SYSTEMATIC INVESTIGATIONS OF ^{14}C MEASUREMENTS AT THE VIENNA ENVIRONMENTAL RESEARCH ACCELERATOR

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ABSTRACT. A newly operating accelerator mass spectrometry (AMS) facility such as VERA has to go through an extensive testing phase in order to establish optimal conditions for ^{14}C measurements, especially in the field of archaeological samples where an overall precision of 0.5% is desirable.

We discuss the results of our measurements at the milligram carbon level as they relate to long-term stability, reproducibility, precision and isotope fractionation.

INTRODUCTION

VERA is built around a 3-MV Pelletron® tandem accelerator and uses fast sequential isotope injection for all three carbon isotopes (^{12}C, ^{13}C, ^{14}C) with a cycle period of 120 ms. The main features of the facility (Fig. 1), which was built by NEC, comprise a 40-target Cs-beam sputter source, a spherical electrostatic analyzer, a (nominally) double focusing 90° injection magnet with an electrically insulated vacuum chamber for fast sequential isotope injection, the tandem accelerator operated with an Ar gas stripper at 2.7 MV (with generating voltmeter and capacitive pick-off voltage control), a double focusing 90° analyzing magnet, an ExB Wien filter, and a surface barrier silicon detector for ^{14}C detection. The machine is fully software controlled and automatic measurements (unattended overnight) are routinely performed.

After an introductory period (Kutschera *et al.* 1997; Priller *et al.* 1997), significant improvements of the machine performance have been achieved by installing a magnetic quadrupole doublet lens to correct the optics of the injection magnet and also by implementing a more elaborate tuning procedure. Due to a deficiency of the pole pieces, a circular object was imaged into an ellipsoidal one elongated in the x-direction (deflection plane). To overcome this problem, the magnet has recently been equipped with a correcting magnetic quadrupole lens.

All targets measured contained 1–2 mg of carbon catalytically deposited on iron powder (for target preparation, see Wild *et al.* 1998). As a blank material for background corrections, high-purity graphite was used. IAEA C-3 Cellulose was used as the reference standard material for normalizing both δ^{13}C corrections and pMC values, whereas IAEA C-6 Sucrose mainly served as an additional quality check. All isotope fractionation corrections were carried out with δ^{13}C values derived from ^{13}C/^{12}C ratios also measured with VERA, since no stable isotope spectrometer is yet available.

The main goal of the present investigation was the reliable prediction of the uncertainties connected with the measurement of ^{14}C/^{12}C ratios for a single target of an unknown sample material. To this end a useful quantity, the so-called *intertarget scattering*, was introduced.

THE INTERTARGET SCATTERING S_{IT}

For a systematic investigation of the reproducibility and the influence of the target position in the target wheel, N targets are filled with the same target material (*e.g.*, C-6 Sucrose) and are put into different positions in the target wheel. Several runs of *ca.* 200 s are performed on each target (R_j runs on target j). First, for each target we calculate the mean value $\bar{x}_j$ and the statistical error S_j^{stat}:

