

GAS INLET SYSTEM FOR AN ACCELERATING MASS-SPECTROMETER

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The work thoroughly describes a complex facility developed at the Institute of Applied Physics NAS of Ukraine to obtain rectified carbonic oxide (CO_2) of various origins from carbon-bearing objects (archeological artefacts, natural environments, objects of cultural heritage, biomedical and pharmacological objects). CO_2 after a direct inlet in a gas carrier (helium) through a capillary system into an ionizer of an accelerating mass-spectrometer (AMS) provides highly accurate analysis of a gaseous phase test sample for carbon ^{14}C isotope. Two basic sample preparation techniques for carbon-bearing objects were compared to be analyzed by the AMS technique: a traditional graphitization and more modern gas inlet technology. The advantage of the latter is shown for a quick test of a trace amount.

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1. INTRODUCTION

Detection, extraction and qualitative estimation of trace quantity of a radioactive material are the subject of modern analytical radiation chemistry. Minor isotopes present in samples in $10^{-12} \dots 10^{-15}$ of basic isotopes concentration are difficult to detect and estimate qualitatively. This problem may be solved mainly with a highly sensitive and very informative method of a mass-spectrometric analysis, an accelerating mass-spectrometry (AMS), in particular.

Mass-spectrometric analysis of a substance is based on separation and registration of atoms or molecules in ionized state by their mass/charge ratio (m/q). Despite its strong contribution to solution of wide variety of analytical problems, some fundamental and technical tasks remain unsolved in a traditional mass-spectrometry. They include insufficient sensitivity, limited resolution, separate registration of isobars and molecule ions that coincide in mass with an isotope measured.

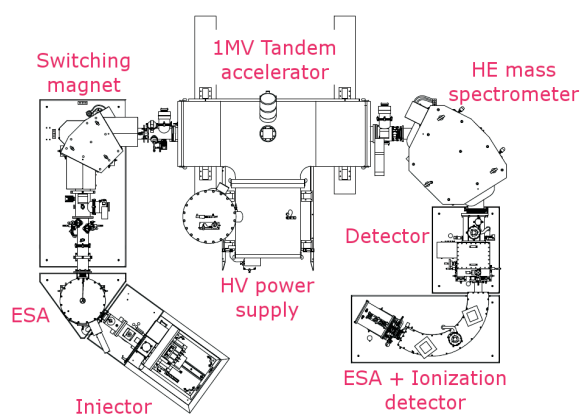
Measurement of rare isotope that are $10^{-12} \dots 10^{-15}$ of concentration of base long-lived cosmogenic radio nuclides, for instance, with current concentration independent of initial content in the Earth belongs to specific tasks requiring a mass-spectrometry of high resolution and sensitivity [1-3].

AMS is advantageous in high sensitivity, capability of operating with trace amounts of a sample, flexibility and tunability to different tasks [4]. Accelerating mass-spectrometry studies rare isotopes of long half-life without considerable radioactivity (for instance, ^{10}Be , ^{36}Cl , ^{41}Ca ($t_{1/2} = 1.04 \cdot 10^5$) [1].

Accelerating mass-spectrometer Tandetron 1.0 MV 4110Bo – AMS created by High Voltage Engineering Europe (the Netherlands) at the Institute of Applied Physics (IAP) NAS of Ukraine, Sumy (Common Use Center "Accelerating Mass-Spectrometry") is a compact, flexible and tunable [5, 6] facility of new generation to obtain accurate data on samples of milligram and submilligram weight (Fig.1,a,b). The AMS technique allows qualitative analysis of radioactive and stable long-live isotopes of high absolute (10^{-12} or ppt) and relative ($10^{-14} \dots 10^{-15}$) sensitivity [4]. The facility has some new authentic engineering solutions realized to compare favourably with its forerunners. For instance, elimination of molecule noise (it is $^{12}CH_2$ and ^{13}CH for ^{14}C test) is preliminary achieved not by high charge state and accelerating potential but by an ion charge exchange chamber and high density of rough gas. In general, suppression of isobars and molecular ions is observed in an ion source, in a charge exchange chamber of an accelerator and in a detection chamber in a detecting system. High resolution at isotope detection considerably surpasses resolution of mass spectrometers operating under all conventional ion separation schemes. "Hybrid" ion source (model SO-110) analyses a sample in solid and gaseous state, as well [7].

