Bats: A new tool for AMS data reduction

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ABSTRACT

A data evaluation program was developed at ETH Zurich to meet the requirements of the new compact AMS systems MICADAS and TANDY in addition to the large EN-Tandem accelerator. The program, called "BATS", is designed to automatically calculate standard and blank corrected results for measured samples. After almost one year of routine operation with the MICADAS C-14 system BATS has proven to be an easy to use data reduction tool that requires minimal user input. Here we present the fundamental principle and the algorithms used in BATS for standard-sized radiocarbon measurements.

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1. Introduction

The first data reduction software used at ETH Zurich was developed 20 years ago for the accelerator mass spectrometry (AMS) measurement on the large 6 MV EN-Tandem [1]. Though the software was powerful for its time, it lacks some nice-to-have features, is rather cumbersome and time-consuming in operation. More important, the data reduction for our compact AMS systems MICADAS [2] and TANDY [3] demands for modified procedures to perform high-precision measurements. A new, computer platform independent data reduction software was therefore programmed to meet these new requirements.

Little information is available about the full data reduction procedures applied by different AMS laboratories starting from the raw data of an AMS measurement [4,5]. Very often only rudimentary information is given [6–10]. However, data reduction for high-precision measurements in accelerator mass spectrometry is not trivial because the measurement is not primarily limited by counting statistics. The stability of the instrument over time and possible small contaminations during sample preparation have become of equal importance for high-precision low energy AMS of radiocarbon.

The new data reduction software BATS is tailored for the needs of the Zurich measurement procedure as it is outlined below for radiocarbon samples. However, it can be adapted virtually to all measurement procedures as they are implemented at other AMS laboratories, when the corresponding data import filters are added.

2. Program overview

BATS, written in the computer platform independent programming language JAVA, is able to calculate the final results of AMS measurements for individual unknown samples with their uncertainties based on the multiple measurement of a set of samples. This set is typically one cassette or one sample wheel with the related number of samples, including standards and blanks. There is also the option to combine several subsequently measured sample sets, if measurement conditions were stable enough to consistently evaluate them simultaneously. Beside the straightforward normalisation and the blank subtraction procedure a number of corrections can by applied to the initial data. These corrections are executed on the results of the single measurements of individual samples, before sample means are calculated. The idea behind this approach is to separate systematic effects from the fundamental uncertainty of the results based on its counting statistics. Such systematic effects, if present, can cause a significantly higher standard deviation of the raw results from repeated measurement of a single sample than expected from their internal counting statistic. Under favourable conditions, the applied corrections reduce the standard deviations towards the internal (counting statistic based) uncertainty. BATS shows this based on chi-square-tests comparing the uncertainty from counting statistics with the standard deviation.

2.1. Systematic effects

Systematic effects can be responsible for offsets of the measured results. The approach of BATS is to visualise and determine any expected systematic effect independently, based on measured parameters of selected samples (e.g. blanks or standards). This disentangles different systematic effects and therefore allows correction by relatively simple mathematics.

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Three types of systematic effects can be corrected with BATS:

1. Time dependent drifts of the observed isotopic ratio measurements.
2. Systematic deviations of measured isotope ratios from variations of extracted beam currents.
3. Distortions of the $^{14}C/^{12}C$ ratio due to misidentified events (in the following termed background) as they can result from e.g. scattered ^{13}C ions resulting from the break-up of ^{13}CH molecules.

The program shows plots of the measured ratios ($^{14}C/^{12}C$ and $^{13}C/^{12}C$) as function of time or current. Possible time dependant trends can be identified easily and accounted for by linear approximations. The required corrections depend mainly on the measurement conditions of the instrument and have to be applied mainly on older and larger accelerators, as new and small accelerators are running more stable over time [2].

Several AMS laboratories regularly observe a dependency of the measured ratios on the beam current intensity. Reasons for this can be manifold. For example the accelerator with the stripper may have a limited acceptance for the relatively large beam currents of ^{12}C (compared to the ^{13}C or ^{14}C). This effect would result in higher $^{14}C/^{12}C$ ratios with increasing beam current.

Some instruments can measure on the high-energy side the current of $^{13}C^+$ coming from brake-up of $^{13}CH^-$ injected together with the ^{14}C. BATS allows to plot the detected $^{14}C/^{12}C$ ratios against the measured $^{13}C(H)/^{12}C$ ratio for blank samples. If a linear correlation is observed, the background from scattered molecular fragments reaching the detection system can be quantified and a subsequent correction can be applied for all types of samples including the blanks.

2.2. Blank subtraction

The program allows the user to introduce and use various models for sample chemistry blanks, such as would be needed for small samples of variable sizes [11], and for sputter sample holder contamination, relevant for sputtering on absorbed CO_2.

