

Another 6 years of radiocarbon secondary-standard AMS with two spectrometers

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ARTICLE INFO

Keywords:

Accelerator mass spectrometry
AMS
SSAMS
Radiocarbon
C14
14C

ABSTRACT

The Scottish Universities Environmental Research Centre (SUERC) has analysed >100,000 individual graphite preparations with two accelerator mass spectrometers. Analysis quality is maintained by a programme of secondary-standards measurement, and annual assessment of the resulting large dataset can provide insight into subtle effects. The same analyses that are used to derive external errors within individual batches of samples, or to monitor inter-batch variance, are also employed in aggregate to determine overall instrument and process performance. The recent 2021 findings are consistent with prior years', including the apparent contradiction that secondary standard analysis can be both consistent and slightly discordant between the two instruments. However, individual sample radiocarbon measurement on both machines remains accurate and typically 3 ‰ precise.

1. Introduction

The SUERC Radiocarbon Laboratory for sample preparation and the AMS Laboratory for sample measurement choose to operate a consistent protocol for organic sample analysis. Therefore, it suffices to monitor performance with only a few different reference materials consistently prepared and measured, but these data are produced in abundance. >4000 individual graphite preparations of two radiocarbon international intercomparison materials have been measured on the SUERC tandem and single-stage (SSAMS) accelerator mass spectrometers since 2016. These results are first and foremost used for quality control and quality assurance in routine random sample analysis but given the power of the large dataset produced they can also be employed to elucidate subtle inter-spectrometer variance and any longitudinal affects. This is assessed annually. These are the 2021 data, with a summary of another 6 years of results [1].

Letham Moss peat humic acid extract has featured in several laboratory intercomparisons and is our most measured secondary standard. Each sample of this is now prepared by individual combustion and subsequently measured as are our unknown samples. For reference, the published ICS Stage 2, VIRI T and SIRI N consensus ages are 3368 BP,

3360 ± 16 BP and 3369 ± 4 BP respectively [2], and the VIRI T consensus Fraction Modern specific activity is 0.65821 ± 0.000333 Modern [3]. The predominantly radiometric ICS contributions considerably scatter about the consensus age, and it is noticed that the uncertainties of the two VIRI T values are inconsistent. The SIRI N consensus specific activity is not published, but the consensus age is consistent with 0.65745 ± 0.00030 Modern. At less than one radiocarbon half-life old the humic acid is typical of samples measured. Moreover, the scatter of the multiple humic acid samples prepared and analysed with each batch of unknown samples is used to derive an additional external error on the acid analyses that is then also applied to the other measurements in the batch for realistic measurement confidence.

Contemporary 1.1635 ± 0.000084 Modern TIRI A barley mash [4] is the other material frequently measured. Whereas the humic acid is principally used to establish batch measurement quality, but can also be used to monitor long-term performance, the barley mash measurements are explicitly intended to be an inter-batch quality check that can also serve as additional intra-batch standard. To this end the barley mash is combusted in bulk and stored as gas for the best long-term sample consistency across batches, with aliquots of this graphitised with the

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<https://doi.org/10.1016/j.nimb.2022.12.014>

Received 19 May 2022; Received in revised form 7 December 2022; Accepted 13 December 2022

Available online 30 December 2022

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batches. No allowance is made in measurement normalisation and background-correction for the barely mash special provenance, which is not ideal, but is unnecessary given the role served by this secondary standard. Certainly, it is expedient to process already combusted material when preparing numerous analysis samples from common material.

Finally, the SUERC AMS Laboratory also makes radiocarbon and other long-lived radionuclide measurements of samples prepared in other SUERC chemistry laboratories and elsewhere. Those analyses are also scrutinised for additive external error using secondary standard materials. However, these workflows must accommodate diverse projects with a considerable variety of sample types and sizes, instead of having samples conform to a single, or a few, common protocols. Accordingly, the choice and preparation of secondaries is then adjusted to each project, with the outcome that no individual secondary standard is measured in the quantities sufficient to be considered here. Conversely, a new third laboratory instrument, the prototype bespoke positive-ion mass spectrometer [5], should produce radiocarbon data in enough quantity in due course.