Technology of gas inlet used here eliminates a complicated and cumbersome common process of graphitization. In particular, this express-method may be used in pharmacology and other biomedical AMS applications [7, 8]. A ^{14}C isotope test in AMS is based on a total carbon fraction obtained from a sample as gaseous carbon oxide (IV) (CO_2).

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a



b

Fig.1. Accelerating mass-spectrometer Tandetron 1.0 MV 4110Bo – AMS: a) block-diagram; b) general view

Before CO_2 extraction, the sample requires primary cleaning by consecutive mechanical separation of macro- and microimpurities and by chemical acid and alkali pretreatment [4]. Then, depending on whether the sample is of organic or carbonate (mineral) nature, it is either burnt (as organic) or decomposed by acids (as carbonate). Organic materials are burnt in vacuum quartz vessels in the presence of copper oxide (II) (CuO) as an oxygen source or in relevant vessels for organic burn-up of conventional element analysers widely used in organic chemistry. Obtained CO_2 is purified from impurity gases, in particular, from nitrogen oxides, halogen, oxygen via a filter system, absorbers (silver wire, $PbCrO_4$ etc.) and cryogenic technology with liquid nitrogen for carbon dioxide freezing and turbomolecular as well as dry forevacuum pumps for residual gas venting.

Most laboratories use graphitization technology that is difficult to realize, since the facility consists of high melting gas, precision vacuum locks (quartz or metal), vacuum-meters, temperature controllers, pipe furnaces for 400 and 600°C heating, Peltier

elements, and must hold residual pressure up to $5 \cdot 10^{-2} Pa$.

By contrast with graphitization technology, gas inlet does not provide a solid-phase carbon; purified CO_2 is fed directly into an ionization source that makes the process cheaper and less cumbersome, though degrading analysis accuracy to some extent [9,10]. Still, many AMS laboratories today improve this approach and achieve impressive results [8,11]. Note, that for dating and chronological analysis, graphitization technology is primarily applied; while for biological AMS applications a gas inlet has found wider application [12-15]. The main disadvantage of the gas inlet is lower negative ion current that conditions prolonged measurement time and lower measurement accuracy as compared to that of solid-phase samples. Among advantages of the gas inlet are lower mass of a sample required for representation of results, lower time for a sample preparation [11]. Still, in Switzerland, at a facility MICADAS (MINI-Carbon System) permitted parameters that allowed elimination of a gap between techniques of graphitization and gas inlet during analysis of gaseous samples of 1...50 μg ; thus, amount of ^{14}C may be defined in samples on the level of tens of nanograms [16,17].

One of the achievements of the gas inlet used in AMS, apart from medical proteomics issues, is a need in development of highly sensitive tracing techniques for protein and its metabolism products or post-translational modification in vivo. Researchers from the Center for Accelerator Mass-Spectrometry, Lawrence Livermore National Laboratory (the USA) showed that LS-AMS facility specifications permit ^{14}C amount measurement in submicrogram (10...21) amount of protein. Comparison of conventional graphitization and gas inlet technologies has shown their complete coincidence. Still, productivity of the gas inlet technique is notably higher than that of conventional graphitization [18].

