13,12}\text{CO}_2$ transitions, and requiring extremely high stability for proper background subtraction.

Figure 7 Simulated background from $^{12}\text{C}^{16}\text{O}_2$ transitions P(20), P(40), P(60), P(80), and P(100) at $p=100$ Pa and $T=340$ K. P(20) of $^{14}\text{C}^{16}\text{O}_2$, assuming $^{14}\text{C}/^{12}\text{C}=10^{-12}$, is shown as a reference.

Signal stability and reproducibility

One important parameter that is of central importance for analytical measurements is the accuracy and precision of the method, requiring well defined reproducibility and stability over the analysis time.

We encountered significant instabilities in the OG signal even though stable operation was ensured for the laser's power and wavelength, as well as for the plasma's electrical properties. This can be seen from the variation of the OG signal over time at five different pressures as shown in figure 8 (a). These variations led to questions regarding the effect of plasma-induced changes in gas chemistry. Traditionally, it would be expected that the concentration of the various radicals and other species in the plasma change in a monotone way with respect to time and continuously evolve towards equilibrium. However, our findings indicate the existence of more complex mechanisms. One important reaction which occurs in the sample cell after plasma ignition is the decomposition of CO_2 into CO and O. This process was found to have a considerable effect on the observed OG signal. The RGA was used to measure the partial pressure of CO_2 and CO after plasma ignition as shown in figure 8 (b) and (c) for two different pressures. The CO_2 amount was found to 1) drop immediately and steeply upon ignition of the plasma and 2) stabilize and subsequently decrease slowly over time. Furthermore, oscillations in the CO_2 and CO partial pressures over time were observed (Figure 8 (c)). The latter effect was more pronounced at lower pressure as well as having a shorter onset time. It could be argued that the oscillations may stem from instabilities in the RF oscillator circuit, but the fact that the CO_2 and CO oscillations were 180° out of phase suggest that they are more likely driven by the kinetics of the chemical reactions in the plasma.

Concerning the oscillations, it is noteworthy that in spite of the known collision rates at these pressures, such “slow” oscillation in the reaction from CO_2 to CO is taking place on periods of tens to hundreds of seconds depending on the base pressure. Oscillatory reactions between CO_2 and CO are known to occur on surfaces with metal catalysts (Hendriksen et al. 2010). Such reaction oscillations have previously not been observed in the bulk gas phase, with or without a catalyst. This is suspected to be the first time $\text{CO}_2 \leftrightarrow \text{CO}$ reaction oscillations are observed in a non-surface environment. This phenomenon is currently being investigated at our laboratory.

Figure 8 Oscillating intensity in the OG measurements (a) where the start, frequency and duration of the oscillations were dependent on the pressure. The partial pressures of CO_2 and CO as a function of time at pressures $p=100$ Pa (b) and $p=50$ Pa (c), measured with the RGA, are shown to the right. Here, time t_0 indicate plasma ignition.

The resemblance between the oscillations seen in the RGA measurements (Figure 8 (c)) and the instabilities in the OG signal (Figure 8 (a)), in terms of waveform, onset time and oscillation frequency, makes it fair to assume that both phenomena have the same origin, namely the plasma induced oscillation in the concentration of CO_2 . Such chemical reaction

oscillations necessitate the establishment of a parameter range where they do not occur or are stable over time scales corresponding to a measurement sequence.

Another issue that was noted was the fact that performing two consecutive measurements, with identical settings for the lasers, RF oscillators, etc., but with a repeated gas fill could lead to variation of around 20% in the OG signal. This was probably due to the fact that the plasma parameters were sensitive to small pressure changes, and that it was difficult to obtain exactly the same pressure in two consecutive fills. It should be noted that these problems might be mitigated by measurements in dynamic, instead of static, mode.

Pressure

One of the parameters affecting the OG signal is the gas pressure. Based on the description given by Murnick et al. and Ilkmen (Murnick et al. 2008, Ilkmen 2009), the signal intensity should be proportional to the pressure. In our system, we have observed a rather limited pressure range in which ICOGS measurements can be performed, spanning from a few tens up to a few hundred Pa. At RF-frequency of 38 MHz the operational range was 20-200 Pa, whereas for pressures up to 500 Pa, one needs to reduce the RF frequency to about 15 MHz. At lower pressures the OG signal shows instability rendering it not useful, whereas at higher pressures the plasma could not be ignited with our oscillator. However, these limitations were set by the design of the oscillator circuit, and could probably, if required, be reduced by redesigning or changing the plasma source.

Gas composition

There are a variety of gas compositions that could be investigated for studying CO₂ samples, in analogy to the gas chemistry of the CO₂ laser (Duarte 1995). Here we have used two alternatives; 1) Pure CO₂ gas, and 2) a mixture of 90-95% N₂ and 5-10% CO₂. We are in the process of evaluating the two mixtures. The latter leads to an increase in the signal strength due to N₂ molecules' collisional excitation of the CO₂ molecules – one of the main principles behind CO₂ lasers – whilst adding an additional absorption background from nitrogen. Pure CO₂, on the other hand lacks the added background but has a weaker signal.

CONCLUSION

The ICOGS setup in our laboratory is operational but not fully developed. Various aspects and operational details of the ICOGS have been studied and presented. A number of issues need to be addressed before performing analytical radiocarbon measurement of CO₂: Firstly, the absorption background, originating from non ¹⁴CO₂ entities such as the ro-vibrational absorption bands of ¹³CO₂ and ¹²CO₂, as well as pressure dependent N₂ background (for gas mixtures) have to be thoroughly characterized. Secondly, the signal stability and reproducibility have to be improved. This includes the oscillatory variations in the amount of CO₂ in the gas cell (CO₂ ↔ CO). Thirdly, calibration data should to be secured, using the in-house AMS facility. Work on addressing these issues is currently underway, with the aim of

using ICOGS for measuring μg -size sample in the 1-2 Modern range. We have so far been unable to detect ^{14}C unambiguously in the range of 0.2-20 Modern.

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