Radiocarbon, Vol 66, Nr 5, 2024, p 1395–1405 DOI:10.1017/RDC.2023.45
Selected Papers from the 24th Radiocarbon and 10th Radiocarbon & Archaeology International Conferences, Zurich, Switzerland, 11–16 Sept. 2022

ROUTINE QUALITY ASSURANCE IN THE SUERC RADIOCARBON LABORATORY

B G Tripney[1]* • E Dunbar[1] • E M Scott[2] • P Naysmith[1]

[1]Scottish Universities Environmental Research Centre, Scottish Enterprise Technology Park, East Kilbride, Glasgow, G75 0QF, Scotland, UK
[2]School of Mathematics and Statistics, University of Glasgow, Glasgow G12 8QQ, Scotland, UK

ABSTRACT. The SUERC Radiocarbon Laboratory reports approximately 3000 unknown samples per year with an additional 1200 samples processed for quality assurance purposes. In addition to the primary OxII standard (SRM-4990C) required for AMS batch normalization, secondary "known-age" standards have been used over many years to evaluate individual batch quality. These have included wood (as prepared alpha-cellulose), barley mash, humic acid, a background mammoth bone, known-age bones, and a whisky sample. In this paper, we present some of the results gathered over routine laboratory operation (for more than 10 years) and examine the results illustrating how they are being used to monitor and quality assure performance. Since many of these samples have also been used in the Glasgow intercomparisons, we will also reflect on the results, as well as the actual and potential uses of such samples.

KEYWORDS: intercomparison, quality assurance, standards.

INTRODUCTION

In continuously operated laboratory processes, the ability to routinely and frequently measure replicate samples of different materials brings many benefits, including monitoring process changes (shifts and changes in variability). In the radiocarbon (^{14}C) community, laboratories use OxI and OxII, as primary standards, but laboratories additionally make use of secondary standards and reference materials (or working standards). Working standards are important tools for any laboratory. They are used to check and calibrate all stages of the dating procedures, including pretreatment and ultimately to assess stability of performance. Checking all parts of the dating process, including pretreatment, and thinking of the diversity of materials and ages, suggests that laboratories require a suite of working standards. In this paper, we present a report of the SUERC working standards.

SUERC QUALITY ASSURANCE SAMPLES

SUERC uses a variety of well-characterized samples for quality assurance (QA) purposes. This has been a regular part of the Radiocarbon Laboratory's processes (Dunbar et al. 2016) since the start of its accelerator mass spectrometry (AMS) program in the early 2000s. Prior to the launch of the AMS program, the laboratory also used working standards, but of course the challenges were different given the sample size requirements. A mix of samples derived from intercomparison studies, and a selection of "in-house" materials are used to fulfil a number of purposes including informing on the quality of individual AMS batches, monitoring particular processes, and estimating the laboratory background.

While some QA samples are used only in relevant batches, many are used as part of a standard AMS batch configuration. Targets are arranged in 13 groups of 10 with the first three positions of each group given over to QA. One position per group is occupied by the SRM-4990C OxII required for AMS batch normalization, with another two positions taken by samples derived from intercomparison studies. The regular use of these samples provides a long-term record of performance. The standard batch composition is shown in Table 1.

*Corresponding author. Email: Brian.Tripney@glasgow.ac.uk

Table 1 Standard 134-position AMS batch composition for SUERC Radiocarbon Laboratory.

Material	Lab code	No. per Batch	Purpose
Oxalic Acid II	M	14	Batch normalization
Humic Acid	HA	13	QA, long-term monitoring, and batch error estimation
Bulk Barley Mash	BBM	6	QA and long-term monitoring
Background	BK	7	Background correction
Background Bone	MB	2 (min.)	Bone background correction
Unknown/Other QA	—	89	Monitoring of individual processes
<left empty>	—	3	Space for AMS Laboratory use

Intercomparison Samples

Samples used in intercomparison studies have been subject to a set of selection criteria (Scott et al. 2018). In addition to being relevant and of sufficient quantity, the samples distributed must be homogeneous in radiocarbon. The variety of materials should cover the different types and ages that a laboratory may encounter. Preferably, materials of known-age (e.g., dendrodated wood) are used but, in the case of working standards, it is also possible to use well-characterized reference materials from laboratory intercomparisons. Using the estimated consensus ages that arise from an intercomparison results in a set of reference materials that are suitable for use in laboratory quality assurance systems.

