

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 $^{14}\text{C}/^{12}\text{C}$ ratios with a minimum expenditure of human resources and beam time. The concept is similar to that proposed by Pursor 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 ΔE -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 (160-200 μs long). Provided

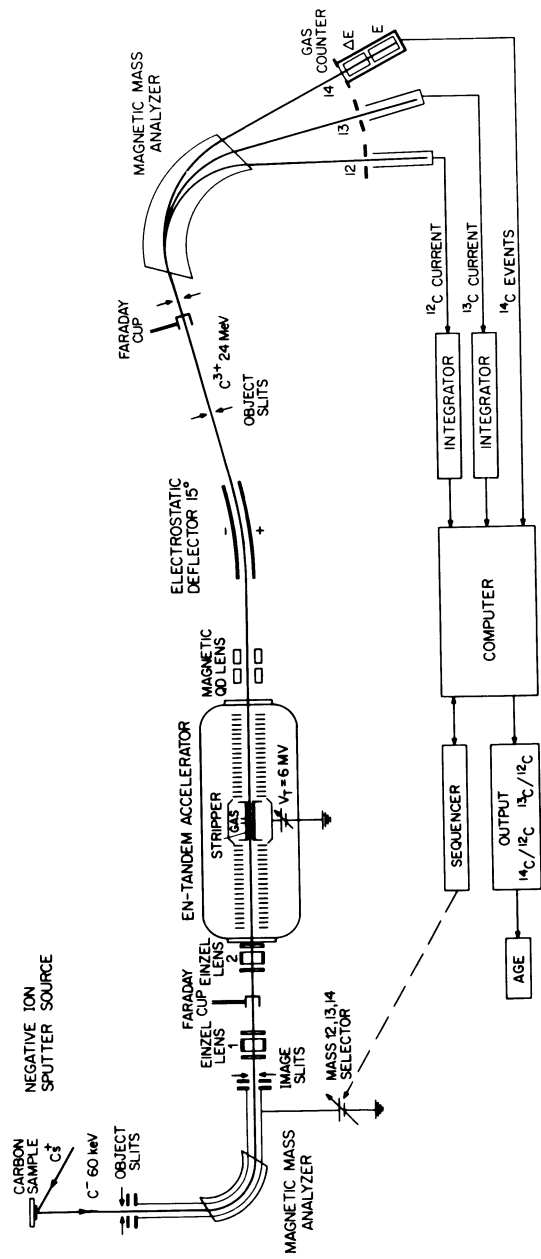


Fig 1. Layout of the accelerator based dating facility

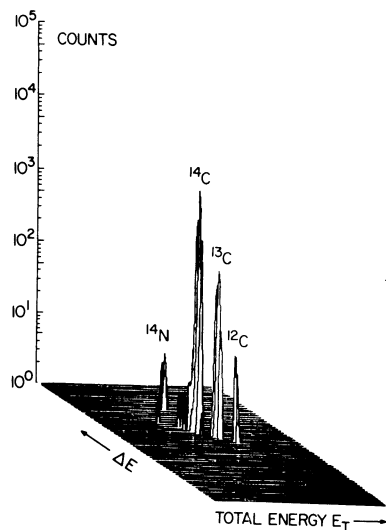


Fig 2. Two-parameter logarithmic plot of a particle spectrum from a graphitic wood sample ($\sim 135\%$ M) observed with the ΔE -E heavy ion gas detector. The electrostatic and magnetic analyzing system was set for particles having an energy of 18MeV, charge state 3^+ and mass 14.