For normal samples, a weighted mean of the background corrected $^{14}C/^{12}C$ from all measured blanks is computed (see Eq. (1)). In general, this blank value is subtracted from all measurements.

2.3. Isotope fractionation

Many instruments have the capability to perform precise $^{13}C/^{12}C$ ratio measurements. With these measurements fractionation effects can be detected. They might occur during sample preparation, during sputtering of the sample material in the ion source, or as a response of the measurement system due to the changing conditions as the material is sputtered away (e.g. crating and related changes in ion optics). To take these effects into account, BATS calculates $\delta^{13}C$ corrected $^{14}C/^{12}C$ ratios for all samples and standards of a set.

2.4. Standard normalisation

Using these *blank and $\delta^{13}C$ corrected ratios* the final standard normalisation factor is calculated.

First, the weighted mean ratio of all individual standards is calculated. Second, the mean of means is calculated. In case there is no significant difference between a single measurement and the mean of means, the corresponding normalisation factor is used for all the measurements to obtain corrected single-measurement results. Otherwise it has to be tested, if individual standards will not reflect the true nominal ratio or if there is an external error contributing in addition to the internal counting statistic error. The sources for an external error are often difficult to determine as they can be either related to sample and target preparation or to the measurement itself.

2.5. Uncertainty

The uncertainty of a given sample is basically deduced from the counting statistic of the sample and the blank and standard variations.

The scatter of the blank represents the variation in sample contamination during preparation and storage as well as ion source contamination. The blank scatter is normally not determined from a single measurement, but it can be derived from multiple measurements.

The uncertainty of the mean of all standards is used for normalisation of the individual samples. In addition the standard deviation of multiple standards is used to determine any additional external uncertainty that represents reproducibility of single samples. The sources for the external error are manifold and often difficult to determine. They originate in sample preparation and sometimes also in the measurement itself. In case of stable and temporarily short measurement of high-quality samples, the external uncertainty is negligible. On the other hand, a temporarily long lasting high-precision measurement is typically limited by the external uncertainty, whereas the sample and standard mean is determined precisely.

2.6. Sample mean and report

The sample mean is calculated from the normalised single measurement and can be reported in different ways. The final data can be saved either to file (text, excel, xml) or be written into a database. All applied corrections are logged. Single results can directly be sent to the Oxcal program for calibration of the radiocarbon age [11].

3. Calculations

In the following, we will describe the evaluation of our standard radiocarbon measurement procedure as they are performed at the ETH MICADAS system. The program has many additional options, but they apply either for other AMS systems (e.g. our large EN-Tandem) or for other isotopes. The MICADAS runs over days and no retuning is required during measurements. No time or current corrections have to be applied.

If not stated otherwise, in the following weighted mean values are calculated:

$$\langle X \rangle = \sum_i \frac{(X_i \cdot p_i)}{\sum_i p_i} \qquad (1)$$

where the weight of a single measurement p_i is the ^{12}C charge during the measurement of ^{14}C, computed from the measured ^{12}C current and the measuring time ($p_i = current(^{12}C) \cdot time \propto {}^{12}C$). By using such weighted averages, the dependency of the final results on the arbitrary defined measurement sequence is avoided.

3.1. Measurement and data import

A typical radiocarbon measurement on the MICADAS at ETH Zurich is done as follows:

- A cassette has 20 samples, including least two standards and two blanks.
- All samples of a cassette are measured at least four times (additional passes are added depending on the required precision).

- A single measurement is subdivided into 10 cycles of 30–60 s each (again depending on the desired precision).
- True raw data are the acquired scaler counts provided by the current-to-frequency converters which measure $^{12}C_{LE}$, ^{12}C, ^{13}C and $^{13}C(H)$, respectively, as well as the ^{14}C counts provided from the data acquisitions system and the counts from a lifetime clock which defines the total measurement time. The measurement control software converts the scaler values to better readable initial measurement parameter such as $^{12}C_{LE}$, ^{12}C, ^{13}C and the $^{13}C(H)$ currents for each cycle [12]. The initial parameters are stored in a database.
- Stored procedures are used to calculate mean values for a single measurement from the corresponding set of cycles and to store them inside the database.

BATS imports the summary data of all single measurements of all samples from the database. Standards, blanks and unknowns have an identifier code. Thus, BATS can retrieve standard normalisation and blank information directly from the database. In general, all corrections are applied to the results of the single measurements of all samples, before any related means are calculated.

