ACCELERATOR MASS SPECTROMETRY WITH ^{14}C AND ^{10}Be IN UTRECHT

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The Utrecht facility for accelerator mass spectrometry is now in operation for routine measurements of ^{14}C and ^{10}Be in natural samples. Sample preparation techniques have been introduced. A 1% precision for ^{14}C/^{12}C ratios is routinely achieved. In the last year, more than 500 samples have been prepared and measured for various applications in archeology, geology and paleontology.

1. Introduction

The Utrecht facility for measurement of radionuclides, in particular ^{14}C and ^{10}Be, has been further developed and adequate precision for a large class of applications has been attained. The setup [1], based on an HVEC EN tandem accelerator, combines good beam transmission with the ability to measure the different isotopes in a rapidly alternating sequence.

The first measurements showed that, with such a setup, a stable measurement of isotope ratios was obtained: the ratios were not sensitive to slow variations in isotope production and beam transmission. Isotope ratios were measured with a stability of at least 0.5% over one hour runs. However, the reproducibility between samples of the same material turned out to be poor and to depend on a number of interrelated parameters. Some of these are associated with instrumental effects, but the dependence of the beam emittance on sample shape and composition turned out to be the dominant effect.

2. Instrumental developments

The asymmetric focusing of the 90° injection magnet has been corrected by means of field clamps so that symmetrical focusing in both the horizontal and vertical plane is achieved according to the original design. The resulting beam transport is better matched to the accelerator acceptance.

The current integrators which are used to perform the current measurement of a stable isotope during a short beam pulse (e.g. 0.1 ms for ^{12}C) have been redesigned. Two units have been made [2] which have each one single three decade input range. The linearity is better than 0.2% over the full range.

The beam emittance has been measured for several samples using a device with associated electronics according to Billen [3]. Variations of emittance due to change in position and composition of samples were observed. It has also been observed that with flat samples such differences are considerably reduced.

To facilitate future measurements with flat samples a new inverted sputter source has been constructed. The design is similar to that previously constructed [4] except that the vacuum at the sample surface is improved to 3×10^{-7} mbar and the sample can be scanned during measurement. The sample wheel contains 16 target stations which can be selected under remote control. The sample can be positioned with an accuracy of 0.1 mm [5].

3. Sample preparation

Preparation techniques have been introduced for carbon and for beryllium.

3.1. Carbon

The various types of parent material are submitted to sometimes delicate chemical processing [6] and finally combusted to CO_2. A graphitization system [7] has been installed to reduce CO_2 to graphite. It is based on the catalytic reduction of CO_2 at 920 K with finely divided iron powder in the presence of excess hydrogen. Complete reduction is obtained in less than 2 hours by forced circulation of the gases and condensation of water vapor at 200 K. The mixture of iron and graphite is pressed in a 2 mm^3 hole in an aluminum holder. These samples give a reproducible and stable C$^-$ beam. The yield is comparable with that from commercial graphite. Special attention is given to the ratio of Fe : C (2 : 1) and the flatness of the samples. Preparation by very old samples reproducibly yield an age limit of about 45k yr.

3.2. Beryllium

Chemical methods are used for the extraction and isolation of ^{10}Be from siliceous material. Depending on the amount of material needed to obtain measurable quantities of ^{10}Be two different methods are used. In both methods the material is firstly spiked with a known amount of ^{9}Be which largely exceeds the ^{9}Be in the sample itself. This spike is typically 1.00 g of a 1000 ppm solution of ^{9}Be and is used both to monitor the chemistry and later on to deduce the amount of ^{10}Be from the measured ^{10}Be/^{9}Be ratio.

Small samples (less than 3 g) are completely dissolved with conc. HF + $HClO_4$ at 400 K. Larger samples are processed via a leaching procedure to extract ^{10}Be from the outer layer of sediment grains. In this procedure the extraction occurs with HCl + $HClO_4$, also at 400 K, followed by repeated washing with HCl. Although the leaching procedure is attractive since it is less elaborate than the total dissolution method, it still has to be proven that a ^{10}Be extraction efficiency exceeding 95% can be routinely obtained [8].

Once the extraction is completed the beryllium is separated [9] from other more abundant elements (e.g. Al, Fe). The precipitate is twice treated with dilute HF and evaporated twice in the presence of $HClO_4$ to remove traces of ^{10}B. Finally Be(OH)$_2$ is precipitated from a HCl solution using NH_4OH (pH = 9) and oxidized in a platinum crucible at 1000 K. Mixed with silver powder (BeO : Ag = 1 : 5) it is pressed in an aluminum cup. With these BeO samples currents of about 100 nA are obtained.