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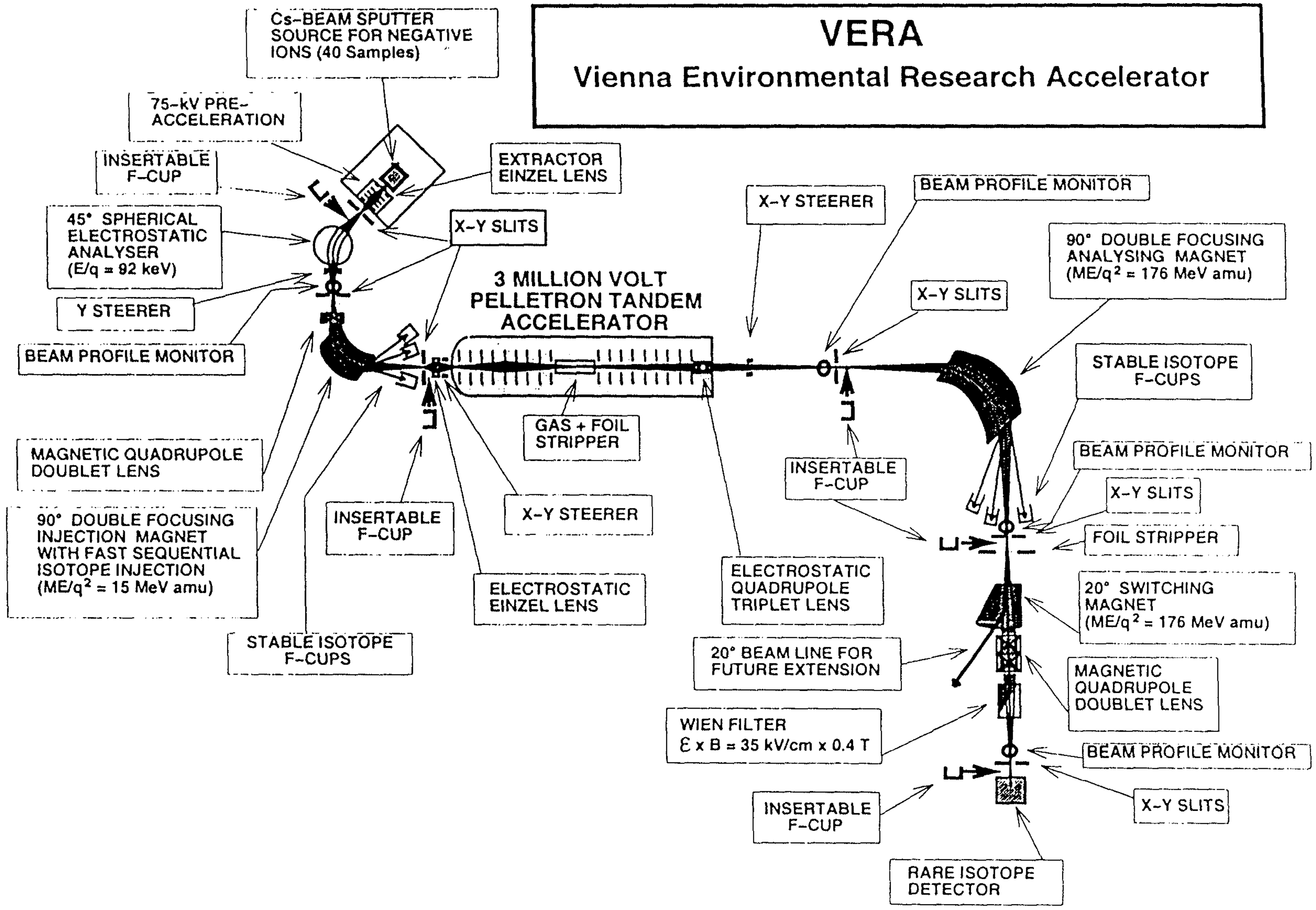

Phillippe Collon

Fig. 1. Schematic layout of the Vienna Environmental Research Accelerator (VERA). The recently installed magnet quadrupole doublet lens is located between the 45° spherical electrostatic analyzer and the 90° double focusing injection magnet.

$$\bar{x}_j = \frac{1}{R_j} \sum_{k=1}^{R_j} x_{j,k} \tag{1a}$$

$$S_j^{stat} = \sqrt{\frac{1}{\sum\limits_{k=1}^{R_j} \frac{1}{(S_{j,k}^{stat})^2}}} \quad \text{with} \quad S_{j,k}^{stat} = \sqrt{\frac{x_{j,k}}{{}^{12}C_{j,k}^{3+}}} \tag{1b}$$

where $x_{j,k}$ denotes the measured $^{14}C^{3+}/^{12}C^{3+}$ ratio in the k^{th} run of target j, and $S_{j,k}^{stat}$ denotes the corresponding statistical error.

Next, the mean of the individual targets for the specific sample material, $\bar{x}$, the standard deviation from the mean, S, and the mean statistical error, S_{stat}, are computed:

$$\bar{x} = \frac{1}{N} \sum_{j=1}^{N} \bar{x}_j \tag{2a}$$

$$S = \sqrt{\frac{\sum\limits_{j=1}^{N} (\bar{x}_j - \bar{x})^2}{N-1}}, \qquad S_{stat} = \sqrt{\frac{N}{\sum\limits_{j=1}^{N} \frac{1}{(S_j^{stat})^2}}} \ . \tag{2b, 2c}$$