2. Method

SUERC accelerator mass spectrometry with the 5 MV tandem and with the 250 keV SSAMS is per [6] & [7] respectively, and radiocarbon dating is per [8]. Essentially all organic sample ^{14}C -AMS is relative to OXII SRM and VIRI K ancient wood background-corrected, and an algorithm automatically sequences sample measurement for constant analysis quality where possible (rather than for consistent sample analysis time). Repeated measurements of unknown age samples and standards are interlaced until sufficient data is generated [1]. It is expedient, for overall productivity, to automatically terminate each sample's analysis when a programmable target measurement quality of typically 3 % precision is achieved. This requirement applies both to the scatter of the repeat measurements of the sample, as determined by the standard error of at least the most recent in sequence repeat measurements of sample $^{14}\text{C}/^{13}\text{C}$ (of typically 40,000 radiocarbon counts each), and to the sample total radiocarbon counting statistics on the sum of counts across the repeats concerned. If, as is usual, the repeat measurements pass a 95 % Chi-square test of consistency then the often smaller Poisson error can be propagated as measurement uncertainty, else the scatter is used. Of course background-correction, normalisation and $\delta^{13}\text{C}$ correction further inflate the uncertainty, and are all included in the data and plots here. We prefer to propagate measured $^{14}\text{C}/^{13}\text{C}$ ratios only, to also avoid the productivity constraints of reliable ^{12}C detection too, and so $\delta^{13}\text{C}$ correction is with separate off-line stable isotope ratio mass spectrometry. Inevitably this adds a small external error to the AMS results, which is captured by also applying the external error on the measurements of the secondary standards concerned here. Samples are of a consistent ~ 1.5 mg C size permitting convenient background correction by subtraction of background sample $^{14}\text{C}/^{13}\text{C}$ ratio. In summary, per the results below, our processes can be tuned for a desired measurement precision, which is achieved by sample preparation, automated analysis and data processing routinely bettering the goal to offset the subsequent addition of externalities.

Instrument differences, per [6] and [9], are largely expected to not manifest in analysis differences. Both instruments now mount two 134 sample MC-SNICS sputter ion sources, but the second on the SSAMS is yet to be commissioned. On-going measurement tandem ion transport is monitored by comparing pre- and post-accelerator ^{12}C measurement (although ^{12}C measurement is not propagated, as explained), while the simpler SSAMS is routinely limited to masses 13 & 14 acceleration only. The tandem eliminates molecular interference to radiocarbon measurement by stripping ions into a high charge state that molecules cannot survive, whereas the SSAMS employs a thicker stripping gas to destroy molecules by repeated collisions, resulting in the same measured sample chemistry background [1]. Tandem radiocarbon detection is of

$^{14}\text{C}^{4+}$ so that any $^7\text{Li}^{2+}$ ions can be separated in the gas ionisation detector and additionally counted as a monitor of any sample glass contamination that might fractionate the measurement, whereas SSAMS radiocarbon detection is necessarily of $^{14}\text{C}^+$. However, extremely few results are affected. Measured 60 % efficient tandem Ar stripping and accelerator ion transport is twice as effective as the lower ion velocity SSAMS N_2 stripping and ion transport, but analysis is typically not sample size limited and both instruments are capable of making 2 % precise $^{14}\text{C}/^{13}\text{C}$ measurements of Contemporary graphite in the usual amount. Moreover, as the SSAMS can accommodate a twice as large 150 μA ^{12}C beam, before ^{13}C measurement becomes non-linear, analysis proceeds at the same rate on both machines. Instrument detector deadtime correction (DTC) is different on the two instruments (SSAMS DTC is by comparing detector single channel analyser hardware triggers with the number of processed counts, and tandem DTC is measured by applying and partially recovering 20 Hz synthetic signals applied to the detector preamps), but is similar at low radiocarbon ion event rates.

However, the SSAMS single-channel PIPS ^{14}C detector is subject to a ~ 1 /minute dark count not present in the tandem's gas ionisation detector using signal multiple-channel coincidence to avoid noise. This affects both primary and secondary standards measurement, as well as all other sample analysis. Automatically longer measurements of samples of lower radiocarbon specific activity will be more affected, and so the measurement dark count contribution will be approximately inversely proportional to the sample specific activity. Accordingly, the dark count can be expected to cause a slight SSAMS data non-linearity with sample age that is insignificant in normal individual sample analysis but may manifest as raised radiocarbon measurement in large datasets of older samples. However, the dark count and its effect are too small to account for the inter-instrument off-set in the humic acid data below.

