RADIOISOTOPE DATING WITH THE ETHZ-EN-TANDEM ACCELERATOR

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INTRODUCTION

During the last three years the ETH-EN-tandem accelerator facility has been adapted for the quantitative determination of the rare isotopes $^{14}$C and $^{10}$Be in mg samples. The goal of this project is to routinely achieve a 1% accuracy when measuring $^{14}$C/$^{12}$C ratios with a minimum expenditure of human resources and beam time. The concept is similar to that proposed by Purser and Henley (1978). The early evolution of this dating facility was described previously (Suter et al., 1981a,b). This paper is a brief report on the current status of the system and its development.

INSTRUMENTATION

The schematic layout of our dating facility is shown in figure 1, consisting of a Cs sputter ion source producing the negative ion beam attached to the 90° inflection magnet at the low energy side of the machine. The accelerated beam is then separated and analyzed by a combination of a 15° electrostatic deflector, a 90° analyzing magnet and a gas AE-E counter (the current of the abundant isotopes is measured directly in Faraday cups). The use of electrostatic elements only, for focusing and steering of the beam from the inflection magnet to the analyzing magnet ensures that for equal beam injection conditions all paths of the various isotopes are virtually the same up to the magnetic spectrometer. In this way, systematic errors in the determination of the isotopic ratios due to changes of the transmission through the accelerator and the beam transport system can be reduced considerably.

Unfortunately, existing tandem van de Graaff accelerators are not capable of sustaining the intense currents of the abundant stable isotopes. An overall current reduction is undesirable since it affects also the rare isotope. Thus we developed a fast switching system in which the stable isotopes are only injected in short pulses (160-200µs long). Provided
Fig 1. Layout of the accelerator based dating facility
Fig 2. Two-parameter logarithmic plot of a particle spectrum from a graphitic wood sample (~135%M) observed with the ΔE-E heavy ion gas detector. The electrostatic and magnetic analyzing system was set for particles having an energy of 18MeV, charge state $3^+$ and mass 14.

the duty cycle is low (2x10^{-3} in our case), loading effects on the machine are minor. The injection of 10 to 20 pulses/s allows quasicontinuous monitoring of all isotopes of interest. A more detailed description has been given by Suter et al (1983). To check the performance, the stability, the sensitivity, and the reproducibility of the whole arrangement, extensive tests with C and BeO standards were made.

RESULTS

$^{14}$C RESULTS. We measured $^{13}$C/$^{12}$C and $^{14}$C/$^{12}$C isotopic ratios using beams from calibrated graphitic C samples, ie, carbon converted into graphite under high temperature and pressure (1300 °C, 10 kb) (Polach, pers commun). Graphite was used because it yields the highest and most stable negative C currents in our ion source. Samples of charcoal and amorphous carbon obtained by various processes give lower and less stable currents, and also tend to burn out faster. From graphite we ob-
tain up to 40μA negative 12C current, which is injected into the tandem. Up to 30% of the injected particles emerge from the accelerator in the 3+ state with an energy of 18MeV (with an accelerating voltage of 4.5MV). This charge state and energy are selected by the electrostatic deflector (independently of particle mass) and finally mass-analyzed by the magnetic spectrometer.

Figure 2 shows a typical particle spectrum measured with a ΔE-E gas counter telescope using a 135% M 14C standard. Only four well-separated peaks are observed, which can be attributed to 14C, 13C, 12C, and 14N ions of equal magnetic rigidity. The unwanted ions (13C, 12C, 14N) stem from fragments of molecular beams (like 13CH−, 12CH2−, 14NH) or from 12C− and 13C− tails under the 14C which, through multiple scattering, find their way through the electrostatic deflector and the magnet to the counter. The 13C and 12C peaks vary significantly from sample to sample since they are related to the hydrocarbon content of the material used.

The sensitivity of the method is limited in two ways - by 13C background (the tail of the 13C peak in fig 2 can reach into the region of the 14C peak), or by 14C contamination of the sample, be it by cross talk in the source or during sample preparation. The present sensitivity limit of 10−15 to 2×10−16 is mainly determined by sample contamination with 14C.

Figure 3 shows a measurement of 14C/12C ratios for a set of calibrated graphitic samples (Polach, pers commun). The measured ratio is plotted vs the age determined by conventional β counting. The data were fitted to an exponential with only the height as a free parameter. The slope is given by the known 14C half life (Libby). The weighted mean deviation of the data points from the fit is 1%.