3.2. Initialisation

BATS initially calculates the raw radioisotope ratios from the measured radioisotope counts and the measured stable isotope current. Standards and blanks are automatically recognised by the program. Stable isotopes are measured as 1 + ion currents quasi-simultaneously with the ^{14}C [12] and can be transformed to an expected amount of stable isotope for the time t the ^{14}C is measured:

$$^{x}C = \text{current}_x \cdot t/e \tag{2}$$

where e is the elementary charge (1.602×10^{-19} C).

3.3. Background

The rare isotope is first corrected for interferences in the detection system Therefore we exploit additional information derived together with ^{14}C measurement. With our MICADAS system, the $^{13}C^+$ resulting from broken-up molecules ($\rightarrow ^{13}C_{mol}$) is detected independently in a dedicated Faraday cup located in the focal plane of the HE-magnet. On the MICADAS machine, this current shows a linear correlation with the background count rate in the detector. The background corrected ratio is then:

$$R_{mol} = \frac{(^{14}C_{meas} - k_{mol} \cdot {}^{13}C_{mol})}{^{12}C} \tag{3}$$

The factor k_{mol} is in our case an experimentally determined correlation factor and is pretty constant over time and is not changed from measurement to measurement. This applied correction typically reduces the scatter of the processing blank and reduces the overall uncertainty of the measurement.

3.4. Blank

In general, we apply only a relative blank correction:

$$R_{mol,bl} = R_{mol} - \langle R(bl)_{mol} \rangle \tag{4}$$

where $\langle R(bl)_{mol} \rangle$ is the mean of all blank measurements:

$$\langle R(bl)_{mol} \rangle = \sum_i \frac{((R(bl)_{mol})_i) \cdot p_i}{\sum_i p_i} \tag{5}$$

The blank is subtracted from all samples, including standards to simplify the calculations. This simplified calculation is valid if sample sizes are kept constant [13].

3.5. Mass-fractionation

The measured $\delta^{13}C$ for every single measurement is used to correct the $^{14}C/^{12}C$ ratios for fractionation (similar to [14]).

First, the weighted mean of the measured $^{13}C/^{12}C$ of all standards with a given $\delta^{13}C_{std}$ is calculated $\langle (^{13}C/^{12}C)_{std} \rangle$. Subsequently, the $\delta^{13}C$ values for the single measurements are calculated according to:

$$\delta^{13}C = \left(\frac{(^{13}C/^{12}C) \cdot (1 + \delta^{13}C_{std}/1000)}{\langle (^{13}C/^{12}C)_{std} \rangle} - 1 \right) \cdot 1000 \tag{6}$$

$R_{mol, \, bl}$ of the single measurements is then corrected for fractionation:

$$R_{mol,bl,f} = R_{mol,bl} \cdot \left(\frac{0.975}{1 + \delta^{13}C/1000} \right)^2 \tag{7}$$

The fractionation correction normally reduces the standard deviation of the single measurements of one sample significantly (sample inhomogeneity and/or changes of fractionation in the ion source during the measurements). Only the application of this mass fractionation correction allows us to perform high-precision radiocarbon measurements with final uncertainties <2‰.

3.6. Standard normalisation

The weighted mean of all fractionation corrected standard measurements $\langle R(std)_{mol,s,bl} \rangle$ is calculated:

$$\langle R(std)_{mol,bl,f} \rangle = \sum_i \frac{((R(std)_{mol,bl,f}) \cdot p_i)}{\sum_i p_i} \tag{8}$$

Subsequently the corrected ratios $R_{mol,bl,f}$ of all samples are normalised.

$$R_{mol,bl,f,std} = \frac{R_{nom}}{\langle R(std)_{mol,bl,f} \rangle} \cdot R_{mol,bl,f}[F^{14}C] \tag{9}$$

where R_{nom} is the nominal *fraction* ^{14}C value of the standard [15].

3.7. Sample mean

Finally the weighted sample means are calculated according to Eq. (1):

$$\langle R_{mol,bl,f,std} \rangle = \frac{\sum_i ((R_{mol,bl,f,std})_i \cdot p_i)}{\sum_i p_i} \tag{10}$$

where i represents a single measurement.

The mean $\delta^{13}C$ is calculated accordingly:

$$\langle \delta^{13}C \rangle = \frac{\sum_i ((\delta^{13}C)_i \cdot p_i)}{\sum_i p_i} \tag{11}$$

3.8. Uncertainty

First, the uncertainty of the counting statistic ($^{14}C_{meas}$) and the molecular correction is calculated for a single measurement:

$$\sigma_{R_{mol}} = \sqrt{^{14}C_{meas} + (\sigma_{k_{mol}} \cdot {}^{13}C_{mol})^2} \tag{12}$$

$\sigma_{k_{mol}}$ is the estimated uncertainty for the correction factor k_{mol} (see Eq. (3)).