The standard deviation is split into two parts,

$$S^2 = S_{stat}^2 + S_{IT}^2 \tag{3}$$

where S_{IT} is the intertarget scattering, being a measure of the excess of the observed error for $^{14}C^{3+}/^{12}C^{3+}$ ratios over the purely statistical error S_{stat}, resulting in

$$S_{IT} = \sqrt{S^2 - S_{stat}^2} \ . \tag{3a}$$

In order to estimate the uncertainty of S_{IT}, we use the error of the standard deviation (best estimator):

$$\Delta S = \frac{S}{\sqrt{2(N-1)}} \ . \tag{4}$$

Using error propagation and setting the error of the statistical error $\Delta S_{stat} = 0$ we obtain from (3a) and (4) the uncertainty of S_{IT}:

$$\Delta S_{IT} = \frac{S^2}{\sqrt{2(N-1)}} \frac{1}{S_{IT}} \ . \tag{5}$$

In the case of $S^2 < S^2_{stat}$, it is reasonable to assume that

$$S_{IT} = 0 \, . \tag{3b}$$

Still, an uncertainty of this value can be calculated from (3a):

$$S_{IT} \,(\pm)\, \Delta S_{IT} = \sqrt{(S \,(\pm)\, \Delta S)^2 - (S_{stat} \,(\pm)\, \Delta S_{stat})^2} \, . \tag{6}$$

Since ΔS_{stat} is negligibly small, one obtains by using (3b)

$$\Delta S_{IT} = \sqrt{(S + \Delta S)^2 - S^2_{stat}} \, , \tag{6a}$$

which indicates an upper limit for the intertarget scattering (see Fig. 4).

δ^{13}C AND BACKGROUND CORRECTIONS

For the δ^{13}C corrections we start from the following definitions:

$$\delta^{13}C_{sample} = \left(\frac{{}^{13}R_{sample} - {}^{13}R_{PDB}}{{}^{13}R_{PDB}} \right) 1000 \text{‰} \tag{7a}$$

$$\delta^{13}C_{std} = \left(\frac{{}^{13}R_{std} - {}^{13}R_{PDB}}{{}^{13}R_{PDB}} \right) 1000 \text{‰} \, , \tag{7b}$$

where ${}^{13}R$ is the measured ${}^{13}C^{3+}/{}^{12}C^{3+}$ ratio, the subscripts *PDB* and *std* denote the PDB standard and another standard material, respectively, and $\delta^{13}C_{std}$ was taken to be the recommended IAEA value of one of the standard materials we used in our measurements (see the end of this section).

Eliminating ${}^{13}R_{PDB}$ from equations (7a) and (7b) results in

$$\delta^{13}C_{sample} = \left(\frac{{}^{13}R_{sample}}{{}^{13}R_{std}} \left(1 + \frac{\delta^{13}C_{std}}{1000} \right) - 1 \right) 1000 \text{‰} \, . \tag{7c}$$

Finally, the ${}^{14}C^{3+}/{}^{12}C^{3+}$ ratio of a sample is normalized to $\delta^{13}C = -25$ ‰ (Stuiver and Polach 1977) by

$$\bar{x}_{sample,\,-25} = \bar{x}_{sample} \left[1 - \frac{2\,(25 + \delta^{13}C_{sample})}{1000} \right] \, . \tag{8a}$$

Our present precision of δ^{13}C does not require use of the more precise quadratic form of the fractionation correction (see Stuiver and Robinson 1974):

$$\bar{x}_{sample,\,-25} = \bar{x}_{sample}\left[\frac{1-\frac{25}{1000}}{1+\frac{\delta^{13}C_{sample}}{1000}}\right]^{2} \qquad \text{(8b)}$$

On the assumption that either 1) the carbon masses of the sample, the standard and the blank material are all the same and contamination is equal for all those materials (in mass and isotopic composition) or 2) the carbon masses for all these materials may be different, but the contamination is strictly proportional to mass, the following background correction is valid:

$$\bar{x}^{corrected}_{sample,\,-25} = \bar{x}^{recommended}_{std,-25}\,\frac{\bar{x}_{sample,\,-25}-\bar{x}_{blank,\,-25}}{\bar{x}_{std,\,-25}-\bar{x}_{blank,\,-25}}\;. \qquad \text{(9a)}$$