In order to prove that this excellent agreement is not fortuitous, we made several runs to determine the long-term stability of the apparatus and the reproducibility of the results. Figure 4 shows results obtained by measuring 14C/12C and 13C/12C ratios in consecutive 50 s long cycles for one hour. We also determined the transmission of 12C through the machine (ie, the ratio between 12C current at the low energy side of the machine and 12C current after the magnetic analyzer divided by the charge state to compare the number of particles). During a 50 s cycle we obtain 14C counting statistics of ca 3%. The internal and external errors of the 14C/12C mean value were consistent with each other (σint = 1/√Ntot = 0.28%, σext = 0.31%). This shows that systematic variations are smaller than 2%, confirmed by the measurement of the 13C/12C ratio which, although measured only during a fraction
Fig 4. Carbon isotopic ratios and $^{12}$C transmission for individual runs each lasting 50 sec. The mean value for the whole series is $\bar{X} = 1.397 \pm 0.004$ (0.31%) for $^{14}$C/$^{12}$C and $\bar{X} = 1.1116 \pm 0.0002$ (0.02%) for $^{13}$C/$^{12}$C. $\sigma$ is the standard deviation of each single measurement.

of the time (0.1 s out of 50 s), is much better determined than $^{14}$C/$^{12}$C. The standard deviation of a single $^{13}$C/$^{12}$C data point in figure 4 is $\sigma = 0.17\%$ and the standard deviation of the mean is $\sigma = 0.02\%$, although the transmission through the machine fell from 29.6% to 29.1%. This shows the inherent insensitivity of the arrangement to small drifts.

If we compare $^{13}$C/$^{12}$C ratios when changing between samples of equal composition we sometimes find larger variations. If different samples made of the same material are measured consecutively, we find variations of the $^{13}$C/$^{12}$C ratios of up to 1%. Preliminary data indicate that for amorphous carbon the variation is presently ca 2%. The lower reproducibility as compared to the stability is due to the fact that small changes in the sample position in the source slightly change the beam parameters. For amorphous material, reproducibility is worse because the samples burn out more quickly and also show large current variations during the measurement. In order to enhance reproducibility and thereby accuracy, the accelerator voltage regulation system must be improved. A reduction in sensitivity to changes in beam quality is expected by replacing the magnetic high-energy quadrupole lens with an electrostatic one.
RESULTS. The cosmogenic radioisotope, $^{10}\text{Be}(t_{1/2}=1.6\cdot10^6\text{ yr})$, has been mainly used, so far, to study variations in the interaction of cosmic radiation with the atmosphere (Raisbeck et al, 1981). $^{10}\text{Be}$ is washed out by precipitation in a very short time of the order of 1 to 2 years and deposited on the earth. It is found in sediments, in polar ice caps, and even in organic material. The concentration of $^{10}\text{Be}$ in ice, eg, is very low. Raisbeck et al (1981) found a $^{10}\text{Be}$ concentration of $(8-12)\cdot10^{-14}$ atoms per gram water in ice-core samples from Antarctica. Our own measurements (Beer et al, 1983) indicate that it is about an order of magnitude smaller in ice-core samples from Dye 3 (Greenland). Usually, a well-known amount of $^{9}\text{Be}$ carrier (1 to 2 mg/l water) is added and both isotopes are extracted chemically in the form of BeO. Samples with a $^{10}\text{Be}$$/^{9}\text{Be}$ concentration of the order of $10^{-12}$-$10^{-13}$ can be used for analysis without further processing, because the most intense negative ion beam obtained from a sputter ion source is formed by this molecule. However, the intensity of the molecular BeO$^-$ currents observed so far, is considerably lower than that for $^{12}\text{C}^-$ . Whereas negative currents of the order of up to $40\mu\text{A}$ can be obtained for $^{12}\text{C}^-$, a maximum of only ca $1\mu\text{A}$ $^{9}\text{BeO}^-$ has been obtained.

The acceleration of molecular ions with tandem accelerators imposes some additional problems as compared to atomic ions. The molecular ions accelerated in the first section usually desintegrate if stripped to positive charge states of $3^+$ or more in the foil or gas stripper placed at the terminal of the accelerator. Consequently, the energies of the $^{9}\text{Be}$ and $^{10}\text{Be}$ fragments accelerated in the second section are not equal. Since the energy of a molecular fragment of mass $m_1$ and charge state $q$ is given by $E = e(U_1 m_1/m_2 + U_T(qm_1/m_2))$ where $m_2$ is the mass and $eU_1$ the energy of the injected molecule and $U_T$ the acceleration voltage, it follows that this energy difference is ca 0.7% for $q=3^+$ and $U_T=5.5\text{MV}$. Thus, all electrostatic focusing and bending elements placed at the high energy side of the accelerator must be modulated with a correction voltage when switching from $^{10}\text{Be}$ to $^{9}\text{Be}$ to avoid different focusing and bending of the two isotopes.