Considering the above mentioned, IAP NAS of Ukraine have firstly developed a complex facility for AMS sample preparation. The system unites two technologies for sample preparation in one facility via combination of a furnace for high temperature combustion of organics (Fig.2)

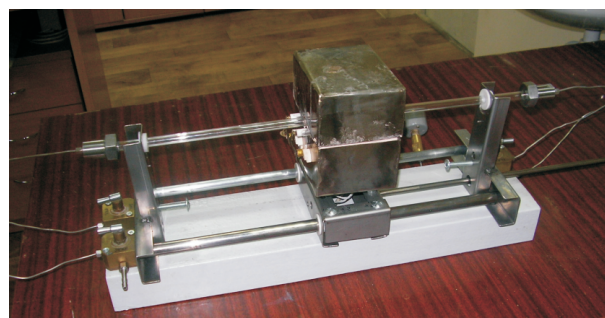


Fig.2. Furnace for high temperature combustion of organics as a part of a complex facility for AMS sample preparation (IAP NAS of Ukraine)

with a CO_2 purification unit based on a gas chromatograph ("Selmichrom-1", JSC SELMI, Sumy, Ukraine), with a subsequent inlet of gas-phase CO_2 into an ioniser of an accelerating mass-spectrometer with an "off-line" mobile system of CO_2 accumulation (Fig.3).

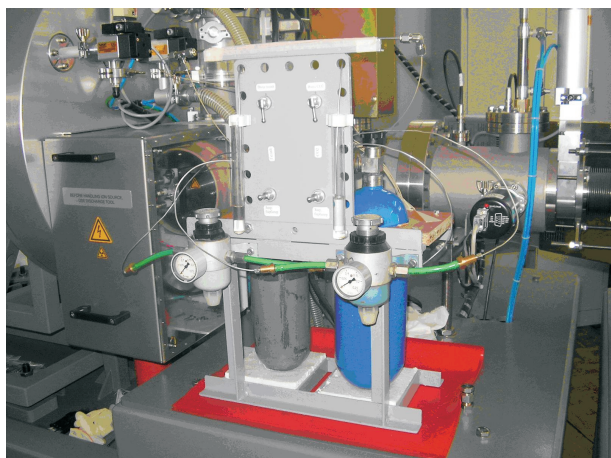


Fig.3. A system of AMS gas inlet in a mass-spectrometer Tandetron Model 4130-AMS

2. DESIGN FEATURES OF THE FACILITY

Fig.4 shows the facility developed for samples combustion and conversion of the obtained carbon into carbon dioxide with its subsequent inlet into an accelerating mass-spectrometer Tandetron Model 4130 – AMS that detects ratio of ^{12}C , ^{13}C , ^{14}C . Gaseous and solid-phase organic samples of 0.1 mg with carbon isotope ^{14}C are an essential part of the analytical process on its content definition with the AMS technique. Here organic compounds are burnt in oxygen in a vacuum furnace; then obtained carbon dioxide is introduced into a gas inlet system (gas inflow) or into a CO_2 graphitisation system (for solid-phase target samples to be obtained). A system of sample preparation comprises elements of quartz and stainless steel 12X18N10T, sealing parts, precision vacuum locks, gas pneumatic switches, temperature controllers, pressure gauges, pipe furnaces 400...1200°C heating. Vacuum part of the system holds the pressure of $5 \cdot 10^{-2} Pa$. Dry fore-vacuum pumps of Pfeiffer type (Germany) are required for high vacuum without any carbonic impurities in the system.

A facility for sample preparation comprises: a high vacuum furnace (A) with a reactor (1) and two quartz tank sections (2). A carbon-bearing sample is placed into one section, copper oxide (II) (CuO uhp, Sigma-Aldrich, USA) is put into another. Operating mode of the furnace may be changed by a gas flux switch (3) (extraction of a sample from a cuvette/high vacuum pumping), temperature controller (4), furnace heater (5), cylinder with inert gas (He) (6), high vacuum port (7), and high vacuum lock valve (8).

