Radiochemical separation and analytical determination of ^{10}Be from proton-irradiated graphite targets

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Summary. High-concentration samples of carrier-free ^{10}Be (up to $1\ \mu\text{g } ^{10}\text{Be}$ per gram graphite) were separated from proton-irradiated graphite targets used at the meson production unit of the Paul Scherrer Institute (PSI). ^{10}Be concentrations were determined both with accelerator mass spectrometry (AMS) and inductively coupled plasma mass spectrometry (ICP-MS). The analytical results from both methods are in good agreement. The highly enriched ^{10}Be -samples will be used in scientific experiments relating to basic nuclear research and nuclear astrophysics in the framework of an international collaboration aimed to exploit accelerator waste material for scientific applications.

Introduction

Until recently, minimal concerted effort has been directed in a program to extract and utilize radionuclides from activated components of particle accelerators. This is mainly the result of the small amounts of suitable irradiated material available. However, with the construction of new large accelerator facilities, spallation neutron sources and radioactive-beam facilities, inventories of activated materials are required from the authorities regarding the waste management. For that purpose several years ago investigations were initiated with the aim of determining the main (γ -ray) activity content of representative targets, shielding materials and beam-dumps of the accelerator facilities at PSI. The potential of these materials as a source for long-lived radionuclides was assessed. ^{60}Fe , ^{26}Al , ^{10}Be and many others were found to be present in considerable amounts [1].

Since PSI operates the most powerful proton accelerator facility in Europe, the “mining of accelerator waste” for long-lived radionuclides seems to be a viable option. In 2006, an initiative called ERAWAST (Exotic Radionuclides from Accelerator Waste for Science and Technology [2]) was started to establish collaboration between several production sites and a user community which is interested in

these rare radionuclides. Among others, Be radionuclides are of great interest in several research areas of nuclear physics and astrophysics as well as in the AMS community where ^{10}Be standard reference materials (SRM) are required. Proton-irradiated graphite targets used at PSI for muon production contain considerable amounts of ^{10}Be . Several irradiated targets are now available and have been analysed for their ^{10}Be content. ^{10}Be -enriched samples are foreseen for application in several scientific experiments.

The work presented here has two aspects. At first, due to the requirements for an intermediate or final disposal, data on the radionuclide inventory of dismantled graphite targets are requested at PSI. Therefore, reliable analytical methods had to be developed for the determination. While samples with relatively small amounts of ^{10}Be can suitably be determined by AMS, for highly enriched samples ICP-MS is the better choice. AMS measurements require in any case the addition of a known amount of stable isotopic carrier, presence of which can also be utilized for the application of special separation techniques, in particular for precipitation procedures, if the quantitative determination of the radionuclide content is the only aim of the separation. However, secondly, we intend to provide suitable amounts of long-lived radionuclides for scientific experiments in the framework of the ERAWAST collaboration. In most of these applications, highly enriched carrier-free samples are necessary, because presence of stable beryllium would effect the measurements. The content of these samples also should be analysed – in these cases by ICP-MS. Since this method requires relatively high amounts of sample material, the best way is to take aliquots directly from the separated samples foreseen for scientific purposes. Therefore, the aim of our work is to describe and compare these two completely independent determination methods including both the measurement technique and the separation procedures.

Experimental

Description of the irradiation equipment

The PSI cyclotron facility provides a high intensity proton beam of 1.8 mA with an energy of 590 MeV. At the two consecutive meson production targets “M” and “E”, the primary

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Fig. 1. Target E unit showing the beam direction and the two locations, from which samples were taken.

proton beam generates intense secondary beams of pions and muons, which are then available for research in particle physics and muon-spin-resonance applications. Downstream of the meson production targets, the proton beam is either defocused and stopped in a beam dump, or refocused and guided to the target of the spallation neutron source SINQ.

The target E station (shown in Fig. 1) consists of a truncated cone of polycrystalline graphite, cooled by thermal radiation. The length of the target in the beam direction is either 60 mm (10.7 g/cm²) or 40 mm (7.1 g/cm²) depending on the intensity requirements of the SINQ facility. Beam losses are up to 43% due to elastic and inelastic reactions in the target and in the shaping collimators.

Sample description

General exposure times of the graphite targets are 1 to 3 years. They become available for analysis after a cooling time of at least 2 years. The integrated beam dose over the irradiation period varies from 4 to 11 Ah (590 MeV proton beam). The main activation products, which persist after the

cooling off time of several years waiting for the decay of ⁷Be (54 days half-life), are ³H (12.3 years), ¹⁴C (5.730 years) and ¹⁰Be (1.5 Ma).

Measurements of the ¹⁰Be separated from graphite were carried out using two different methods; ICP-MS and AMS. Both methods require the addition of the stable carrier isotope, ⁹Be, in known amounts, because these analyses are based on the measurement of isotopic ratios.

