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Design of a secondary ionization target for direct production of a C⁻ beam from CO₂ pulses for online AMS

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Abstract

We designed and optimized a novel device “target” that directs a CO₂ gas pulse onto a Ti surface where a Cs⁺ beam generates C⁻ from the CO₂. This secondary ionization target enables an accelerator mass spectrometer to ionize pulses of CO₂ in the negative mode to measure ¹⁴C/¹²C isotopic ratios in real time. The design of the targets were based on computational flow dynamics, ionization mechanism and empirical optimization. As part of the ionization mechanism, the adsorption of CO₂ on the Ti surface was fitted with the Jovanovic–Freundlich isotherm model using empirical and simulation data. The inferred adsorption constants were in good agreement with other works. The empirical optimization showed that amount of injected carbon and the flow speed of the helium carrier gas improve the ionization efficiency and the amount of ¹²C⁻ produced until reaching a saturation point. Linear dynamic range between 150 and 1000 ng of C and optimum carrier gas flow speed of around 0.1 mL/min were shown. It was also shown that the ionization depends on the area of the Ti surface and Cs⁺ beam cross-section. A range of ionization efficiency of 1–2.5% was obtained by optimizing the described parameters.

Keywords

AMS; Gas ion source; CO₂ direct ionization; Gas target; COMSOL simulation

1. Introduction

Accelerator Mass Spectrometry (AMS) is a spectroscopic technique that precisely measures the ratio of long-lived radionuclides to the abundant isotope (e.g. ¹⁴C/¹²C). For biological studies, ¹⁴C is an excellent molecular label due to its natural low abundance. Sample preparation for AMS routinely follows a time-consuming procedure of oxidizing samples (combustion) labeled with ¹⁴C, followed by graphitization of the CO₂. Conventional AMS is able to produce an intense beam of negatively charged carbon (C⁻) from the graphite by using Secondary Ionization sources (e.g. Cs⁺ beam as the primary ion) [1]. AMS can reach the ultra high sensitivity to count ¹⁴C atoms by efficiently eliminating the spectroscopic interferences [2]. AMS destroys the molecular structure of the isobaric interferences (e.g. ¹²CH⁻₂, ¹³CH⁻) with high energy collisions in the MeV range. Furthermore, the ion

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source works in the negative mode as ^{14}N does not form stable negative ions. Elimination of the graphitization step, by the direct ionization of a continuous flow or a pulse of CO_2 is very important to reduce sample turnaround time and to minimize the sample size required for the analysis. As Ognibene et al. have pointed out [3], direct ionization of CO_2 is also useful as a method to couple the AMS instrument with separation techniques like HPLC following combustion. The amount of carbon contained in any given eluent peak is small and of order of a few micro-grams. Although possible, graphitization of such small samples is time consuming and difficult [4,5]. It is necessary that any direct ionization method for CO_2 must produce a high current of C^- in order to obtain precise isotope ratio measurements. A microwave-plasma has been used to produce C^+ from CO_2 , coming from a Gas Chromatograph; then the C^+ is converted into C^- by using a charge-exchange canal [6]. Other papers [7–13] have demonstrated the feasibility of producing C^- when CO_2 comes in contact with a high energy beam of Cs^+ and with the surface of a transition metal (e.g. titanium). Hughey et al. was the first in coupling this type of ion source with a GC [14,15]. The device used to bring in contact the CO_2 with the Cs^+ and the Ti is called “target”. The design of the targets of the works mentioned above, were based on the Heinemeier or Bronk designs [14,15]. Middleton and Klein [16] compared the C^- signal from CO_2 using a Cs^+ beam for different metals. The relative signals compared with Ti were: 0.72, 0.64, 0.54, 0.24, 0.15, 0.06, and 0.02 for Zr, Sc, Ta, Ni, Mg, Cu, and Au respectively. The advantage of Ti over the other metals lies in its high adsorption efficiency to CO_2 [17]. With this in mind, we designed a new target with a Ti insert that controls the flow of CO_2 for better interaction with the Cs^+ beam and better adsorption onto the Ti surface. This work focuses on target design, the adsorption theory and empirical parameters (helium carrier gas flow, CO_2 amount and Ti target area) that affect the generation of $^{12}\text{C}^-$ from CO_2 .