The SUERC Radiocarbon Laboratory has used 3 such reference materials for internal quality checks. A cellulose and a humic acid have successively been used as the main reference sample, with a barley mash running in a supporting capacity continuously from 2003 onwards. The intercomparison samples employed by the laboratory are summarised in Table 2.

Those samples derived from intercomparison studies not only provide the immediate benefit of comparing results against a known consensus value but, with their continued usage over several years, allow for the monitoring of any long-term trends or drifts in the data.

Belfast Cellulose

For the FIRI study (Scott 2003), a dendrochronologically dated section of Scots pine was supplied by Prof M Baillie, Queen's University Belfast. This 40-year ring span (identifier Q7780) had been dated to 3299 BC–3257 BC and originated from the Garry Bog, Co Antrim, Northern Ireland.

Fine shavings of the wood were taken and subjected to an acid-base-acid pretreatment, followed by a cold bleaching with a solution of sodium chlorite in hydrochloric acid. Repeat bleaching and washing left a white cellulose fraction, which was dried to form FIRI sample I.

With a consensus value of 4485 ± 5 yr BP, this material was deemed a good fit for the predominately archaeological-age unknown samples being processed at SUERC. The pre-prepared Belfast Cellulose (laboratory code BC) was employed by the Radiocarbon Laboratory as one of its main QA samples, with small sub-samples taken and combusted

https://doi.org/10.1017/RDC.2023.45 Published online by Cambridge University Press

Table 2 Main intercomparison samples used in the SUERC Radiocarbon Laboratory Quality Assurance program.

Type	Inter-comparison sample	Consensus	Lab code	Lab mean	No. of measurements	Period in use
Belfast Cellulose	FIRI I	4485 ± 5 yr BP	BC	4495 ± 36 yr BP	1229	2003–2009
Humic Acid	SIRI N	3369 ± 4 yr BP	HA	3370 ± 28 yr BP	4269	2007–present
Bulk Barley Mash	GIRI A	116.43 ± 0.075 pMC	BBM	116.49 ± 0.49 pMC	3209	2003–present

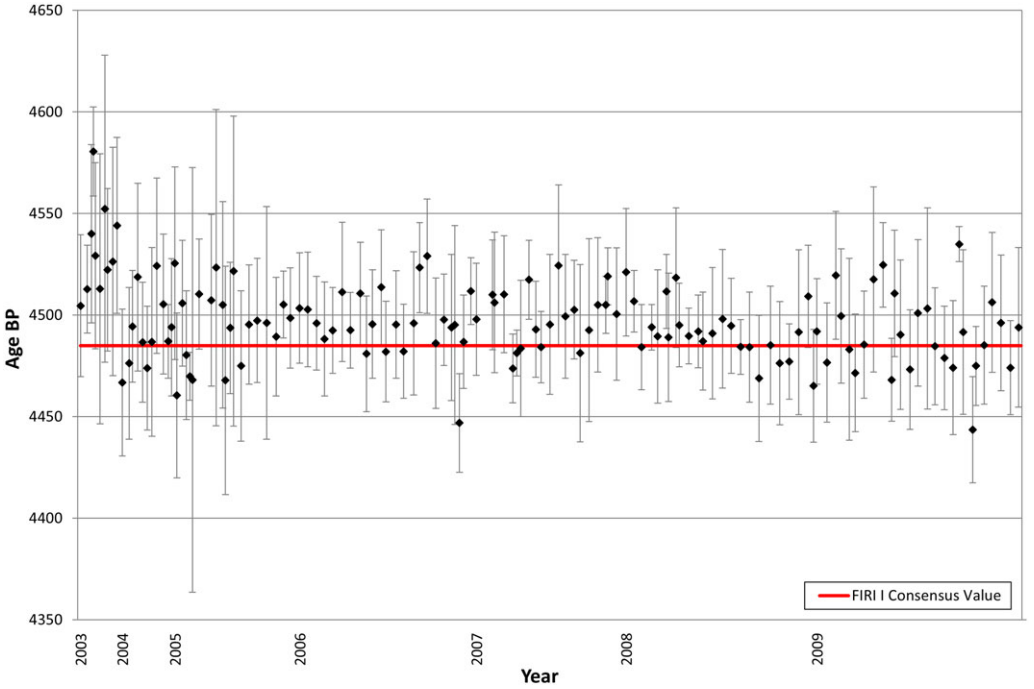

Figure 1 Belfast Cellulose, mean value per AMS batch.