In contrast, samples foreseen to be useful for certain nuclear-based scientific purposes require a procedure which extracts ¹⁰Be without addition of ⁹Be. Therefore, two independent separation methods based on aqueous solution chemistry were developed.

Four different targets were analysed. For each target, one sample came from the outer part (o) (beam entrance). Additionally, one sample each was taken from the inner parts (i) of the targets 1 and 2, respectively, where no direct beam contact took place (see Fig. 1).

Separation procedure for analytical samples (AMS)

Four samples for AMS measurement were prepared, 2 from outer and 2 from inner target positions (see Table 1).

About 20–30 mg of carbon were dissolved in a HNO₃/HCl/HClO₄ mixture while stirring under heating for several hours. 2 mg of ⁹Be were added to each sample. After complete dissolution, Be(OH)₂ was precipitated with diluted ammonia solution and then re-dissolved by addition of HNO₃. The samples were purified by ion exchange on a DOWEX 50 column from boron (¹⁰B is an interfering isobar in ¹⁰Be analysis) as described in [3]. Elution of Be can be performed with diluted HCl solutions in a concentration range of 1–4 M. Due to the relative high expected content of ¹⁰Be, further dilution of these final solutions with stable Be was necessary in order to obtain isotope ratios suitable for AMS measurement. This was done by setting up dilution series in correspondence to the expected ¹⁰Be content. After a second precipitation step, the hydroxides were calcined at 900 °C to form the BeO, the sample form required for insertion into the AMS ion source.

Separation procedure for highly-active carrier-free samples and ICP-MS determination

From every outer sample taking position a sample using carbon target material in gram amounts was prepared. These samples were foreseen both for application purposes and ICP-MS measurement.

5–14 g of carbon were pulverized with a ball mill and then treated with a mixture of HNO₃/HClO₄/H₂SO₄ in a three-neck flask under stirring and heating for several hours. ⁷Be was added to monitor the chemical yield. The outgoing gas flows through a Ba(OH)₂ solution in order to adsorb the carbon dioxide. The remaining solution containing the beryllium and tritium was filtered. Fe³⁺ was added and beryllium hydroxide was co-precipitated together with iron hydroxide by use of ammonia solution. The Fe(OH)₃ was dissolved in 7 M HCl and the iron separated by use of an anion exchange column. After evaporation to dryness and re-dissolving in diluted HNO₃, purification was achieved by the procedure described above for the AMS samples.

Aliquots from these final solutions were mixed with carrier solution and the content of ^{10}Be was determined by ICP-MS.

Measurement techniques

The AMS measurements were carried out at the 6 MV van-de-Graaff EN tandem accelerator at the Institute of Particle Physics at ETH Hngerberg. Typical isotopic ratios detected with this method range between $^{10}\text{Be}/^9\text{Be} = 10^{-14}$ – 10^{-9} . Higher concentrations of ^{10}Be can lead to serious contamination of the facility. Because of this, AMS is suitable mainly for low activity samples. One way to measure highly active samples is dilution, but since a dilution factor of about 10^3 or higher would be necessary for some of the “hot samples” to reach the required activity level, this is not a real option for a routine analysis due to the high risk of cross contamination. Therefore, this possibility was taken into consideration only for two of the highly active samples in order to check the reliability of the methods. Therefore, no samples were prepared from the outer wheel parts of targets 1 and 4.

The samples with high expected content of ^{10}Be were measured with ICP-MS at the PSI Hotlab (Laboratory for Materials Behaviour). The detection limits were determined by repeated measurements of blank solutions and were 200 ng of ^{10}Be , due to the relatively high background of ^{10}B , which cannot be separated from ^{10}Be with the mass resolution of the ICP-MS. All 4 high-activity samples from the outer part of the wheels were analyzed by this method.

Results

Table 1 shows the analytical results for the determination of the ^{10}Be content from the 6 graphite target samples. The values are given in Bq/g, which means the activity of ^{10}Be in relation to the amount of sample material (ie the mass of the graphite sample). For both methods, an overall measurement error of 10% was estimated, which consists of the error of the measurement itself, the errors in the sample preparation and dilution procedures as well as a background correction.

For those samples where both AMS and ICP-MS measurements were undertaken, ie the outer part samples 2o and 3o, the results determined by both methods agree well with each other and therefore show the reliability of the analytic

methods as well as confirm the selected separation techniques. Detailed analyses of further graphite targets should be carried out in the same manner: highly active samples with ICP-MS, low-content probes with AMS.

In the preparative separations without stable carrier (samples 1o, 2o, 3o and 4o), chemical yields based on ^7Be activities ranged between 35 and 50%. In column 4 of Table 1, the total amounts of ^{10}Be -atoms for the outer position samples are shown, which can be used for experimental purposes. For the planned scientific experiments, described below, this separation efficiency is sufficient. However, for systematic determinations of the radionuclide inventory of the graphite targets aimed to characterize these materials with respect to a final or intermediate disposal, the separation methods have to be optimized. These studies will also cover measurements of the tritium and ^{14}C content and will allow comparisons with theoretical predictions which are still under development.