2. Materials and methods

2.1. CO_2 pulse injection system

The scheme of the CO_2 injection system is shown in Fig. 1a. A tank containing pressurized CO_2 (Instrument grade 99.99% purity, Airgas Co.; Bowling Green, USA) was connected to an electrically actuated GC injection valve with a 100 μL sample loop (Valco Instruments Co., Waterbury, USA). The pressure inside the sample loop was measured with 2 pressure analog-to-digital transducers (MKS, Andover, USA) connected at both ends. The CO_2 flow was controlled with two microcontrol valves. A dedicated computer program continuously read the CO_2 pressure and converted it to grams of carbon based on ideal gas calculations. The pressures at both ends of the sample port, during the filling step, were kept within a relative difference of 4%. The software also was able to read and control the flow-meter (Alicat Scientific, Tucson, USA) dedicated for the He carrier gas coming from a pressurized He tank (Ultra high purity, Airgas Co.; Bowling Green, USA). The injection system and the high-vacuum gas feedthrough of the ion source were connected with a fused silica capillary (3 m long, 0.25 mm id, 0.35 mm od). The feedthrough contained a stainless steel tubing of 30 cm long, 0.5 mm id, 1.6 mm od.

2.2. Gas targets and inserts

The machined targets consisted of a Ti piece inserted in an aluminum support. The targets were mounted in a standard MCGSNICS sample wheel of a modified NEC ion source [18]. Two configurations of titanium inserts were proposed. Fig. 1b and c illustrate the cavities inside the aluminum supports and the holes drilled in the inserts. The conventional diverging-flow configuration (Fig. 1b) was based on a Bronk et al. [12] design. The inserts were made starting from Ti rods of $\varnothing$ 1.59 mm diameter $\times$ 4 mm long and compressing them to an oval cross-section of 0.8 mm $\times$ 1.6 mm. The frontal face of the insert defines the Cs⁺ contact area. A novel insert with directed-flow configuration (Fig. 1c) was machined out from Ti rods of $\varnothing$ 3.17 mm $\times$ 4 mm long (99.99%, Alfa Aesar, Ward Hill, USA) by drilling 4 entrance holes for the gas ($\varnothing$ 0.63 mm) and one hole at the front ($\varnothing$ 1.32 mm $\times$ 1.2 mm deep). The face of the frontal hole defines the Cs⁺ contact area. A Ti insert with the same configuration but with a smaller front area was made by drilling the frontal hole at a diameter of 0.79 mm. All the targets and inserts were cleaned by soaking in 10 mL of isopropanol in a 25 mL plastic bottle for 1 h with periodic shaking.

2.3. Ion source conditions

Computer simulations and description of the gas-capable ion source of our AMS instrument were described previously [18]. However, the experiments in this work were carried out using only: the ion source; the first acceleration region; the first mass-scan magnet and the Faraday cup as indicated in Fig. 1a. The experimental conditions were: Cs metal vaporization temperature 170 °C, Cs thermal surface-ionizer power of 134 Watts, Cs⁺ beam energy 9 kV, negative ions acceleration voltage 40 kV and magnet field 4149 Gauss. These ion source parameters were determined based on the performance of solid graphite targets [19].