Another contrast with tandem AMS is that the SSAMS is operated slightly detuned for radiocarbon measurement [7]. This is to mitigate PIPS detector interference from ions with rigidities in analytical elements only very slightly different to ^{14}C . Ultimately this limits the SSAMS instrument radiocarbon measurement background to little better than the sample chemistry background. The tandem radiocarbon AMS instrument background, measured with sputtered unprocessed geological carbon, is several half-lives lower.

3. Results

All the 2021 humic acid AMS is accurate, in that the 146 SSAMS and the 280 tandem measurements are each normally distributed with median values within 1- σ uncertainty of the reference values. Indeed, the averages bisect the VIRI and SIRI results. This is shown in Fig. 1 along with the fits. The median value is the 50th percentile value of data plotted in value sequence, and a non-linear horizontal axis that renders a normal distribution as a straight line makes deviations from normality readily apparent across the whole range of data values.

The SSAMS mean is 0.6578 Modern with 2.7 % average 1- σ uncertainty and 3.0 % standard deviation, i.e. on average an additional 1.4 % external error would need to be added in quadrature to the propagated sample analysis uncertainties to produce uncertainties indicative of overall instrument and process performance for the year. The tandem values are 0.6574 Modern mean, 2.8 % average uncertainty, 3.0 % standard deviation, and 1.1 % external error, i.e. radiocarbon AMS is routinely to the same average 3.0 % precision on both instruments.

Both the 70 SSAMS and the 112 tandem measurements of processed barley mash bulk gas are normally distributed with the fits shown in Fig. 2. As before, the intercomparison consensus value and the median measurement agree within measurement uncertainty. The SSAMS mean is 1.1649 Modern with 2.8 % average 1- σ uncertainty and 4.0 % standard deviation, i.e. a 2.9 % annual external error. The tandem values are 1.1654 Modern mean, 2.8 % average uncertainty, 3.4 % standard deviation, and 2.0 % external error, i.e. the twice as large bulk barley mash

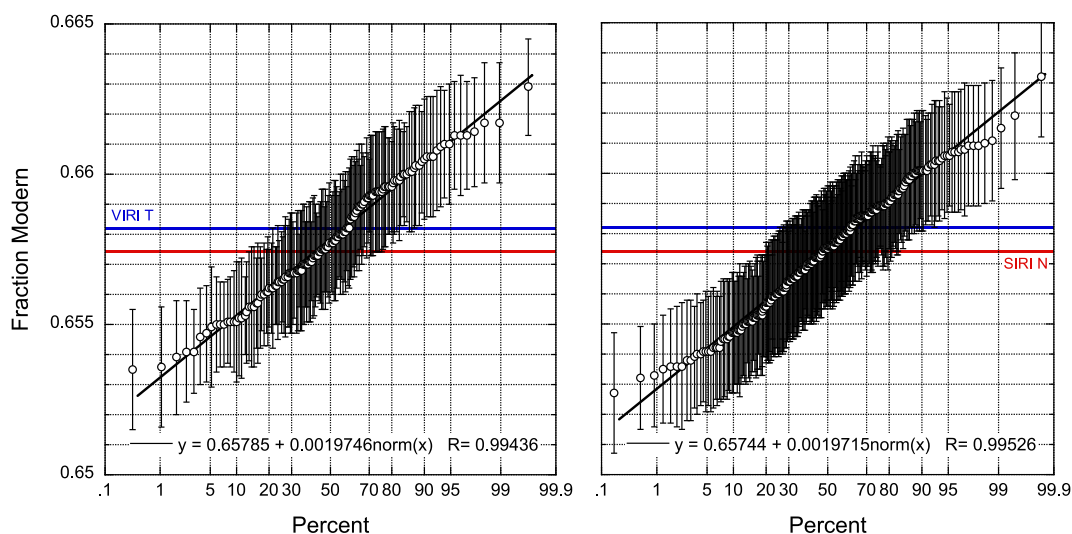


Fig. 1. Probability plots of the SSAMS (left) and tandem (right) measurements of SIRS N / VIRI T humic acid in 2021, and their consensus values. The plotted 1- σ uncertainties are propagated $^{14}\text{C}/^{13}\text{C}$ measurement, background-correction, normalisation and $\delta^{13}\text{C}$ correction uncertainties. The excess scatter on humic acid samples measured with sample batches is employed to derive the additional external error to be applied to the whole sample batch.

