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Novel simplified absorption-catalytic method of sample preparation for AMS analysis designed at the Laboratory of Radiocarbon Methods of Analysis (LRMA) in Novosibirsk Akademgorodok

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ABSTRACT

A new absorption-catalytic method of sample preparation for AMS ^{14}C analysis has been designed. The semi-automatic graphitization equipment consists of catalytic combustion, selective absorption/desorption of CO_2 and graphitization zones. Sample combustion followed by CO_2 separation takes less than 30 min that allows plenty of samples to be processed in a short time. The average CO_2 conversion to graphite turned out to be 75%. Achieved value of background induced by contamination with contemporary carbon is about 1.2 pMC. The proposed method is reproducible according to results for the OX-I and OX-II oxalic acid standards measured from 2015 to 2018 and has been successfully used for dating lake sediments. The results agree with the data of other laboratories. The penetration of model aerosol particles inhaled at low dose by mice has been studied by means of the designed method.

1. Introduction

Accelerated mass spectrometry (AMS) is the exquisite method for the detection of long-lived isotopes at part-per-quadrillion sensitivities with good precision [1]. AMS is traditionally used for studying the past by means of radiocarbon dating: geology, paleoclimatology, paleontology, and archaeology [2–6].

In the last decade biomedical applications based on tracing ^{14}C-labeled compounds through natural systems *via* AMS have been developing [7–9] to elegantly solve complex problems including: the metabolic fate of drugs and viruses up to several months [10], the formation of carcinogen-DNA adducts [11,12], the penetration of model aerosol particles inhaled at low dose by mice [13] and cell renewal time [14,15]. Attomole sensitivity of AMS greatly reduces the chemical and the radiological dose required for isotope tracing enabling human studies to be implemented. Non-invasive diagnostics of *Helicobacter pylori* infection, bringing on gastritis, gastric and duodenal ulcers, through monitoring $^{14}CO_2$ in exhaled air by AMS following the administration of ^{14}C-urea with low level of radioactivity, can be conducted in children [16]. The cutting-edge trend in preclinical drug testing is a microdosing technique allowing the metabolism of subpharmacological amount of radiolabeled drug to be studied *in vivo* [10]. Very early microdose studies in healthy volunteers enhance value of a drug's selection for subsequent development, and lead to a reduction in animal use, without compromising the scientific quality of the data obtained [17].

Wide use of AMS ^{14}C for biomedical applications, associated with analyzing a huge number of samples, requires fast and simple procedure of sample preparation and analysis. The most common approach for the sample preparation is the conversion of organic samples to thermally and electrically conductive graphite for generating an intense ion beam when exposed to a cesium sputter ion source [18]. Graphite production can be performed independently of the expensive accelerator time and far from the possible contamination of unrelated samples [19]. Organic samples are traditionally

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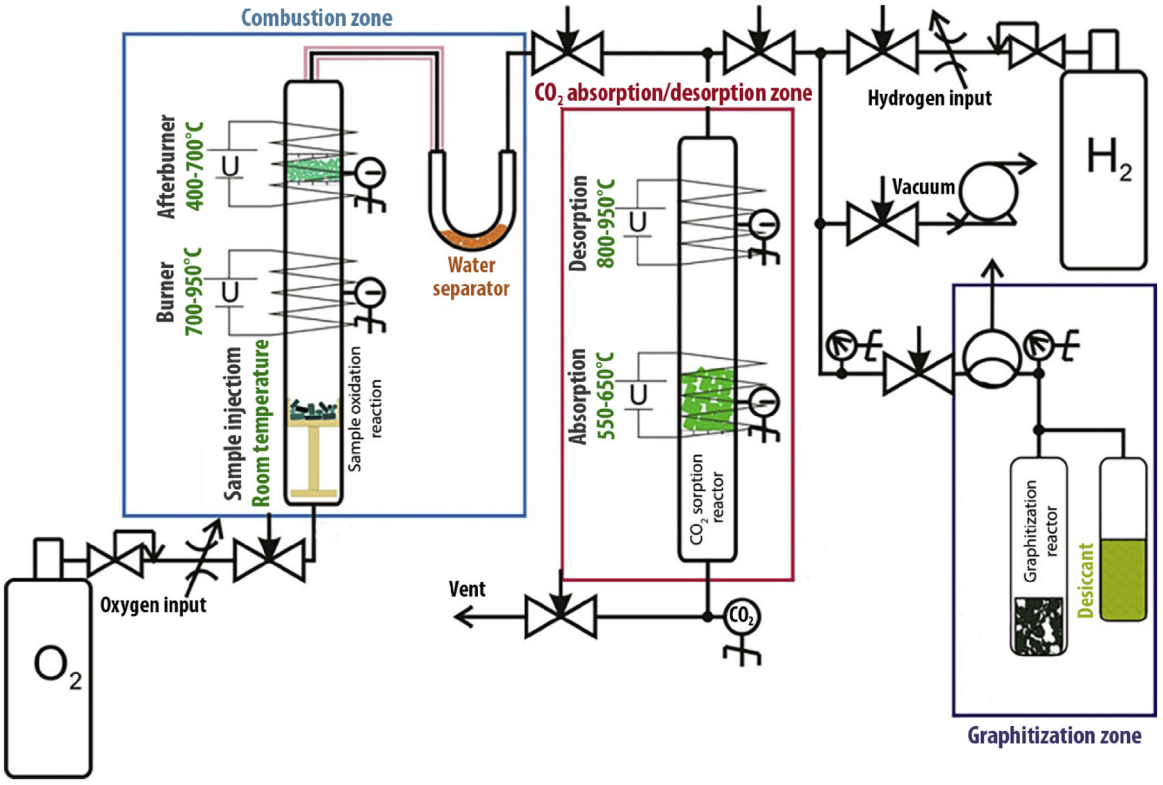