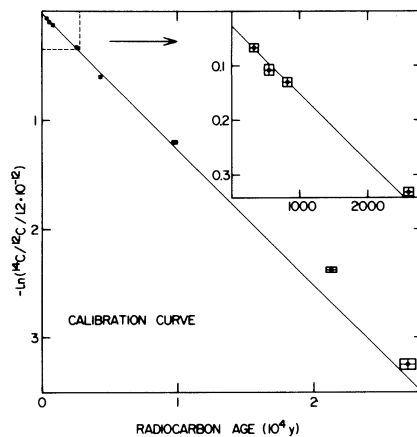


Fig 3. Calibration curve. The $^{14}\text{C}/^{12}\text{C}$ ratios are given in units of modern carbon ($1.2 \cdot 10^{-12}$). The carbon age of the samples was determined by beta counting. The solid line is a fit to the data using $t_{1/2} = 5568$ yr. For the samples shown in the insertion, the β counting accuracy is better than ± 75 yr. For the older samples, it lies between ± 80 and ± 590 yr. The measuring time for each sample was only 500 sec.

the duty cycle is low (2×10^{-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 $^{13}\text{C}/^{12}\text{C}$ and $^{14}\text{C}/^{12}\text{C}$ isotopic ratios using beams from calibrated graphitic C samples, ie, carbon converted into graphite under high temperature and pressure (1300 $^{\circ}\text{C}$, 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 40 μ A negative ^{12}C 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 ^{14}C standard. Only four well-separated peaks are observed, which can be attributed to ^{14}C , ^{13}C , ^{12}C , and ^{14}N ions of equal magnetic rigidity. The unwanted ions (^{13}C , ^{12}C , ^{14}N) stem from fragments of molecular beams (like $^{13}\text{CH}^-$, $^{12}\text{CH}_2^-$, ^{14}NH) or from $^{12}\text{C}^-$ and $^{13}\text{C}^-$ tails under the ^{14}C which, through multiple scattering, find their way through the electrostatic deflector and the magnet to the counter. The ^{13}C and ^{12}C 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 ^{13}C background (the tail of the ^{13}C peak in fig 2 can reach into the region of the ^{14}C peak), or by ^{14}C 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 ^{14}C .

Figure 3 shows a measurement of $^{14}\text{C}/^{12}\text{C}$ 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 ^{14}C 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 $^{14}\text{C}/^{12}\text{C}$ and $^{13}\text{C}/^{12}\text{C}$ ratios in consecutive 50 s long cycles for one hour. We also determined the transmission of ^{12}C through the machine (ie, the ratio between ^{12}C current at the low energy side of the machine and ^{12}C current after the magnetic analyzer divided by the charge state to compare the number of particles). During a 50 s cycle we obtain ^{14}C counting statistics of ca 3%. The internal and external errors of the $^{14}\text{C}/^{12}\text{C}$ mean value were consistent with each other ($\sigma_{\text{int}} = 1/\sqrt{N_{\text{tot}}} = 0.28\%$, $\sigma_{\text{ext}} = 0.31\%$). This shows that systematic variations are smaller than 2%, confirmed by the measurement of the $^{13}\text{C}/^{12}\text{C}$ ratio which, although measured only during a fraction

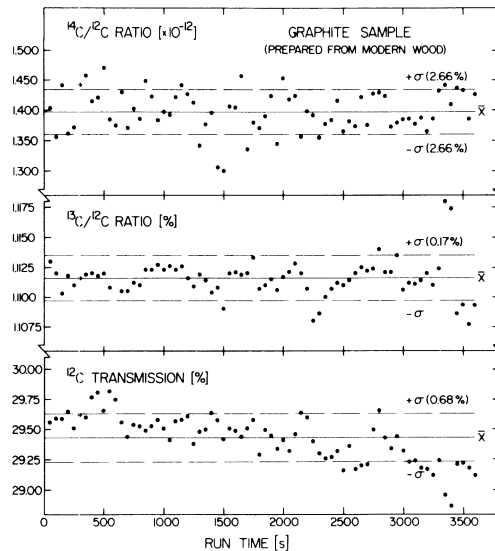


Fig 4. Carbon isotopic ratios and ^{12}C transmission for individual runs each lasting 50 sec. The mean value for the whole series is $\bar{X} = 1.397 \pm 0.004$ (0.31%) for $^{14}\text{C}/^{12}\text{C}$ and $\bar{X} = 1.1116 \pm 0.0002$ (0.02%) for $^{13}\text{C}/^{12}\text{C}$. σ is the standard deviation of each single measurement.

of the time (0.1 s out of 50 s), is much better determined than $^{14}\text{C}/^{12}\text{C}$. The standard deviation of a single $^{13}\text{C}/^{12}\text{C}$ 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 $^{13}\text{C}/^{12}\text{C}$ 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 $^{13}\text{C}/^{12}\text{C}$ 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.