The uncertainty for the sample mean is then:

$$\sigma_{\langle R_{mol} \rangle} = \frac{\sum_i ((\sigma_{R_{mol}})_i \cdot p_i)}{\sum_i p_i} \tag{13}$$

Second, the scatter of the blank samples $\langle R_{mol}\rangle_i$ is used to account for the variability of the blank contamination of the samples:

$$\sigma_{\langle R(bl)_{mol}\rangle} = \frac{\sum_i \left(\langle R_{mol}\rangle_i - \langle R(bl)_{mol}\rangle\right)^2}{n-1} \tag{14}$$

The blank scatter can be a long-term empirical value because it is mainly caused by sample preparation and only to a minor extend by the actual measurement itself.

The uncertainty of the blank scatter is added, and corrected for fractionation:

$$\sigma_{\langle R_{mol,bl,f}\rangle} = \sqrt{\sigma_{\langle R_{mol}\rangle}^2 + \sigma_{\langle R(bl)_{mol}\rangle}^2} \cdot \left(\frac{0.975}{1+\langle \delta^{13}C\rangle/1000}\right)^2 \tag{15}$$

In most cases the $\sigma_{\langle R_{mol,bl,f}\rangle}$ underestimates the true uncertainty. Therefore, third, an additional external error is added.

$$\sigma_{\langle R_{mol,bl,f,ex}\rangle} = \sqrt{\sigma_{\langle R_{mol,bl,f}\rangle}^2 + \sigma_{ex}^2} \tag{16}$$

The external uncertainty σ_{ex} covers additional unassigned errors (e.g. caused by measurement instabilities or by variation in target preparation). It can be estimated from the scatter of individual standard means based on chi-square-tests, that compares the uncertainty of the $\sigma_{\langle R_{mol,bl,f}\rangle}^2$, that is mainly based on counting statistic, with the observed standard deviation of the mean, that should be in accordance with $\sigma_{\langle R_{mol,bl,f,ex}\rangle}$. In practice, often only few standards are measured and it is difficult to make a good estimate for the σ_{ex} σ_{ex} (that is in our case in the range of only 1‰). The σ_{ex} is then best estimated from long-term experience, as this value represents the instrumental properties under normal and stable conditions. For high-precision measurements, the σ_{ex} is estimated directly from an increased number of standards measured together with the unknowns.

Finally, the uncertainty of the standard normalised mean is finally:

$$\sigma_{\langle R_{mol,bl,ex,std}\rangle} = \langle R_{mol,bl,f,std}\rangle$$
$$\times \sqrt{\left(\frac{\sigma_{\langle R_{mol,bl,f,ex}\rangle}}{\langle R_{mol,bl,f}\rangle}\right)^2 + \left(\frac{\sigma_{\langle R(std)_{mol,bl,f,ex}\rangle}}{\langle R(std)_{mol,bl,f}\rangle}\right)^2 + \left(\frac{\sigma_{R_{nom}}}{R_{nom}}\right)^2} \tag{17}$$

where

$$\sigma_{\langle R(std)_{mol,bl,ex}\rangle} = \frac{\sum_s \left(\left(\sigma_{\langle R_{mol,bl,f,ex}\rangle}\right)_s \cdot p_s\right)^2}{p_s} \tag{18}$$

is the uncertainty of the weighted mean of all standards $\left(\sigma_{\langle R_{mol,bl,ex}\rangle}\right)_s$ and where $\sigma_{R_{nom}}$ is the uncertainty of the R_{nom}.

We would like to note, that the uncertainty of the standard normalised mean does not include any uncertainty introduced by the sample pre-treatment (if not applied to the blanks and standards as well).

4. Results and conclusions

Over the last year the BATS program has proven to be an easy to use data reduction program. Little user input is required to get good and reliable end results. In more than 90% of all routine radiocarbon measurements on MICADAS, no user input is required. Only for high-precision measurements (<2‰) we usually have a closer look at the data to more precisely estimate the external uncertainty mainly coming from sample preparation. Data tables with chi-square-tests and 2D-plots help to visualise and monitor the quality of the data.

Because the program is designed to automatically calculate and update the results the quality and status of the acquired data can be monitored quasi-online. This allows us to see, if the desired precision including the complete error propagation has been reached. The possibility to monitor the data quality and to calculate the full error propagation quasi online is a fundamental and important development that enables us to perform high-quality and high-precision measurements on our compact AMS systems.

In a next step, the program will be applied for data analysis/reduction of other isotopes than radiocarbon. An open, public version will be published soon as well. The import options will be extended and some calculations will be adapted to meet the requirements of other AMS systems.

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