to produce graphite targets. By late-2005 the laboratory's standard AMS setup had evolved to require 13 of the BC secondary standards per batch, one per group, with the measurement results not only providing a check against an expected consensus value, but the standard deviation of these also informing the reportable error on the unknowns in the batch. Use of the BC sample continued until the end of 2009 when it was superseded by a humic acid sample. The measurements from this seven-year period are shown in Figure 1. The figure shows the variation in results over time, and the slight mean shift compared to the consensus value. The overall variation (standard deviation of 36 years) is slightly larger than the mean quoted error of 25 years.

Humic Acid

Humic acid is a useful sample type for inter-comparison studies as its preparation results in a homogeneous material that can be sub-sampled for distribution to study participants. Several humic samples have been used in studies over the years (Naysmith et al. 2019).

In this case, a well-humified peat was collected from Letham Moss, Central Scotland. A freshly cut sample was taken, with the depth limited to around 20 cm to reduce age variation. Following humic acid extraction as described in Harkness et al. (1989), the resultant material was used initially as part of the International Collaborative Study (ICS) (Scott et al. 1990), and subsequently in VIRI (sample T; Scott et al. 2010) and SIRI (sample N; Scott et al. 2017).

The SUERC Radiocarbon Laboratory first measured the Letham Moss Humic Acid as a QA sample in 2007. A small quantity of the prepared Letham Moss Humic Acid is taken and combusted to produce CO_2 for each graphite target. From 2010 onwards, 13 of these humic

https://doi.org/10.1017/RDC.2023.45 Published online by Cambridge University Press

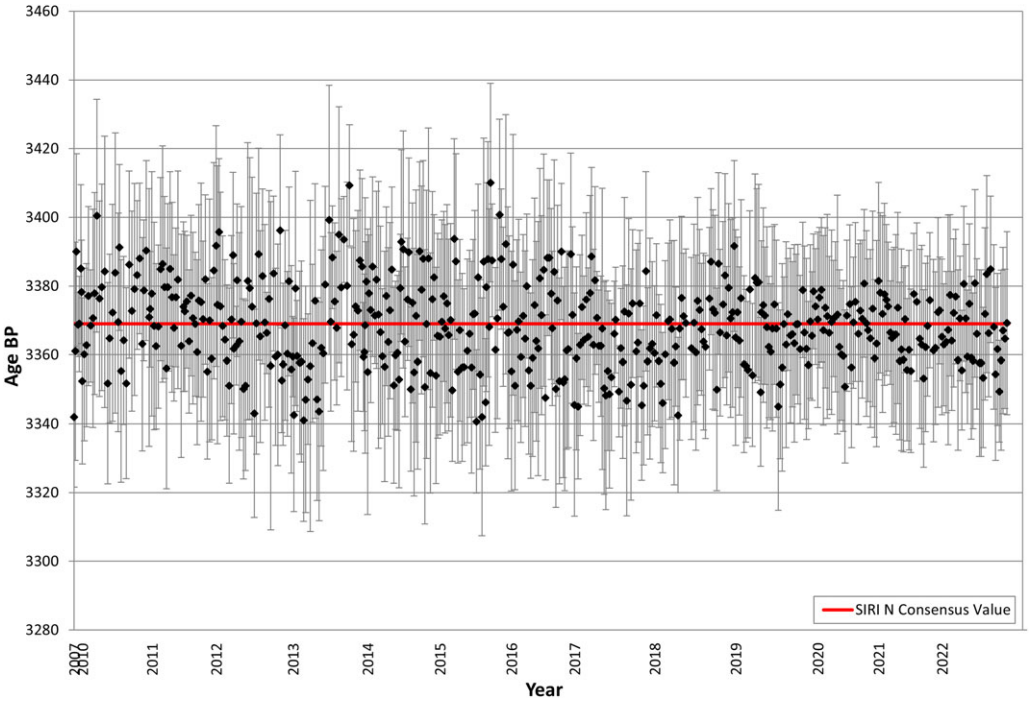

Figure 2 Humic Acid, mean value per AMS batch.

acid targets (lab code HA) are required for a standard AMS batch, as this took over the role of the BC samples in determining the batch error. The overall laboratory mean of 3370 ± 28 yr BP shows good agreement with the SIRI N consensus value of 3369 ± 4 yr BP. A distribution plot of the humic acid measurements since 2007 is shown in Figure 2.

