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Design of a secondary ionization target for direct production of a C^- beam from CO_2 pulses for online AMS

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ABSTRACT

We designed and optimized a novel device "target" that directs a CO_2 gas pulse onto a Ti surface where a Cs^+ beam generates C^- from the CO_2. This secondary ionization target enables an accelerator mass spectrometer to ionize pulses of CO_2 in the negative mode to measure $^{14}C/^{12}C$ 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 CO_2 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 $^{12}C^-$ 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.

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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. $^{14}C/^{12}C$). For biological studies, ^{14}C 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 ^{14}C, followed by graphitization of the CO_2. 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 ^{14}C atoms by efficiently eliminating the spectroscopic interferences [2]. AMS destroys the molecular structure of the isobaric interferences (e.g. $^{12}CH_2^-$, $^{13}CH^-$) with high energy collisions in the MeV range. Furthermore, the ion 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 $^{12}C^-$ from CO_2.

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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 MCGS-NICS 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 Ø 1.59 mm diameter × 4 mm long and compressing them to an oval cross-section of 0.8 mm × 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 Ø 3.17 mm × 4 mm long (99.99%, Alfa Aesar, Ward Hill, USA) by drilling 4 entrance holes for the gas (Ø 0.63 mm) and one hole at the front (Ø 1.32 mm × 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 CO_2 was added by

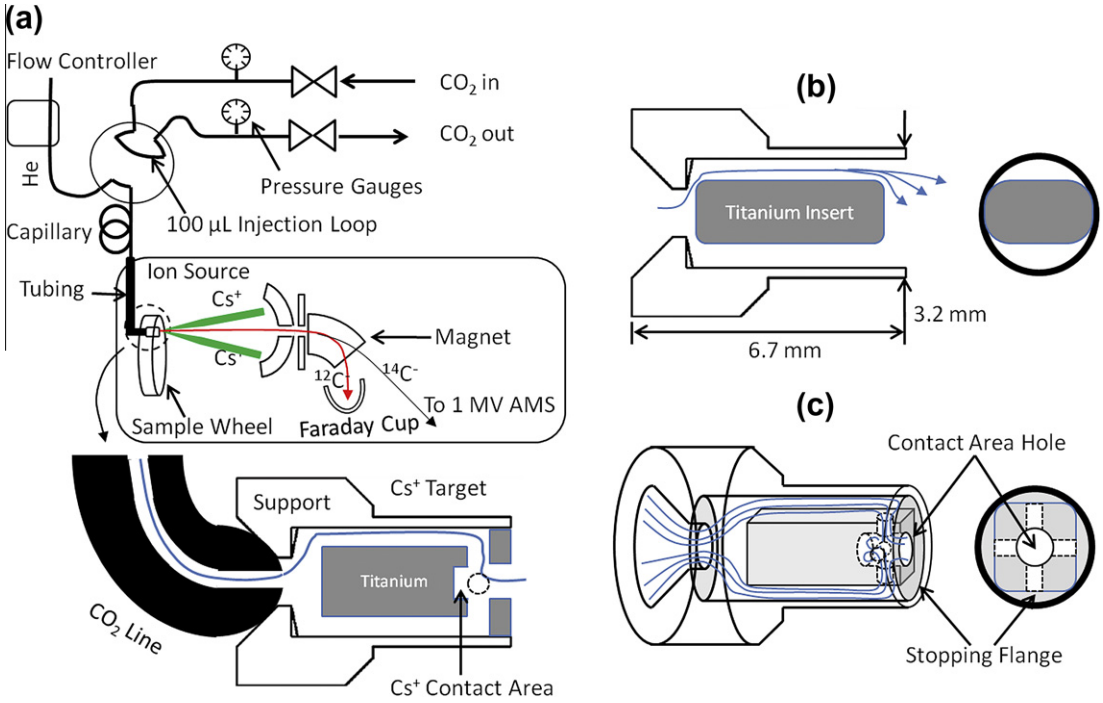

Fig. 1. Scheme of the experimental set-up. (a) Gas line connecting the CO_2 injection set-up with a target and a Cs^+-beam target (green), producing a beam of C^- (red). Gas targets consisting of an Al support and a Ti insert. (b) Diverging-flow configuration and (c) directed-flow configuration.