2.4. COMSOL flow simulations inside the target

Comsol™ (COMSOL Inc., Los Angeles, USA) is a finite element analysis, solver and simulation software. Navier–Stokes partial differential equations were used for compressible and laminar flow conditions. The simulation of the target was defined in 2D axisymmetric geometry. The entrance of the target was taken as the flow boundary for a constant laminar inflow of He at 0.5 mL/min which is the flow to be leaked inside the ionization source. The exit of the target was taken as a pressure boundary at 1×10^{-6} Torr which is the background pressure of the ion source when flow is leaked inside. The convection and diffusion simulation of CO₂ was added by starting a pulse of CO₂ with concentration distributed with a Gaussian function and the CO₂ behavior was simulated in a time dependent fashion until 7 s. Comsol™ applies a dynamic method to mesh the geometry to be solved thus the mesh density was not constant but denser at regions of high curvature. In total, it used 2×10^6 mesh units in an area of 4 cm². All the physicochemical properties of the involved gases were added from the Comsol material library. Only the solid surfaces in contact with the flow were defined and all were designated as boundary conditions without including adsorption interactions with the walls.

3. Results and discussion

3.1. Flow simulations inside the target

The design of the target was mostly done with the help of computer simulations. The simulations helped us to decide between a diverging-flow or a directed-flow configuration (Fig. 2). In our simulations, the pulse of CO₂ was started from the entrance of the target at an initial concentration following a Gaussian function (Eq. (1)) where t is time and c_0 , b_0 and t_0 are

$$c=c_0e^{-b_0(t-t_0)^2} \quad (1)$$

constants that affect the total amount of CO₂, the width and center position of the pulse peak, respectively. These constants were set at values that emulated the empirical results. Fig. 2d shows that by selecting the values of b_0 and t_0 , 2000 s⁻² and 0.08 s, respectively; the simulated pulse emulated the same FWHM as the experimental average (3 s as in Fig. 3b). Experimentally, a specific number of moles of CO₂ were pulsed and injected into the target; however, in the simulations, the CO₂ could not be inputted as moles but as a distribution of concentration (Eq. (1)). The moles of injected CO₂ contained in such simulated pulse could be calculated by integrating the CO₂ flux (mol/m² s) while the pulse passes across a cross section of the target, and then integrating over the time (T) that the CO₂ pulse needs to pass such cross section (Eq. (2)):

$$moles=\int_0^T \oint flux \cdot \partial A \partial t \quad (2)$$

The value of c_0 that corresponded for a certain experimental CO₂ injection was found by trial and error until the double integral equaled the amount of experimentally injected moles of CO₂.

Fig. 2a and b show the calculated CO₂ concentration profiles along the fluidic cavities inside the targets at the time point when the pulse has just reached the front face of the titanium surface. The concentration profiles are in a rainbow-color code. For the directed-flow configuration, most of the CO₂ in the pulse is located in the blue region and for the diverging-flow configuration, the CO₂ band is defined by the green region. The concentration profiles along the red¹ lines on Fig. 2a and b are graphed in Fig. 2c. Comparing the minimum values of both graphs, it can be seen that at the Ti surface for the directed flow, the gas concentration profile is 1.7 times higher than for the diverging-flow configuration. The velocity arrows of the diverging-flow configuration show that during the gas expansion, only a fraction of the gas molecules will travel towards the surface. On the other hand, by directing the flow through ducts towards the surface, more molecules get adsorbed on the surface at the location where the Cs⁺ beam impacts the Ti surface (front face), which should lead to increased CO₂ ionization efficiency. The simulations (data not shown) also indicated that the peak of the CO₂ concentration broadens when the size of the cavities inside the target increases. For that reason, the sizes of the cavities were selected as small as the machine shop could make them.