$\bar{x}^{recommended}_{std,-25}$ is the $^{14}C/^{12}C$ ratio derived from the absolute international standard activity and the ^{14}C value recommended by the IAEA for a specific sample material, normalized to −25‰. This equation is also valid for calculating the ^{14}C content in pMC (% of modern carbon)

$$^{14}C^{corrected}_{sample} = {}^{14}C^{recommended}_{std}\,\frac{\bar{x}_{sample,\,-25}-\bar{x}_{blank,\,-25}}{\bar{x}_{std,\,-25}-\bar{x}_{blank,\,-25}}\;. \qquad \text{(9b)}$$

The corresponding recommended values for the IAEA standard materials used in our systematic investigations are (Rozanski 1991):

IAEA C-3 Cellulose: $\delta^{13}C = (-24.91 \pm 0.49)$‰; (129.41 ± 0.06) pMC
IAEA C-6 Sucrose: $\delta^{13}C = (-10.80 \pm 0.47)$‰; (150.61 ± 0.11) pMC

RESULTS AND DISCUSSION

The upper part of Figure 2 shows the dependence of the intertarget scattering S_{IT} on the bouncer voltage. The measurements were performed on 17 targets containing the same sample material, IAEA C-6 Sucrose. No $\delta^{13}C$ or background corrections were applied to these data. The clear minimum in S_{IT} (maximum of reproducibility) at *ca.* 0.95 kV corresponds to a maximum of the $^{14}C^{3+}$ transmission through the machine, as depicted for the measurement of a single target in the lower part of Figure 2. In our routine setup for ^{14}C measurement, various parameters of the AMS system (electrostatic analyzer, bouncer voltage, electric and magnetic lenses, steerers) are tuned for maximum readings of ^{13}C currents. Interestingly, in this procedure the same optimal bouncer voltage was reached, thus confirming the quality of our routine tuning procedure.

Long-term measurements were carried out on single targets in a regular ^{14}C-dating run (Fig. 3). From these measurements it can be concluded that 1) targets containing *ca.* 1 mg carbon can be measured for at least 1 h; 2) even a decline in the $^{12}C^-$ current by a factor of nearly 3 (see the rye grain curve in the lower part of Fig. 3) has essentially no influence on the $^{14}C^{3+}/^{12}C^{3+}$ ratio measured at our machine; and 3) there is no significant deviation from purely statistical error (see caption to Fig. 3).

The upper part of Figure 4 plots the absolute $^{14}C^{3+}/^{12}C^{3+}$ values measured before and after the installation of a magnetic quadrupole lens in the injection magnet. Proceeding from the absolute interna-