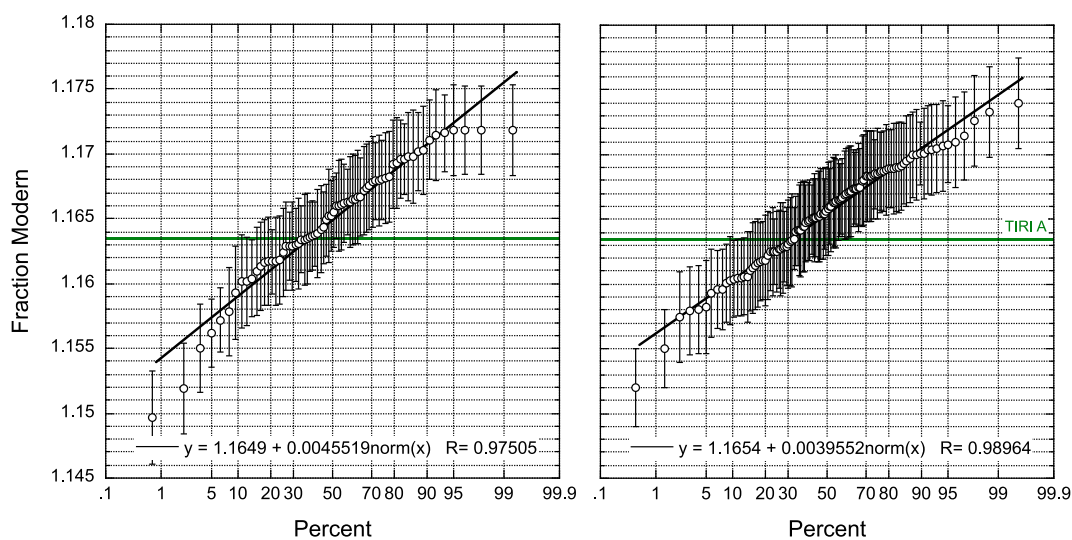


Fig. 2. Probability plots of the SSAMS (left) and tandem (right) measurements of TIRI A barley mash in 2021, and the consensus value. The plotted 1- σ uncertainties are propagated $^{14}\text{C}/^{13}\text{C}$ measurement, background-correction, normalisation and $\delta^{13}\text{C}$ correction uncertainties. Bulk barley mash CO_2 is principally employed to monitor inter sample batch AMS consistency.

external error is not instrument specific.

The 2021 data are unexceptional, with distributions like those in previous years. Also, the size of the datasets tightly constrains the error on the annual mean, and Fig. 3 shows that the 2021 data is consistent with previous years' results to great certainty. The figure is derived from 2887 humic acid and 1267 barley mash preparations and measurement.

4. Discussion

The materials employed as AMS secondary standards well brackets in radiocarbon-age much of the $>100,000$ graphitised samples measured at SUERC to date. Accordingly, the standards-performance is considered indicative of much of our routine AMS and informs the expressed uncertainty of relevant measurements. However, while the humic acid and barley mash materials are principally employed to test intra and inter-sample batch AMS performance respectively, they are annually measured in such large quantities that they can also elucidate subtle effects. Certainly there are anomalies.

Bulk sample combustion is unrepresentative of usual sample processing, but the external error on the samples thus produced is greater than that of the individual combustions when the reverse may be expected. However, bulk barley mash samples are similarly measured on both instruments to great certainty, which isn't the case for the humic acid. To the $<1\%$ standard error of the annual means graphed, the two instruments' results agree for the younger barley mash but not exactly for the older material. Results on both instruments are accurate, but very slightly different. This has consistently been the case since these measurements began a decade ago.

We speculate that an inheritance of sample preparation may be responsible. Certainly, the three standards concerned, the humic acid, the barley mash, and the oxalic acid primary standard to which they are normalised, are differently prepared. Perhaps some legacy of this survives CO_2 cryofocusing manifesting in graphite that behaves differently in the two instruments. The simplest hypothesis is that humic acid graphite includes more of the unidentified species interfering with SSAMS PIPS radiocarbon detection. The presence of hydrogen in a