3.2. Representative results of the $^{12}\text{C}^-$ beam

A representative example of the beam current of $^{12}\text{C}^-$ ionized from CO_2 pulses is presented in Fig. 3. The $^{12}\text{C}^-$ total charge corresponding to each CO_2 pulse was measured by numerical integration of the peak and subtracting the area under the baseline. The start and end points of the peak were visually selected. The $^{12}\text{C}^-$ current detected by AMS for the analysis of carbon graphite is normally on the order of 100 μA while the peak height of the CO_2 pulses is 40 μA . High precision isotope ratios can only be obtained when the initial beam current is high. This is a disadvantage of our direct ionization of CO_2 compared with the graphite analysis. Fig. 3 also illustrates memory effects. The three first peaks were obtained with a new Ti insert and the fourth peak was obtained with a Ti insert extensively used over 3 days. Fig. 3 shows that the background level for the old insert is higher. We think that this memory has negligible effect on the area calculation because the background is practically flat. On the other hand, the height of the last peak is slightly lower due to degradation of the Ti insert with the constant sputtering, elevating the RSD of the areas to 9.4%. In our experience, the signal does not change during the first 60 min of continuous use of a new target. Therefore, for future applications, one target will be able to withstand one HPLC run. Fig. 3b shows that the peaks had a typical short rise time from the base line to the top (<0.8 s), indicating that the CO_2 pulse band was kept narrow due to the small inner diameter of the capillary used to transport the pulse from the injection system to the ion source. The peak tailing magnitude ($x_2 - x_0$) depended on the amount of injected CO_2 and gas carrier flow. The typical value of the asymmetry factor ($[(x_2 - x_0)/(x_0 - x_1)]$) was ~1.8 or ~3.5, measured at 50% or 10% of peak height, respectively. The peak tailing was the result of the adsorbed CO_2 and the residual gaseous CO_2 that is not immediately pumped away. The $^{12}\text{C}^-$ total charge per pulse, the peak shape and the ionization efficiency were the parameters that we chose to study the performance of the system. Ionization efficiency was defined as the total moles of detected charge (magnet set at $m/z = 12$) relative to the moles of carbon from the injected CO_2 :

$$E = \frac{C^-}{C} = \frac{A \times K}{C} \quad (3)$$

See definition in Eq. (3), where A (μC) is the total charge integrated from the current signal (μA). K is the inverse of the Faraday constant. C (μmol) = PV/RT where P , T are the average pressure and temperature of CO_2 in the sample loop registered by both gauges; V is the volume of the sample loop, and R is the gas constant. In short, the simulations offered a first insight in the differences between the conventional diverging-flow and the new directed-flow configurations. Also, the simulated behavior of the CO_2 pulses inside the target was reproduced experimentally.

3.3. Adsorption theory of CO_2 on Ti

Our hypothesized mechanism for the CO_2 ionization can be described as follow: first CO_2 is brought in contact with a Ti surface and is adsorbed; then the high-energy Cs^+ particles hit the adsorbed CO_2 , triggering its fragmentation into C and O elements. The negative charge in the C atoms might be due to electron capture at the Ti surface level. It is known that fragmentation of triatomic molecules can be induced with collisions with energetic particles

[20]. The charging of the carbon atoms must occur at surface level because the velocity of the electrons in the gas-phase, in a kilovolt potential difference, is too high for being captured by neutral atoms [21]. The adsorption step can be studied using the Jovanovic–Freundlich isotherm models. These two models have been extensively studied individually or in combination in several papers [22–24], and the combination is shown in Eq. (4). The Freundlich model which is an empiric model for gaseous adsorbates has the form $\theta = (\beta P)^\nu$, where β is a proportional constant:

$$\theta = \frac{q_{ads}}{q_{max}} = 1 - e^{-(\alpha P)^\nu} \quad (4)$$

In Eq. (4): α is a factor that depends on the CO₂ adsorption rate over its vapor pressure (Eq. (5)), q_{ads} is the specific amount of adsorbed molecules, q_{max} has the same units as q_{ads} and it is the saturation or monolayer capacity of the adsorbent, θ is the fractional coverage or fraction of occupied sites relative to the total availability, P is the partial pressure of the molecule of interest in the bulk near the Ti surface and ν is the homogeneity parameter. The amount of adsorbed CO₂ (q_{ads}) is proportional to the measured total charge of ¹²C[−] (A), therefore the fractional coverage can be expressed as: $q_{ads}/q_{max} = A/A_{max}$. P is proportional to the amount of injected CO₂ (C); however it cannot be experimentally determined. P can be indirectly measured from the simulation by applying the ideal gas law to the CO₂ transient concentration (Fig. 2d). Finally, P is obtained by averaging the transient pressure. As explained earlier, the simulation conditions and constants values were selected by trial and error until matching the amount of injected CO₂ and the experimental peak shape. The Jovanovic model [22] states that every gas particle that reaches the surface is adsorbed only during an average time of residence (τ). τ can be increased due to collisions with gaseous particles thus the desorbing particle bounces back to the surface:

$$\alpha = \frac{\sigma \tau}{\sqrt{2\pi m k T}} = \frac{e^{(\varepsilon_{ad} - \Delta H_{vap})/RT}}{P_s} \quad (5)$$

In Eq. (5): σ is the adsorbate collision cross section (17 Å² for CO₂), τ is the average residence time; ε_{ad} is the adsorption potential energy, H_{vap} and P_s are the heat of vaporization (4.93 kJ/mol) [25] and the vapor pressure (4.92×10^4 Torr at 298 K) [25], respectively. $m k T$ are the CO₂ molecule mass, Boltzmann constant and temperature, respectively. These concepts are important for fitting our system because the adsorption process will be controlled by the short transient pressure of the CO₂ pulse in contact with the Ti surface.

Examples of the fitting of the Jovanovic–Freundlich model for both configurations are presented in Fig. 4a and b. The parameter α will be extracted from the fittings of Eq. (4); ε_{ad} and τ from Eq. (5). The agreement of the model demonstrates that adsorption must be part of the mechanism of conversion of CO₂ into C[−]. The fitted parameters of the model are presented in Table 1. As in any other adsorption system, the data saturate at a point A_{max} . A_{max} is proportional to the total capacity or the total number of available adsorption sites. At a carrier flow of 0.15 mL/min, A_{max} for the directed-flow configuration #1 is 1.8 times bigger than for the diverging-flow configuration even though the area of the Ti surface is the

same for both configurations. The reason is that some of the adsorption sites of the diverging-flow configuration are poorly exposed to the CO₂ due to the gas-flow configuration; thus the effective number of adsorption sites is lower. The A_{max} for the directed-flow configuration #1 is 2.2 times larger than for the same configuration with smaller area (#2). In these two configurations, the gas-flow is the same but the areas are simply different, therein the difference in number of adsorption sites. The parameter ν measures the homogeneity of the surface. All the Ti surfaces had the same degree of homogeneity (flat and smooth); however the CO₂ gas is differently distributed on the Ti surface for the directed-flow and diverging-flow configurations. Therefore, this difference in distribution translates into different values for the surface homogeneity parameter. Logically, ν presents almost the same value for the directed-flow configurations #1 and #2. Table 1 shows that the parameters α , ϵ_{ad} and τ have practically the same value (0.07 Torr⁻¹, 0.26 eV and 40 ns, respectively) for the different configurations. Eq. (5) states that α , ϵ_{ad} and τ are independent of the geometry and only depends on the thermodynamics of the surface-adsorbate interaction, and the experimental results agree with this. Our τ values agree with Jovanovic [22] who estimated that τ should be 10⁻⁶ to 10⁻¹⁰ s in the case of physical adsorption. Vesselli et al. using Density Functional Theory (DFT), investigated the adsorption energy (ϵ_{ad}) of CO₂ on several metals. Some examples of these values in eV are: 0.09, 0.11 and 0.32 for Cu, Pt and Ni, respectively [26]. Cu seems to have low affinity for CO₂ while Ni has high affinity. In this work, we determined an ϵ_{ad} of 0.26 eV for Ti which means high affinity but lower than Ni. As stated in the introduction [16], it was expected that Ti will have higher affinity than Ni; however the experimental conditions 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 measured 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

Fig. 4 shows the ionization efficiency (E) and total integrated charge per pulse (A) for both target configurations vs 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 Fig. 4 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. (3), the data A vs C of Fig. 4a and b are converted into ionization efficiency (Fig. 4c and d). 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 (Fig. 4a and b) 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 and 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.