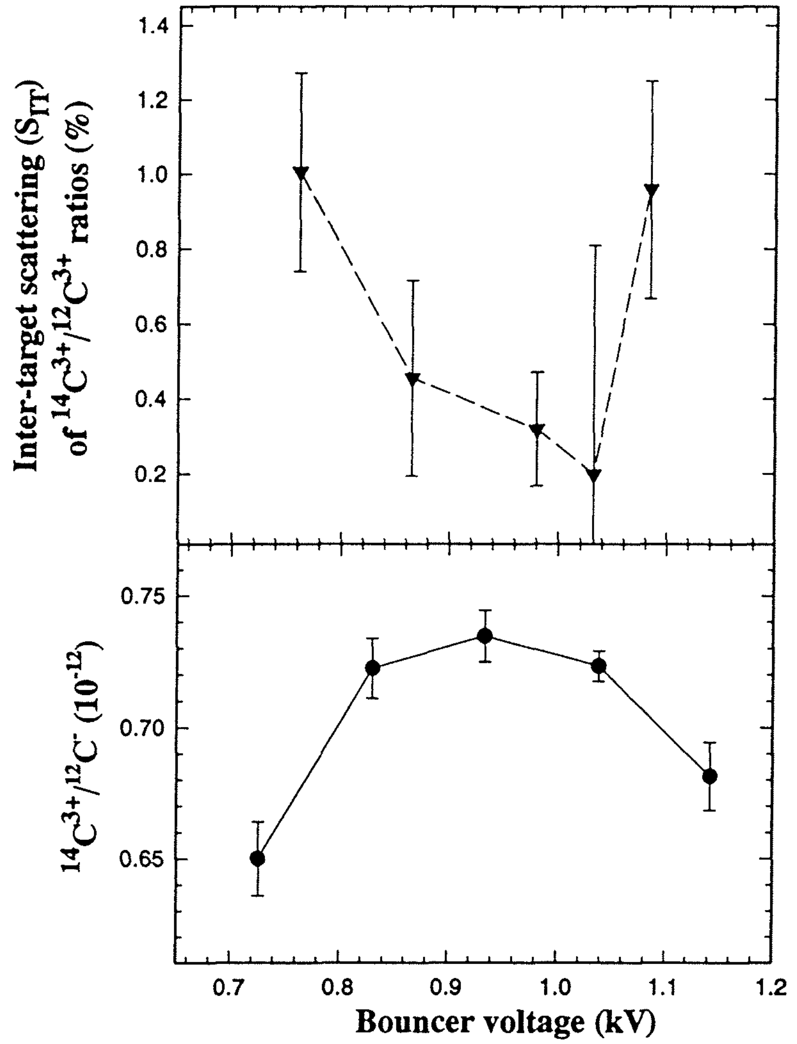

Fig. 2. Dependency of the intertarget scattering (top) and of the transmission (bottom) on the bouncer voltage (for details see text)

tional standard activity of 13.56 dpm per gram carbon (Karlén *et al.* 1964), which translates into a $^{14}C/^{12}C$ ratio of 1.189×10^{-12}, one gets 1.530×10^{-12} for the $^{14}C/^{12}C$ ratio of the IAEA C-3 Cellulose in 1997. The measured $^{14}C^{3+}/^{12}C^{3+}$ ratios shown in Figure 4 approached 90% of the C-3 nominal value, once the injection optics was corrected with the additional lens. Together with the corresponding $^{12}C^{3+}$ transmission through the machine and the intertarget scattering (S_{IT}), plotted in the lower part of Figure 4, the improvements of the machine performance due to the optical correction are evident: the $^{14}C^{3+}/^{12}C^{3+}$ ratios measured over an 8-month period are quite stable, the average transmission amounts to 47% and the intertarget scattering is below the 0.5% limit. It also can be inferred that S_{IT} is the main contribution to the uncertainty in measuring a single target, since the excess over the purely statistical error in the long-term measurements is negligible.

As an additional quality control, $\delta^{13}C$ and pMC values of the IAEA C-6 Sucrose standard are compared to the IAEA C-3 Cellulose standard measured in the same target wheel (see Fig. 5). The values obtained after installing the magnetic quadrupole doublet lens agree well with the values recommended by the IAEA.