^{10}Be RESULTS. The cosmogenic radioisotope, ^{10}Be ($t_{1/2} = 1.6 \cdot 10^6$ yr), has been mainly used, so far, to study variations in the interaction of cosmic radiation with the atmosphere (Raisbeck et al, 1981). ^{10}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}Be in ice, eg, is very low. Raisbeck et al (1981) found a ^{10}Be concentration of $(4-12) \cdot 10^4$ 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 ^9Be carrier (1 to 2 mg/lt 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 μA can be obtained for $^{12}\text{C}^-$, a maximum of only ca 1 μA $^9\text{BeO}^-$ 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 ^9Be and ^{10}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 $E = e(U_1 m_1/m_2 + U_T(q+m_1/m_2))$ 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}Be to ^9Be to avoid different focusing and bending of the two isotopes.

Transmission measurements made with BeO and ^{12}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 $\Delta\text{E-E}$ 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 ($^1\text{H}(^{10}\text{B}, ^7\text{Be})^4\text{He}$) always present in ppm concentrations in metal foils. This reaction is exothermic ($Q = 1.146\text{MeV}$) and both reaction products are able to enter the $\Delta\text{E-E}$ counter telescope. ^7Be is very disturbing since it extends into the ^{10}Be region (Klein, Middleton, and Tang, 1981) limiting the $^{10}\text{Be}/^9\text{Be}$ 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 (~ 2 to 3%) because of the poorer beam quality. For a $^9\text{BeO}^-$ current of $1\mu\text{A}$ 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 $^{14}\text{C}/^{12}\text{C}$ 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 2×10^{-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 $^{13}\text{CH}^-$ 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 (eg ^{36}Cl), for which major modifications will be needed.

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REFERENCES

- Beer, J, Oeschger, H, Stauffer, B, Balzer, R, Bonani, G, Stoller, Ch, Suter, M, and Wölfli, W, 1983, Comparison of ^{10}B and ^{14}C variations, in Stuiver, Minze and Kra, Renée, eds, Internatl radiocarbon Conf, 11th, Proc: Radiocarbon, v 25.
- Klein, M, Middleton, R, and Tang, H, 1982, Modifications of an FN tandem for quantitative ^{10}Be measurements, Nucl Instr Meth, v 193, p 601-616.
- Middleton, R, Klein, J, Tang, W, 1981, Instrumentation of an FN tandem for the detection of ^{10}Be , ANL/PHY-81-1, p 57-86.
- Purser, KH, and Henley, PR, 1978, in Gove, HE, ed, First Conf on Radiocarbon Dating with Accelerators, Proc Univ Rochester, p 165-186.
- Raisbeck, GM, Yion, F, Lieuvin, M, Ravel, JC, Fruneau, M, Loiseaux, JM, 1981, ^{10}Be in the environment: Some recent results and their applications, ANL/PHY-81-1, p 228-243.

- Suter, M, Balzer, R, Bonani, G, Stoller, Ch, Wölfli, W, Beer, J, Oeschger, H, and Stauffer, B, 1981a, Radioisotope Dating using an EN-tandem accelerator, IEEE transaction on Nucl Sci, NS-28, p 1475-1477.
- Suter, M, Balzer, R, Bonani, G, Stoller, Ch, Wölfli, W, Beer, J, Oeschger, H, and Stauffer, B, 1981b, Improvements in the application of a tandem Van-de-Graaff accelerator for ultra-sensitive mass spectrometry, ANL/PHY-81-1, p 87-95.
- Suter, M, Balzer, R, Bonani, G, Nessi, M, Stoller, Ch, Wölfli, W, André, M, Beer, J, Oeschger, H, 1983, Precision measurements of rare radioisotopes with a tandem Van-de-Graaff accelerator, IEEE Transaction on Nucl Sci, NS-30, in press.