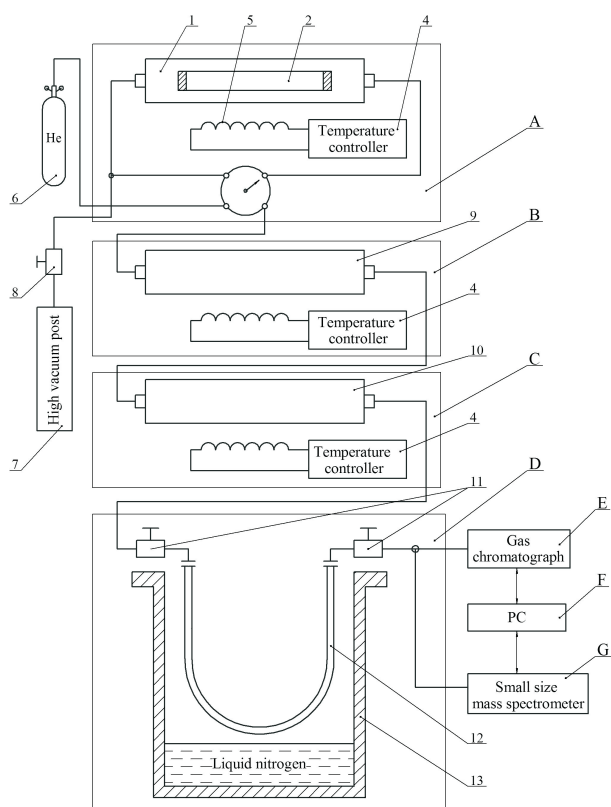


Fig.4. Diagram of a facility for a sample combustion: Unit A : high vacuum furnace; (1) – reactor; (2) – joint cuvette; (3) – gas flux switch; (4) – temperature controller; (5) – furnace heater; (6) – cylinder with inert gas (He); (7) – high vacuum post; (8) – high vacuum valve. Unit B : filter-drier – (9). Unit C : purification filter – (10). Unit D : a sample accumulator: high vacuum valves – (11); a freezing loop – (12); vessels with liquid nitrogen – (13). Unit E : gas chromatograph. Unit F : PC. Unit G : small size mass spectrometer

A sample is burnt in an evacuated reactor of the furnace and the cuvette with copper oxide (II) is heated. CuO is used for oxygen production to oxidize carbon in the sample; - a filter-drier (B) comprising a container with silica gel (9) and a temperature controller (150°C). The filter-drier is intended for water vapour catch. An electrical heater purifies the filter from water vapor accumulated; - filter for halogenic compounds (B) comprising a container filled with silver threads (wool diameter 0.05 mm, 99.9% trace metals basis, Sigma-Aldrich, USA) heated up to 700...800°C; - a sample accumulator (D) comprising a freezing loop (12), high vacuum valves (11), vessels with liquid nitrogen (13). CO_2 comes into the freezing loop that is in vapours of liquid nitrogen and settles on its walls at temperature below - 50°C. Accumulated CO_2 is collected in the loop. The loop can be immersed into the vessel with liquid nitrogen at various depths thus the temperature in the freezing loop may be varied. A platinum temperature controller measuring temperature on the loop surface is provided in the facility design; - a gas chromato-

graph (E) for qualitative CO_2 content in the sample accumulator; - a PC (F); - a small size mass spectrometer (G) detecting impurities in a sample and ratio of $^{12}C/^{13}C$.

A small size mass spectrometer on permanent magnets was developed at IAP NAS of Ukraine [19,20]. The mass spectrometer (Fig.5) is a one stage static magnet facility of 60 mm radius, a 120° turn angle, an input beam and output beam angles of 30° and a mass-analyzer arm of 51.6 mm. The facility records a mass range of 11...45 a.m.u. with resolution of 200. Isotope sensitivity threshold is at least equal to 10^{-4} . Dimensions with an electronics module are $(300 \times 450 \times 450) mm^3$. Energy consumption is less than 60 W. Mass is 30 kg.