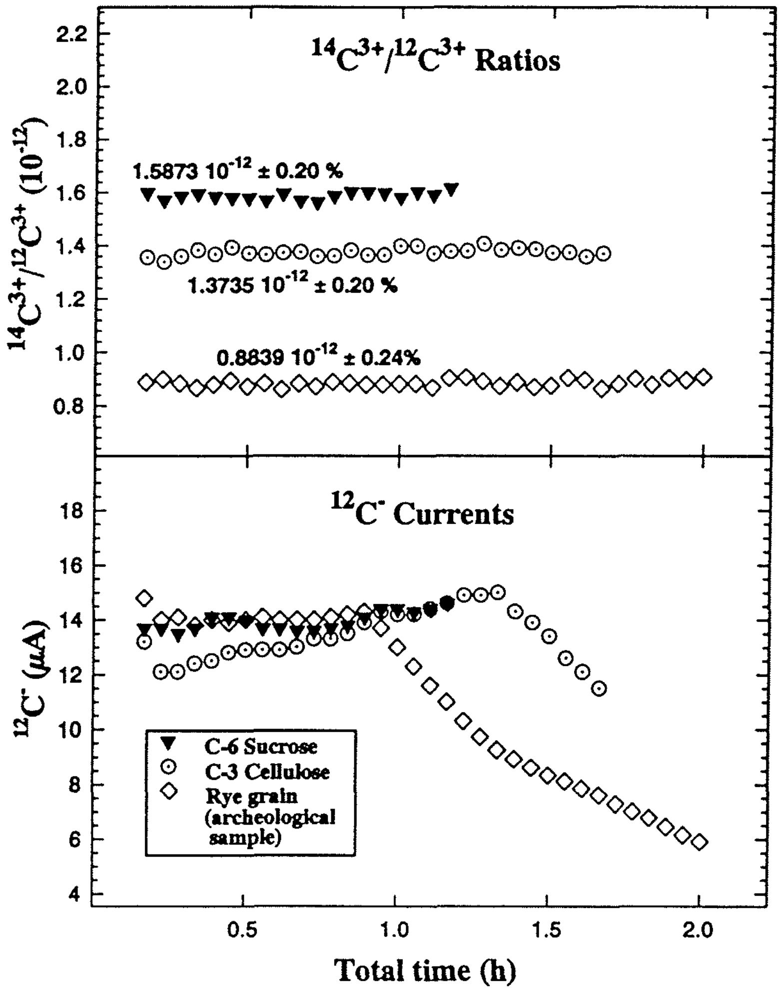

Fig. 3. Long-term measurements on single targets. The numbers shown in the top half of the figure indicate the $^{14}C^{3+}/^{12}C^{3+}$ ratios (normalized to $\delta^{13}C$ = −25‰) and the relative standard deviation of the mean. The corresponding relative statistical errors of the mean are 0.19%, 0.18%, and 0.22% for the C-6 Sucrose, the C-3 Cellulose, and the rye grain target, respectively.

It should be emphasized that all the data points shown in Figures 3–5 were obtained in regular ^{14}C-dating runs with fully automated operation (except for the measurement in April 1996). They include all the measurements performed without any rejection of data, therefore strengthening the reliability for ^{14}C measurements at the 0.5% precision level on a single target at VERA.

CONCLUSION

Mainly due to improvements of the ion beam optics and the tuning procedure of our machine, the goal of ^{14}C measurements at the 0.5% precision level for $^{14}C/^{12}C$ ratios with the new AMS facility VERA has been reached. Systematic investigations on single targets containing 1–2 mg of carbon show no significant deviation from purely statistical error, even after more than 1 h of total measuring time. However, the obtainable precision is limited by the intertarget scattering, *i.e.*, the excess of the observed error for $^{14}C^{3+}/^{12}C^{3+}$ ratios of several targets containing the same sample material over the purely statistical error. This scattering is the main contribution to the uncertainty in measuring a single target.