Prospective applications of ^{10}Be -enriched samples

The half-life of ^{10}Be

AMS ratios of $^{10}\text{Be}/^9\text{Be}$ in environmental samples are nearly in all cases normalised to accepted standard reference materials which are either purchased commercially or prepared in-house. Given that the first family of $^{10}\text{Be}/^9\text{Be}$ AMS standards were prepared from enriched ^{10}Be solution (at the few percent level) and subsequently diluted, their nominal $^{10}\text{Be}/^9\text{Be}$ ratios were calculated from measured ^{10}Be specific activities prior to dilution and the amount of ^9Be (^{10}Be -free) added as a dilutant. Hence, the nominal AMS standard ratios are directly linked to the absolute value of the ^{10}Be half-life. Up till 1990, the accepted half-life for ^{10}Be was 1.51 Ma. In 1990, NIST released a certified $^{10}\text{Be}/\text{Be}$ ratio for a prepared standard material, SRM-4325, and in addition accompanied this SRM certificate with a new ^{10}Be half-life of 1.34 Ma. Challenges to this new half-life were reported soon afterwards [4]. Very recently new attempts have been made at indirectly measuring the absolute $^{10}\text{Be}/^9\text{Be}$ value of the NIST SRM 4325 and in turn, the ^{10}Be half-life [5, 6]. A definitive resolution for the ^{10}Be half-life debate awaits a careful and accurate measure of a ^{10}Be activity and a subsequent ^{10}Be atom concentration of the source material. Due to the criticality of the half-life value, influencing the ^{10}Be measurements world-wide, a remeasure of the ^{10}Be half-life is of high importance. For this task, a sufficient amount of sample material is essential, and with respect to this, providing high active ^{10}Be -samples such as we can obtain could contribute to these efforts.

Investigation of exotic nuclear structures by using a ^{10}Be beam

The properties of light exotic nuclei are one of the most interesting research topics in nuclear physics, especially their ability to form a neutron or a proton halo with a dilute mass distribution extending far outside the core of the nucleus. Halo nuclei generally have small binding energies and their excited states are unbound [7, 8]. Access to long-lived nuclei will open new opportunities to explore this promising

Table 1. Analytical results from several carbon targets and available amounts of ^{10}Be for scientific experiments; unit: [Bq/g carbon] – columns 4 and 5 indicate the total amount of ^{10}Be obtained from the respective sample and available for experiments (o – outer part of the target wheel - beam entrance; i – inner part of the target wheel – no direct beam contact).

Sample	^{10}Be [Bq/g] ICP-MS	^{10}Be [Bq/g] AMS	Total amount of atoms	Total amount in μg
1o	220 ± 22	–	6.7×10^{16}	1.1
1i	–	95 ± 10		
2o	291 ± 29	316 ± 32	8.4×10^{16}	1.4
2i	–	7 ± 1		
3o	506 ± 51	495 ± 50	6.5×10^{16}	1.1
4o	2049 ± 205	–	1.0×10^{18}	16.7

Fig. 2. New design of target E, operated from 2003 till end of 2005 (integrated proton beam dose: 25 Ah).

research area, for instance by use of a ^{10}Be beam. Among others, studies of nuclear potentials, charge-symmetry properties and spectroscopy of light and cluster nuclei will be possible using this new radioactive beam. First studies for beam development would require about 5×10^{16} atoms of ^{10}Be [9].

Laser-based studies of ^{10}Be charge radii

Breakup cross-section measurements on the helium, lithium and beryllium isotope chains by Tanihata [8, 10] showed strongly increased *matter* radii for ^8He , ^{11}Li and ^{11}Be which lead to the discovery of neutron-halo in the 1980s. Although these radii have been known for more than twenty years now, the *charge* radii measurements of these nuclei have become feasible just very recently due to the development of refined new techniques in on-line laser spectroscopy. From a comparison of these charge radii measurements to the neighboring non-halo isotopes, the effect of the halo-neutrons on the inner core can be studied. For measurements of the halo-nuclides in the beryllium isotope chain, a laser-based system will be used. This system consists of a desorption laser ion source in combination with a linear radio-frequency trap, a cooling and a spectroscopy laser. The study of the long-lived isotope ^{10}Be will be tested off-line using a highly enriched sample of 1×10^{15} atoms ^{10}Be [11].

Future sample taking and separation

An improved target design is shown in Fig. 2. The gaps allow unconstrained dimensional changes of the irradiated part of the graphite as well as a simple sample preparation for analytics and preparative separation. This target was in

operation from March 2002 till December 2005. Due to the extraordinary high accumulated beam dose (25 Ah), samples from this target will become available for chemical separation of ^{10}Be in the mg mass range after a cooling time of about 2 years.

For these prospective tasks, alternative separation methods concerning both analytical measurements and preparative isolation (e.g. combustion of the carbon or leaching of pulverized samples with diluted acids) should be also investigated.

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