

of the works referenced here are very different. This work was based on experimental and simulation to calculate the adsorption energies. The work from Vesselli et al. was purely DFT calculations and the work from Middleton measured the relative intensities empirically and they did not measure the adsorption energies. In short, the adsorption theory explained the experimental differences between the target-flow configurations. The inferred parameter values were in agreement with independent works. This suggests that adsorption is an important step in the ionization process.

3.4 Optimization of the Ionization

FIGS. 13A, 13B, 13C and 13D (FIG. 4 in the manuscript) shows the ionization efficiency (E) and total integrated charge per pulse (A) for both target configurations versus carbon mass (C). The precision of the amount of injected carbon is taken as the relative difference between the pressure readings of the gauges connected to the sample loop. The injection precision is not graphed in FIGS. 13A, 13B, 13C and 13D (FIG. 4 in the manuscript) as carbon-mass error bars; however, while carrying out the experiments, it was kept lower than 4%. The carbon-mass range starts at 150 ng as the precision of the CO₂ injection is higher than 4% at lower masses. By means of Eq. 2, the data A vs C of FIGS. 13A, 13B, 13C and 13D (FIG. 4 in the manuscript) are converted into ionization efficiency (FIGS. 4c and 4d). The data suggest that CO₂ adsorbs on the Ti efficiently (constant efficiency) when it reaches a pressure threshold (maxima of E vs P graph). This threshold seems to be 9.8 Torr and 5.0 Torr for the directed-flow and diverging-flow configurations respectively. Before the threshold, E increases with the increase of A. After the threshold, the CO₂ starts to saturate the surface causing the efficiency to start dropping. The linearity of the signal vs amount of carbon (FIGS. 13A, 13B, 13C and 13D (FIG. 4 in the manuscript) is useful for analysis and quantitation of CO₂. We propose that this linearity could be useful to quantify organic molecules by detecting the CO₂ produced from its combustion and at the same time to measure the rare carbon isotope ratio using an AMS. As proof of principle, the linear dynamic range (LDR) is marked with dashed green lines. The LDR was chosen for the set of points that gave a correlation coefficient (r^2) between 0.97-0.98 and starting from the minimum carbon mass. The LDR range (150-1000 ng) and sensitivity (slope and slope confidence) of the directed-flow configuration is better than for the other configurations. As explained above, the reason is that the signal of the other configurations is inhibited by the aerodynamics and the smaller area of the Ti surface, thus their curves saturates faster. The efficiency maximizes near 2.5% at around helium flow of 0.07 to 0.1 mL/min. At high flow, the contact time of CO₂ with the Ti surface is shorter and as overall effect, ionization becomes inefficient. Also, at higher flows, the background pressure in the source increases; affecting the mean free path of 12C⁻ ions. In the range of 0.05-0.35 mL/min, the pressure linearly increased 1 order of magnitude until reaching 5.0×10^{-6} torr. This is the range where the ionization efficiency decreases. At He flow values below 0.05 mL/min, the pressure was almost constant (6.0×10^{-7} torr). At these low flow rates of the carrier gas, CO₂ experiences diffusion considerably and the peak shape broadens. For compatibility purposes with HPLC and GC, the capacity to detect short pulses is important in order to maintain the resolution of the chromatographic technique. The peak shape optimizes at 0.1 mL/min because the peak height is maximum and the FWHM is cut at the half. If this ion source is coupled to a CO₂ pulse-producing analytical system, the carrier flow speed is likely to be determined by the analytical system. This ion source could be used at any flow rate between 0.02 to 3

mL/min and the FWHM will be in the range of 4-10 s. The behavior of the tail vs flow is the same as for the FWHM and the tail ranges between 2.6 and 6.4 s (data not shown). The peak tail was measured as $(x_2 - x_0)$ and $\text{FWHM} = x_2 \times x_1$. For our data set, it can be demonstrated that $(x_2 - x_0) = 0.64$ FWHM because the asymmetric factor ($[(x_2 - x_0) / (x_0 - x_1)] = 1.8$) is relatively constant. In order to take full advantage of the adsorption process, it is best to ensure that the whole Ti surface is sampled by the Cs⁺ beam. The position of the target was moved step by step at positions downstream of the Cs⁺ beam waist. Beyond the beam waist, the Cs⁺ beam cross-section is bigger. The efficiency was improved because a Cs⁺ beam with higher cross-section can sample more adsorbed CO₂. Throughout the results of this work, the ionization efficiency or yield has ranged from 1 to 2.5% for carbon mass higher than 400 ng when using the directed-flow configuration with high Ti area. For masses lower than 400 ng, the same configuration with lower area presented 1% efficiency. It can be found, in the literature, efficiencies of 8% for continuous flow at low speed, containing tens of μg of carbon; and 1.5-6% for the μg range of carbon. Kjeldsen reported efficiencies between 0.5-1.5% for long pulses or continuous-flow. In the case of short pulses, Kjeldsen showed lower efficiencies in the range of 0.2-0.8%. For a microwave-plasma ionization of CO₂ with charge inversion, the reported overall efficiency was 0.4%. It is expected that the ionization of a continuous flow of CO₂ at low speed will be more efficient than the ionization of a fast CO₂ pulse. As mentioned before, a low gas flow maintains a better vacuum and mean-free-path for the ion beam transmittance. Also, at low gas flows, the CO₂ has higher interaction time with the Ti surface and the Cs⁺ beam. Our target performance felt in the low range of efficiencies reported for continuous flow systems.

4. Conclusions

A "target" for direct ionization of CO₂ in the form of 12C⁻ was designed by computer simulations, adsorption theory and empirical research. It was found that the ionization is optimized with a novel flow geometry that directs the CO₂ flow on a Ti surface where a Cs⁺ beam is bombarding; rather than a diverging-flow configuration. The fitting of the Jovanovic-Freundlich model provided values of adsorption energy and average residence time for CO₂ on Ti of 0.26 eV and 40 ns respectively. The agreement of the fitting with the data; and the agreement of the measured constants with other works suggest that adsorption plays a major role in the ionization mechanism. By optimizing the parameters that affect the CO₂ interaction with the Ti surface and Cs⁺ beam (amount of CO₂, gas flow, Ti contact area and beam cross-section) effective ionization was obtained in the range of 1-2.5%. The linear dynamic range for the 12C⁻ was from 150 ng to 1000 ng of carbon for the novel directed-flow configuration indicating the potential use of the ionization method to quantify analyte mass and to measure isotope ratios. These results demonstrate the feasibility of using this ionization system for coupling HPLC with an online combustion interface with our AMS instrument for the measurement of 14C/12C molecular isotopic ratios.

While the invention may be susceptible to various modifications and alternative forms, specific embodiments have been shown by way of example in the drawings and have been described in detail herein. However, it should be understood that the invention is not intended to be limited to the particular forms disclosed. Rather, the invention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the following appended claims.