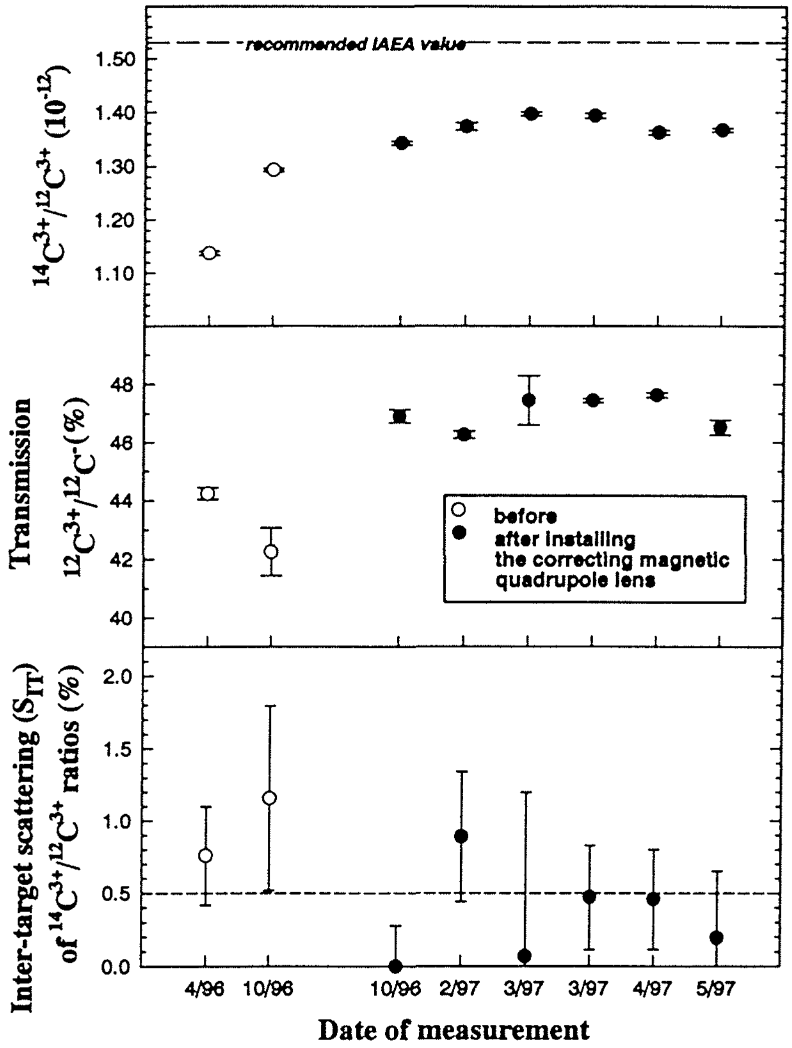

Fig. 4. Performance of C-3 Cellulose standards in regular ^{14}C-dating measurements. For the recommended IAEA value of C-3 Cellulose, see text. The dashed line in the lower third indicates the 0.5% limit for the reproducibility between different targets containing the same sample material.

Currently, the uncertainty of measuring $\delta^{13}C$ with our machine approaches ±1‰ (Fig. 5). A considerably higher precision for $\delta^{13}C$ measurements will soon be available from an offline stable isotope mass spectrometer.

The quality of our systematic tuning procedure is proved by the fact that the maximum in reproducibility (minimum in the intertarget scattering) for the $^{14}C^{3+}/^{12}C^{3+}$ ratios corresponds to a maximum in transmission of $^{14}C^{3+}$ through the machine.

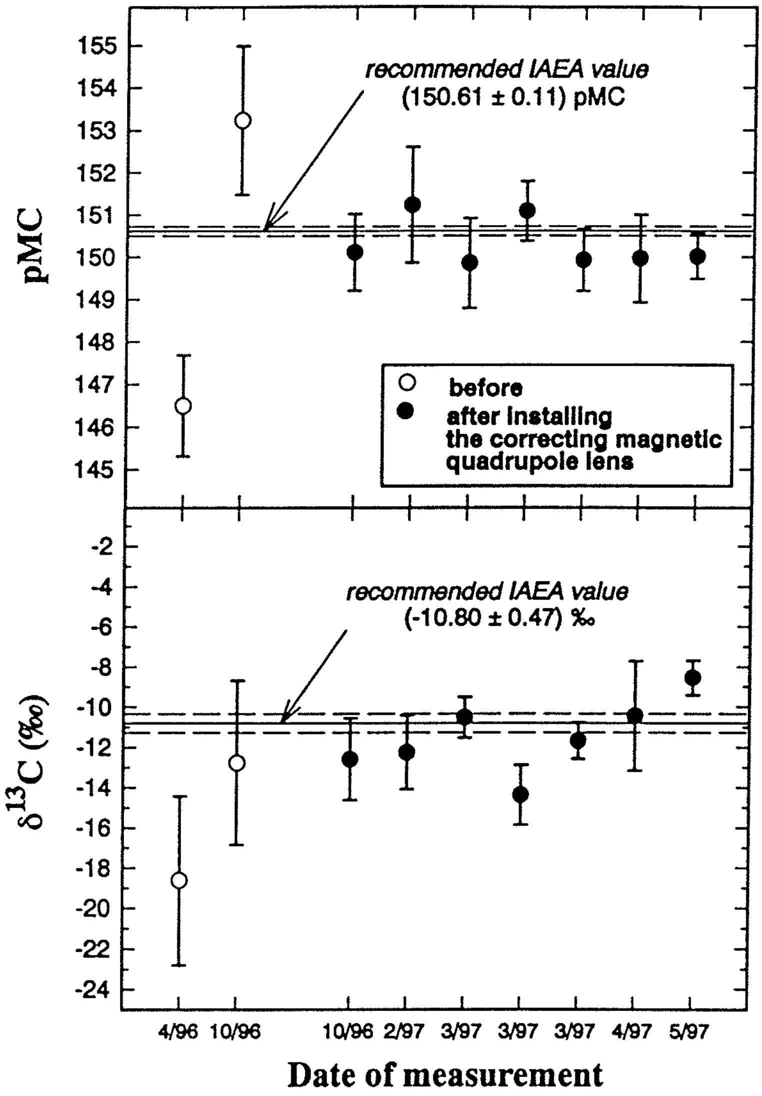

Fig. 5. C-6 Sucrose normalized to C-3 Cellulose. Background corrections following equations (9a) and (9b) have been applied to all data points.

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