Fig. 5a plots the ionization efficiency with respect to helium gas flow. The efficiency maximizes near 2.5% at around helium flow of 0.07–0.1 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 (Fig. 5b). At lower flow speeds the ionization efficiency does not increase considerably. 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. Fig. 5b shows that this ion source could be used at any flow rate between 0.02 and 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 FWHM = $x_2 - x_1$. 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 (0 mm in Fig. 6). 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 [27]; and 1.5–6% for the µg range of carbon [9]. Kjeldsen et al. [28] reported efficiencies between 0.5% and 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 [29] 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 through 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 compound-specific ¹⁴C measurement.

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Fig. 1.

Scheme of the experimental set-up. (a) Gas line connecting the CO₂ injection set-up with a target and a Cs⁺-beam target (green), producing a beam of C⁻ (red). Gas targets consisting of an Al support and a Ti insert. (b) Diverging-flow configuration and (c) directed-flow configuration.

Fig. 2.

Computer simulations of two target configurations. (a) Diverging-flow configuration showing the CO₂ concentration (mol/m³) spatial profile inside the cavities. The black arrows represent the direction of the velocity vectors. (b) Same as (a) for a directed flow. (c) Concentration profile just on the titanium surface (red line) for both configurations. (d) Example of CO₂ concentration time-profile along the red line. The bars indicate the spatial variation.

Fig. 3.

Illustration of the reproducibility and peak shape of the $^{12}\text{C}^-$ current detected by the Faraday cup. (a) He carrier at 0.1 mL/min was flowed into a directed-flow configuration and each peak contains ~ 800 ng of carbon. The relative standard deviation (RSD) of the areas of the first 3 peaks is 5.0%; including the last peak, it is 9.4%. (b) Scale expansion for one peak. The parameters (x_1 , x_2) of the asymmetric factor are measured at the half of the peak maxima.

Fig. 4.

Adsorption model fitted to the data of $^{12}\text{C}^-$ total integrated charge (A) vs CO_2 average pressure (P). LDR is represented with a green dashed line. P is the average pressure of the transient CO_2 pulse. P was obtained from simulations that corresponded to the amount of injected CO_2 in ng of carbon (C). (a) A vs P vs C (c) E vs P vs C for directed-flow configuration with a large Ti surface area (1.8 mm^2). (b) A vs P vs C (d) E vs P vs C for diverging-flow configuration with Ti surface area of 1.9 mm^2 . He flow 0.15 mL/min .

Fig. 5. Effect of the gas flow over (a) ionization efficiency (E) of produced $^{12}\text{C}^-$ and (b) peak shape parameters. 800 ng of carbon per CO_2 pulse, Ti insert with large area surface.

Fig. 6. Effect of the target position over the ionization efficiency for the directed-flow configuration. He flow 0.15 mL/min, 800 ng of carbon per CO₂ pulse.

Table 1

Fitting parameters for the Jovanovic–Freundlich and linear models.

Target configuration	Ti area (mm ²)	A _{max} (μC)	r ² ^a	ν	α (×10 ⁻² Torr ⁻¹)	ε _{ad} (eV)	τ (ns)	LDR ^b range (ng)	LDR ^b slope (μC/ng)	Slope conf. (%)
Directed flow #1	1.8	180	0.93	1.75	6.9	0.26	39	150–1000	0.15	6.7
Diverging flow	1.9	100	0.90	1.00	7.2	0.26	40	150–500	0.11	9.0
Directed flow #2	0.49	80.0	0.91	1.75	7.0	0.26	39	150–800	0.088	10

^aCorrelation coefficients for the adsorption model.

^bLinear dynamic range.