Barley Mash

To ensure that the inter-comparison series covered the full range of the radiocarbon dating process, a natural sample was sought that would provide a modern value. Barley mash, a by-product of the whisky industry, was chosen. This "mash" material consists of the solid residue of the whisky fermentation process and is produced from a single year of barley growth. A number of these barley mash samples have been used in inter-comparison exercises over the years, with four samples collected in different years from the Glengoyne distillery and two more recently from the Glen Elgin and Linkwood distilleries.

Table 3 presents information on all the barley mash samples that have been used in the 30 years of Intercomparison studies (Scott et al. 2018).

The Glengoyne barley mash, introduced in the Third International Radiocarbon Intercomparison (TIRI sample A) and subsequently used in GIRI (sample A; Scott et al. in review), has been used by the laboratory as an additional quality assurance sample from 2003 onwards and has run concurrently across both the BC and HA samples, adding a repeat "modern" sample to the QA suite.

https://doi.org/10.1017/RDC.2023.45 Published online by Cambridge University Press

Table 3 Barley Mash samples used in intercomparison studies over the last 30 years.

Sample code	Year collected	Sample description	Consensus pMC	1σ error
TIRI A	1991	Barley Mash Glengoyne	116.35	0.0084
FIRI G	1998	Barley Mash Glengoyne	110.7	0.04
FIRI J	1998	Barley Mash Glengoyne	110.7	0.04
VIRI A	2001	Barley Mash Glengoyne	109.1	0.04
VIRI C	1998	Barley Mash Glengoyne	110.7	0.04
VIRI S	2001	Barley Mash Glengoyne	109.96	0.042
SIRI D	2006	Barley Mash Glengoyne	103.9	0.063
GIRI A	1991	Barley Mash Glengoyne	116.43	0.075
GIRI C	2017	Barley Mash Glen Elgin	102.22	0.072
GIRI F	2019	Barley Mash Linkwood	101.62	0.117