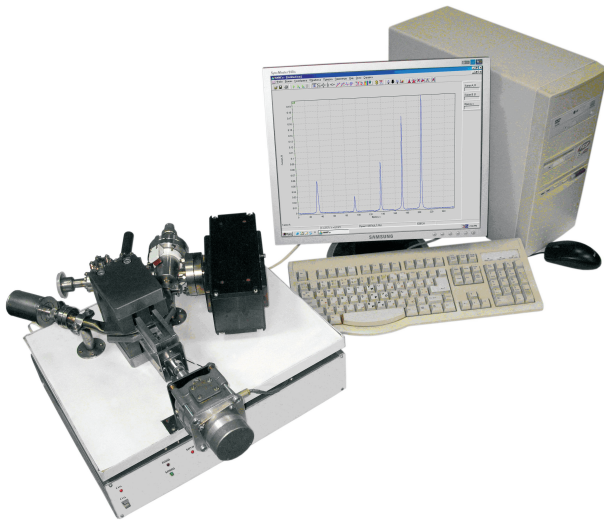


Fig.5. General view of a small size mass spectrometer

3. MEASUREMENT PROCEDURE

Since ^{13}C is about 1% of the total amount of carbon in a sample, the ratio $^{13}C/^{12}C$ may be precisely measured with a traditional mass-spectrometry [21]. Ratio $^{13}C/^{12}C$ and $^{14}C/^{12}C$ in plants differ from that of the atmosphere because of different absorption efficiency of three carbon isotopes. This effect is named as isotope fractionation [21, 22]. For a degree of fractionation in some sample to be defined, amount of both isotope (^{12}C and ^{13}C) is measured and the obtained ratio $^{13}C/^{12}C$ is compared to a standard ratio known as PDB (Pee Dee Belemnite). Fractionation at radiocarbon dating is estimated by ratio $^{13}C/^{12}C$, since ratio of stable isotopes ^{13}C and ^{12}C remains constant with time after metabolic block. Basic ratio $^{14}C/^{12}C$ (observed in a living body by the time of death) may be derived from it: degradation of a sample of ^{13}C as compared to ^{12}C is proportional to difference of atomic weight of two isotopes; therefore, a degradation of ^{14}C is twice higher than that of ^{13}C [21]. Fractionation of ^{13}C marked as $\delta^{13}C$ is calculated as [22]:

$$\delta^{13}C = \left(\frac{\left(\frac{^{13}C}{^{12}C} \right)_{sample}}{\left(\frac{^{13}C}{^{12}C} \right)_{PDB}} - 1 \right) \times 1000\%. \quad (1)$$

Since standard PDB has an extremely high rate of ^{13}C ($^{13}C/^{12}C$ PDB = 11,2372%), measured sample values of $\delta^{13}C$ are mostly negative.

Typical values of $\delta^{13}C$ were experimentally found for many plants and for different parts of animals like ossein; however, when a particular sample is studied, reference data should not be used but value of $\delta^{13}C$ is required to be measured directly.

The loop with the sample analyzed in the small size mass spectrometer is transferred to an analytical unit of the accelerating mass-spectrometer (Fig.6); then an outlet of the sample accumulator is connected through the gate G1 to a gas pipe line of an inflow block IB1.