Fig. 1. The scheme of the semi-automatic device for sample preparation.

converted to graphite as follows: solid or liquid tissue is dried, oxidized to carbon dioxide, CO_2 gas is separated from impurities and reduced to graphite [20]. Dried organic samples are typically combusted in sealed quartz tubes containing CuO at 900 °C for an hour [21]. Carbon dioxide purified by means of passing through a series of cryogenic traps followed by the conversion to graphite commonly produced by the "overnight" reduction of CO_2 by hydrogen or zinc over an iron catalyst [22–25]. Multi-stage graphite production is time and resource consuming step of AMS analysis. The modern and convenient approach for sample preparation is to use of an elemental analyzer for sample combustion and gas separation [26], however sample analyzer is a quite expensive device.

To simplify and cheapen the procedures mentioned above we suggest absorption-catalytic method of sample preparation. The main features of novel approach are fast catalytic combustion of the sample and "inverted" carbon dioxide purification representing one-step CO_2 separation from oxidation products by means of the selective absorbent. Detailed description of the semi-automatic equipment and protocol of sample preparation is presented below.

2. Methods

The scheme and photograph of the semi-automatic device for sample preparation are shown in the Figs. 1 and 2, respectively. The device operates in a semi-automatic mode in the similar way described in [27,28]. Sample preparation is carried out as follows.

2.1. Catalytic combustion of the sample

The combustion reactor is the quartz tube with an internal diameter of 8 mm and a length of 60 cm placed in the cylindrical furnace. The afterburning catalyst is loaded on the top of the quartz tube. The quartz crucible with 5–10 mg of the sample is placed in the cold zone (20–25 °C) of the combustion reactor by an iron pin. The system consisting of reactors for the sample oxidation and CO_2 sorption is blown through with pure oxygen to remove any residual carbon from CO_2 sorbent and afterburning catalyst. Gas flow rate of about 30 ml/min being maintained constant during sample combustion by means of solenoid valves. Before sample combustion, the CO_2 sorption quartz reactor is moved down from the desorption zone (800–950 °C) to the sorption zone (550–650 °C), provided zero CO_2 signal is observed by the carbon dioxide output sensor. Then the sample is moved up to the hot zone (600–950 °C) by means of the magnet to burn. The products of incomplete combustion are subjected to afterburning in the catalytic combustion zone at 700–400 °C by the catalyst ICT-12-8 kindly provided by JSC "Katalizator" with 5 CuO : 10 Cr_2O_3 : 20 $CuCr_2O_4$: 65 Al_2O_3 percent composition by mass allowing carbon, CO and other pyrolysis products to be completely oxidized even in the presence of chlorine and sulfur compounds [29,30]. The capacity of the catalyst to absorb SO_2 forming sulfates of aluminum and copper at operating temperatures of 400–500 °C is a significant advantage when working with bioorganic samples containing a lot of sulfur. The combustion method described above provides the complete and rapid combustion (10–15 min) of any organic sample including even the pitch coke. The products of complete combustion pass through the thermally insulated line to the separator of water and heavy-boiling compounds representing a U-shaped tube placed into crushed ice/NaCl mixture having the temperature of −20 °C. After that the gaseous mixture runs to the CO_2 sorption reactor.

2.2. Selective absorption of CO_2

2 g of the selective CO_2 sorbent based on CaO designed earlier [31,32] is placed to the quartz tube with an internal diameter of 8 mm and a length of 60 cm equipped with two cylindrical outer furnaces. The temperature of furnaces is set 550–650 °C and 800–950 °C in the absorption and desorption zones, respectively.