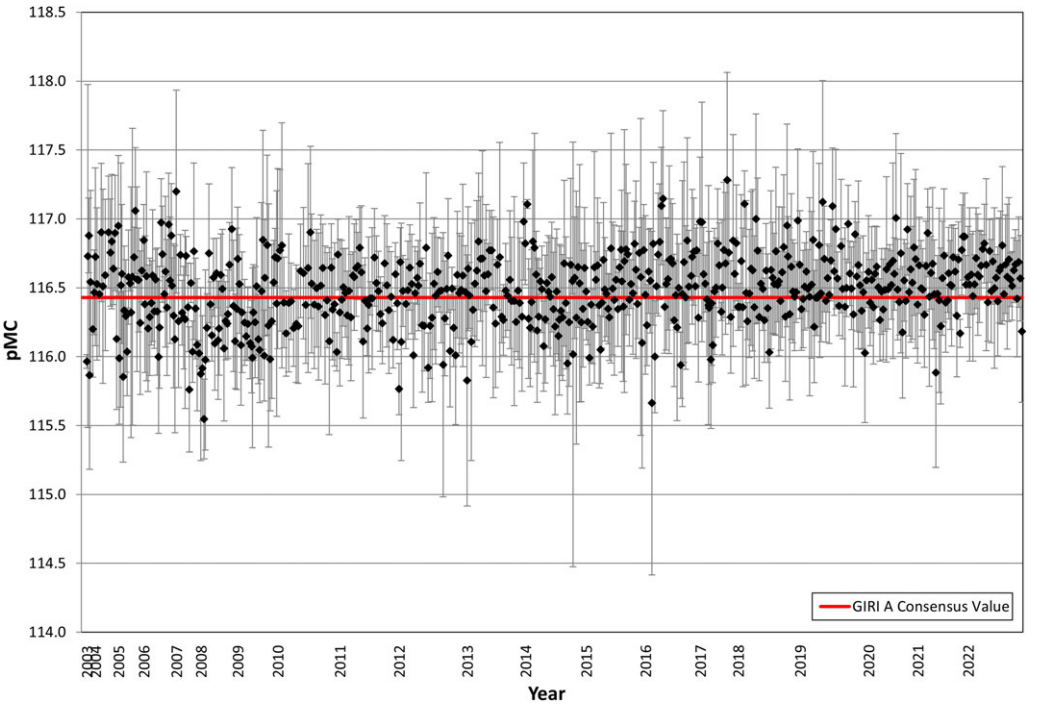

Figure 3 Bulk Barley Mash, mean value per AMS batch.

While the BC and HA samples are combusted similarly to unknown samples, the barley mash is treated differently. Sufficient material is combusted to generate 2 L of CO_2 with smaller aliquots sub-sampled to prepare replicate graphite targets. Once prepared as a Bulk Barley Mash gas (lab code BBM), routine measurement provides a more focused check upon the graphitization and AMS operational parameters of the dating process, removing the variables of pretreatment and combustion. Figure 3 shows 20 years of measurements on the BBM sample. The barley mash samples have also played an important role in modern grain studies (Dunbar et al. in review).

https://doi.org/10.1017/RDC.2023.45 Published online by Cambridge University Press

Table 4 Background samples used by SUERC Radiocarbon Laboratory.

Type	Mean $F^{14}C$	No. of measurements
Interglacial wood	0.0014 ± 0.0006	3648
Icelandic doublespar	0.0016 ± 0.0007	157
Background bone	0.0033 ± 0.0013	895

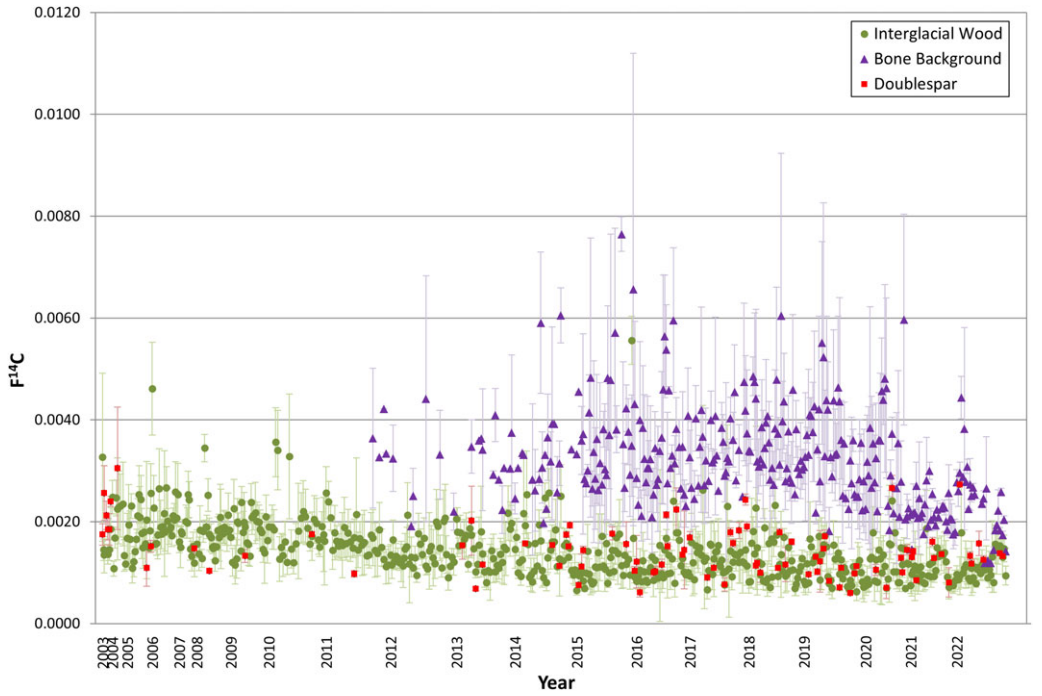

Figure 4 Background samples, mean values per AMS batch.