Transmission measurements made with BeO and $^{12}\text{C}$-beams confirmed earlier observations (Middleton, Klein and Tang, 1981) that the transmission of a molecular beam is significantly poorer (about a factor of 4) than for elemental ions. The lower velocity of the heavier molecules in the first section of the accelerator and the Coulomb explosion of the molecules when passing through the stripper are responsible for this effect.
All analyzed BeO samples have been contaminated with Boron on the ppm level. Boron oxide forms negative ions with about twice the efficiency of BeO (Middleton, Klein and Tang, 1981). The $^{10}$B beam cannot be separated from the $^{10}$Be beam by the magnetic spectrometer. Because the high $^{10}$B intensity would overload the detector, the beam must be stopped in a suitable absorber before it reaches the $\Delta E$-$E$ counter.

Following a suggestion of Middleton, Klein and Tang (1981), we are using a gas (Ar) absorber cell into which an ionization chamber is incorporated. $^{10}$B can then be used as a pilot beam for optimal tuning of the accelerator, beam transport, and isotope switching system. On the other hand, although this beam is only of the order of a few pA, it produces a disturbing background in the entrance foil of the gas cell which limits the detection sensitivity for $^{10}$Be. The background results from a nuclear reaction of $^{10}$B with hydrogen ($^{1}$H($^{10}$B,$^{7}$Be)$^{4}$He) always present in ppm concentrations in metal foils. This reaction is exothermic ($Q = 1.146$MeV) and both reaction products are able to enter the $\Delta E$-$E$ counter telescope. $^{7}$Be is very disturbing since it extends into the $^{10}$Be region (Klein, Middleton, and Tang, 1981) limiting the $^{10}$Be/$^{9}$Be concentration sensitivity to ca $10^{-14}$. Obviously, this limit can be improved considerably if some way is found to reduce the Boron contamination in the BeO samples or (and) the hydrogen content of the entrance foil of the gas absorber.

At present the accuracy of measurements of Be samples with $^{10}$Be concentration is determined mostly by statistics, because of the relatively low BeO$^-$ currents. Systematic errors are larger than for carbon ($\approx 2$ to 3%) because of the poorer beam quality. For a $^{9}$BeO$^-$ current of 1μA and a $^{10}$Be concentration of $10^{-14}$ only 20 counts per hour are recorded with the particle detector. Thus, the development of ion source with a negative ion efficiency comparable to that for carbon is very desirable.

The first results of measurements on ice samples from Dye 3 (Greenland) are discussed by Beer et al (1983).

CONCLUSION

We have shown that it is possible to convert a tandem Van de Graaff accelerator to a highly sensitive and accurate tool for rare isotope mass spectrometry. Using the concept of Purser and Henley (1978) we have obtained an accuracy of 1% for $^{14}$C/$^{12}$C ratios using graphitic C samples. An improvement to 0.3% seems possible without major modifications. The $^{14}$C concentration sensitivity is presently $10^{-15}$ to $2 \times 10^{-16}$, depending on the composition and preparation of the sample.
Limitation is mainly by sample contamination with $^{14}$C except for samples with a high hydrocarbon content. Molecular $^{13}$C fragments from the parasitic $^{13}$CH$^-$ beam are the limiting factors here.

With $^{10}$Be we have achieved sensitivities of $10^{-13}$ to $10^{-14}$, depending on the amount of $^{10}$B contamination in the sample. In this case systematic errors were between 2 and 3%. Present limitations in our apparatus are determined, on the one hand by the long-term variations in the sputter ion source, and on the other hand by the present long-term stability of the accelerator. The performance of the source can be improved by better sample preparation techniques and by changes in the source geometry. Higher accelerator stability requires a new stabilization system and the installation of an electrostatic quadrupole lens at the high energy end of the machine to reduce its sensitivity to small instabilities. Further improvements might be achieved by using computer-aided procedures to tune the accelerator and beam transport system so that the beam path for all isotopes is equal. We also intend to measure heavier isotopes (e.g. $^{36}$Cl), for which major modifications will be needed.

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REFERENCES