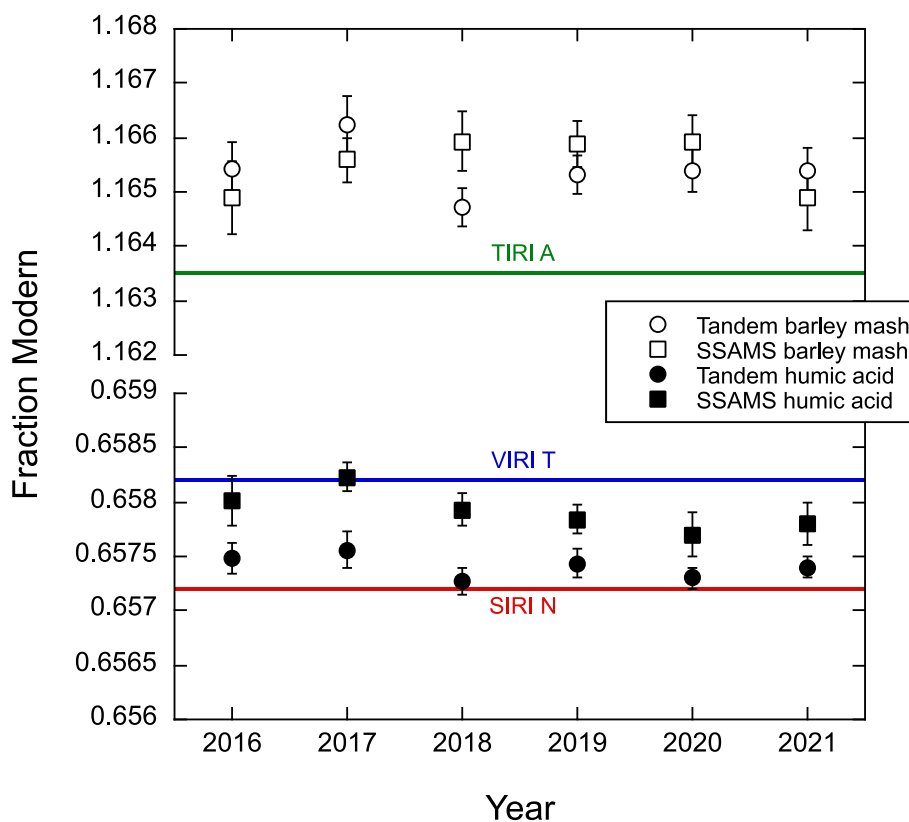


Fig. 3. The mean and standard error of annual analyses of SIRI N / VIRI T humic acid and TIRI A barley mash with the SSAMS and tandem accelerator mass spectrometer in recent years. 2021 data is consistent with prior results, including the apparent contradiction that one secondary standard measures indistinguishably on both instruments, while the other doesn't quite.

sputtered sample cathode is known to promote this [9], but there is no correlating humic acid excess CH^- signal (as determined by routine pre-accelerator mass 13 measurement during mass 14 accelerator sequential injection). Alternatively, sample impurities might indirectly affect the isotope-ratio measurement by fractionating the carbon isotope ratio in a manner that is spectrometer-specific. This seems implausible, not the least because the measured $\delta^{13}\text{C}$ of the gases from either secondary standard are routinely similar to each other, as are the measured AMS beam currents, but the stable carbon isotope ratio of the graphite prepared from these is not systematically evaluated on the accelerator mass spectrometers for the reason given.

Finally, Naysmith et al [2] have previously reported on the annual variation of the humic acid measurements averaged over both instruments without considering the two populations of results and their changing weighting to the average from year to year. They declared a 3369 ± 5 BP consensus age. In comparison, this six-year tandem and SSAMS mean and standard errors are 3369 ± 1 BP and 3363 ± 1 BP respectively. The 6 years inter-instrument variance at this age is consistent with the 3366 ± 5 BP mean and standard deviation of the three historical international laboratory inter-comparisons listed previously. Moreover, the even slight discordance also highlights the challenges of establishing the reference materials consensus values in the first place: if, under the near optimal conditions for consistency, the same SUERC personnel preparing common materials and measuring radiocarbon according to the same protocols can produce appreciably divergent results on two instruments, then the diversity of data within the field is only to be imagined, the inter-comparisons notwithstanding.

As has been described, humic acid samples are individually combusted while the barley mash CO_2 is made in greater quantity at a time and stored for use, and in further contrast OXII CO_2 is by wet oxidation. A campaign of consistent preparation of these materials in sufficient quantities could address the speculative cause of the reported inter-

instrument performance. Nevertheless, the agreement between the two quite different spectrometers operating with different ion charge-states, differently overcoming molecular interferences and dead-time correcting their results, is remarkable. Essentially individual sample measurements with both instruments remain indistinguishable, and accurate. Also, irrespective of the external errors and any inter-instrument variance, the consistency of the aggregated data over the years is testament to the long-term reproducibility of the underlying processes at SUERC.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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