4. Experimental method

In order to reduce the dependence of the emittance on differences in samples a limiting diaphragm is positioned behind the source. At the expense of a factor of 10 current loss reproducible tuning is obtained which does not critically depend on the sample used. Moreover, the cratering of the samples did not effect the isotope ratios during the measuring times used. This may be due to relatively small amounts of cratering during the periods of, at maximum an hour, and to the axial symmetry of the inverted sputter source used.

For tuning the stable isotope beam is used to optimize beam transmission from the source, through the accelerator, towards the final detection system. Beam profile monitors are used at several places in the beam line to inspect the beam centering. Fine tuning is carried out with the restriction that the beam transmission is unaffected by deflection of the beam over an angle of 20 mrad. This procedure is repeated for the stable isotopes in both vertical and horizontal planes. The so obtained settings also apply to the rare isotope.

Measurements of ^{14}C have been performed at a terminal voltage VT = 5 MV, using a foil stripper and selecting the 4$^+$ state. The 55% transmission obtained is entirely attributed to the stripping efficiency. A typical $^{12}C^{4+}$ current is 5 μA. The yields of the isotopes are measured in rapidly alternating beam pulses: ^{12}C and ^{13}C pulses of 0.1 and 0.9 ms, respectively, alternated with ^{14}C at a repetition rate of 10 Hz. The yields of the stable isotopes are measured in Faraday cups, while ^{14}C is counted in an ionization counter. The yields are digitized and, by means of an on-line PDP11/34 computer, converted into isotope ratios. Measuring periods varied from 20 to 60 min. During a period of one or two days calibration standards and backgrounds are repeatedly measured.

Comparison of the measured ratios of standards with their known values showed about 10% lower ^{14}C/^{12}C ratios and about 5% lower ^{13}/^{12}C values. These values are expected for mass fractionation in the sputter source [10] and the stripping process [11].

The background for ^{14}C lies within 0.2 and 0.6% Modern. Its origin is not understood yet. Tests with graphitization of enriched material showed that memory effects in this system are negligible.

From comparison with standards and correction for background normalized ^{14}C/^{12}C were obtained. These normalized ratios were used to obtain ^{14}C dates, taking into account corrections [14] for isotope fractionation, determined from δ^{13}-values [13] in a conventional mass spectrometer.

The ^{10}Be measurements were performed at $V_T = 5.2$ MV, using a gas stripper and selecting the 3 + state. The stripping efficiency was 10% resulting in typical $^9Be^{3+}$ currents of 30 nA. Due to the low current intensity the ^{9}Be pulse length was set at 10 ms and the repetition rate at 1 Hz. The abundant ^{10}B contaminant was eliminated from the ^{10}Be beam by means of a gas absorber in front of the ionization counter. The gas absorber consists of a gas cell with two 2 μm Havar windows and filled with about 150 mbar Xe, sufficiently to stop ^{10}B and leaving ^{10}Be at a residual energy of 6 MeV. The ^{10}B signal derived from this cell was used to correct for ^{7}Be due to reactions. With this correction the detection limit was ^{10}Be/^{9}Be = 10^{-14}.

5. Precision

Series of measurements with carbon samples of known isotope ratios show for ^{14}C/^{12}C ratios a reproducibility better than 1%. The simultaneously recorded ^{13}C/^{12}C ratios for these samples, which do not depend on statistics, resulted in a 0.5% precision determined by the systematical error only.

The long term precision is observed with the repeated measurement of calibration standards. During a

period of two days, in which the accelerator settings were unchanged, the observed spread of the isotope ratios was 0.5% for ^{14}C/^{12}C and 0.4% for ^{13}C/^{12}C. Here is also observed that the ^{13}C/^{12}C ratios can be used to monitor the reproducibility and and the precision.

In this way the ^{13}C/^{12}C ratios are used to monitor the measurements: ratios deviating from values expected from conventionally measured δ^{13} values indicate suspected measurements.

There exist, however, indications that fluctuations observed in the ^{13}C/^{12}C ratios are correlated with those in ^{14}C/^{12}C ratios. For example the isotope ratios vary with the iron–graphite ratio as has also been observed previously [14]. Further investigations are firstly needed to justify corrections by means of variations in the measured ^{13}C/^{12}C ratios.

The precision for ^{10}Be depends only on the reproducibility of the calibration standards. During a measuring period for ^{10}Be the standards, obtained from irridiation with known neutron doses at IRI [15], are reproduced at about 3%.

6. Summary

The measurements of ^{14}C and ^{10}Be in various (small) samples are routinely performed in Utrecht. Sample preparation techniques have been introduced. Adequate precision, 1% for ^{14}C/^{12}C ratios and 3% for ^{10}Be/^{9}Be ratios is routinely obtained for samples of sufficient concentration. Further improvement of precision may be possible when correction via simultaneously recorded ^{13}C/^{12}C ratios can be performed.

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