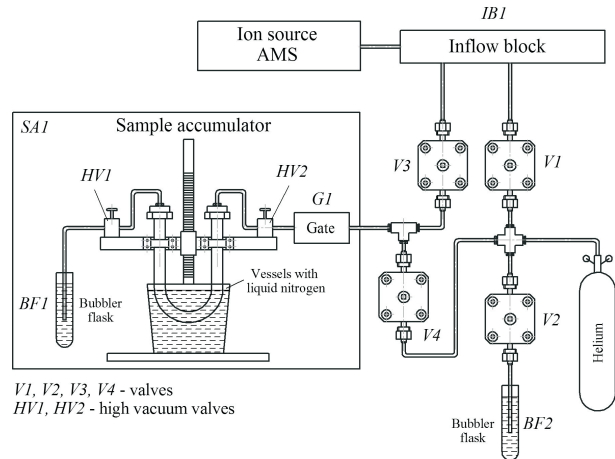


Fig.6. Block of a sample accumulator

The loop with the sample is immersed into vapour of liquid nitrogen and then is cleared with helium during 5 min (flow is $30 cm^3/min$) to evacuate air occurred in the gas pipelines during the sample accumulator transportation to the mass-spectrometer. The clearing process is controlled over the presence of bubbles in a bubbler flask BF1. Helium is driven into the inflow block through the valve V1 (flow is $5 cm^3/min$). The clearing process is controlled over the presence of bubbles in the bubbler flask BF1. The freezing loop is removed from liquid nitrogen vapour and the heater. The valve V3 drives a CO_2 test sample into the inflow block of the mass-spectrometer that is set into a measurement mode. A general rule for gas inlet techniques regardless of method of sample combustion and cleaning (laser ablation, gas-liquid chromatography, hydrolysis, high-temperature combustion) is as follows: CO_2 inflow flux should not exceed $3 \mu l/s$. Higher or lower flux (regardless of a gas carrier) may result in a vacuum failure or an ionizer malfunction. Constant flow of analyzed gas of $3 \mu l/s$. (at 1 atm) is maintained by an adjusted length and diameter of an inlet capillary [18] set in the facility design by a manufacturer. Concentration ratio of helium and CO_2 coming into a measuring loop of the mass-spectrometer depends on design of the inflow block.

4. CONCLUSIONS

The work presents theoretical and applicable issues of gas inlet techniques as promising approach to a sample preparation for accelerating mass-spectrometry (AMS). The described technique is based on a direct input of CO_2 test sample preliminary purified into an ionizing block. Specifications were described for a complex facility developed at the Institute of Applied Physics NAS of Ukraine to obtain rectified carbonic oxide (CO_2) of various origins from carbon-bearing objects of (archeological artefacts, natural environments, objects of cultural heritage, biomedical and pharmacological objects). Two basic sample preparation techniques for carbon-bearing objects were compared to be analyzed by AMS: a traditional graphitization and more modern gas inlet technology. The advantage of the latter is shown for a quick test of a trace amount.

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СИСТЕМА ГАЗОВОГО ВВОДА ДЛЯ УСКОРИТЕЛЬНОГО МАСС-СПЕКТРОМЕТРА

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Подробно охарактеризована разработанная в Институте прикладной физики НАН Украины комплексная установка, предназначенная для получения из углеродсодержащих образцов различного происхождения (археологических артефактов, объектов окружающей среды, предметов культурного наследия, биомедицинских и фармакологических препаратов) очищенного диоксида углерода (CO_2). Полученный CO_2 посредством прямой подачи через систему капилляров в потоке газа-носителя (гелий) в ионизатор ускорительного масс-спектрометра (УМС) обеспечивает возможность проведения высокоточного количественного анализа газофазной пробы на содержание изотопа углерода ^{14}C . Проведено сравнение двух основных технологий пробоподготовки углеродсодержащих образцов для анализа методом УМС: традиционной графитизации и более современной технологии газового ввода, и показано преимущество использования последней для экспресс-анализов микроколичеств образцов.

СИСТЕМА ГАЗОВОГО ВВОДУ ДЛЯ ПРИСКОРЮВАЛЬНОГО МАСС-СПЕКТРОМЕТРА

С.В. Новіков, А.Г. Рябишев, О.В. Запорожець, А.А. Яновська, В.Б. Москаленко, А.В. Бойченко, В.М. Ковальчук, А.М. Калинин, В.Д. Чиванов, С.М. Данильченко, В.Ю. Сторіжко

Детально охарактеризована розроблена в Інституті прикладної фізики НАН України комплексна установка, призначена для отримання із зразків різного походження, які містять вуглець, (археологічних артефактів, об'єктів оточуючого середовища, предметів культурної спадщини, біомедицинських та фармакологічних препаратів) очищеного диоксида вуглецю (CO_2). Отриманий CO_2 шляхом прямої подачі через систему капілярів у потоці газу-носія (гелій) в іонізатор прискорювального мас-спектрометра (ПМС) забезпечує можливість проведення високоточного кількісного аналізу газофазної проби на вміст ізотопу вуглецю ^{14}C . Проведено порівняння двох основних технологій пробопідготовки зразків, які містять вуглець, для аналізу методом ПМС: традиційної графітизації і більш сучасної технології газового вводу, та показано переваги використання останньої для експрес-аналізів мікро-кількості зразків.