Background Samples

The laboratory uses a "background subtraction" method to calculate results (Brown and Southon 1997). In a standard configuration, 7 background samples (laboratory code BK) are prepared and included within each AMS batch, with the measured mean background ratio for the batch removed from all other samples (standards and unknowns) as part of the age calculation process. Due to the intrinsic differences in the pretreatment processes, the background for bones is calculated separately to that for other samples using measurements on appropriate materials.

A summary of the sample materials used to estimate laboratory background is shown in Table 4, with a distribution plot of the results given in Figure 4.

Interglacial Wood

A wood sample, expected to be of background age, was provided by Michael Friedrich, University of Hohenheim as part of the VIRI study and used as Sample K. This is the main

https://doi.org/10.1017/RDC.2023.45 Published online by Cambridge University Press

Table 5 SUERC Radiocarbon Laboratory "in-house" quality assurance samples.

Type	Lab code	Mean	No. of measurements	Period in use
New make spirit	WNMS	1.0613 ± 0.0043	47	2015–present
Kerosine	—	0.0016 ± 0.0003	12	2018–present
Known-age bone	KAB	2134 ± 44 yr BP	40	2003–2011
	SKAB	428 ± 42 yr BP	74	2012–2017
	HSKB	1594 ± 36 yr BP	36	2018–2021
	ESKB	1673 ± 24 yr BP	8	2022–present
Cremated bone	CBS	4122 ± 29 yr BP	20	2019–present

background sample now employed by the laboratory. Sub-samples of the material are processed according to the alpha-cellulose method (modification of Hoper et al. 1998; Dunbar et al. 2016) to remove any contaminant carbon before combustion and graphitization.

Icelandic Doublespar

Where a batch contains unknown carbonate samples, some wood samples may be replaced with geological-age carbonate. Provided by S Jakobssen, Museum of Natural History, Reykjavik for use in the TIRI study (Sample F), this material from an Icelandic spar-mine is subjected to acid hydrolysis to produce CO_2 for graphitization. Typically, a small number of these are prepared annually.

Background Bone

A program of measurement on mammoth bone commenced in 2011 to monitor the contribution of the bone chemical pretreatment processes (modification of Longin 1971; Dunbar et al. 2016) to the laboratory background. It was noted that this bone background value was higher than that for the wood and doublespar background (Naysmith et al. 2017). As of 2013 background bone samples are routinely prepared and included in AMS batches alongside unknown bone samples, with the batch mean bone background substituted as appropriate in the final age calculations to account for the difference in the pretreatment procedure. Originally a mammoth bone from a Marine Isotope Stage 7 (MIS-7) deposit (Cook et al. 2012) was used to this effect and from 2022 this has been processed in conjunction with a section of aurochs horn (courtesy of Headland Archaeology), also of infinite age with respect to ^{14}C.

While the bone background is elevated compared to the wood and carbonate, this may be explained by the more complicated chemical process. More recent analysis of the bone background demonstrates less variability as a number of environmental factors have stabilised (Dunbar et al. 2017).

"In-House" Quality Assurance Samples

In addition to the samples adopted from intercomparison studies and those providing an estimate of background, the SUERC Radiocarbon Laboratory employs several "in-house" samples to further broaden its quality assurance program. These serve a different purpose, namely to provide confidence in laboratory procedures that are more specialized. As such, these QA samples are not part of the standard AMS batch layout but may be added to customise the batch to the unknown sample types being measured. A summary of the "in-house" samples is given in Table 5.

https://doi.org/10.1017/RDC.2023.45 Published online by Cambridge University Press

QA for Whisky Analysis

Whisky differs from most samples analysed by the laboratory in that it is of fairly recent age and a liquid. As such, two further QA samples are processed alongside any unknown whiskies that are measured (Dunbar et al. 2018; Cook et al. 2020).

Each AMS batch containing whisky will include a sample of New Make Spirit (lab code WNMS) produced in 2007, sourced from a Scottish distillery. This is spirit that has not been barrel-aged, so all ^{14}C may be attributed to the barley used for distillation. 15 µL is taken by syringe for combustion.

As a further check, a kerosine sample is used to monitor the laboratory background for the syringe sampling process, with results comparable to the background wood value.

Known-Age Bones

As noted above, the chemistry involved in the pretreatment of bone is quite different to that used for other organic samples. For this reason, starting in 2003, a series of known-age bones have been used to monitor the collagen extraction process. These bones are selected to be of an age appropriate to the majority of samples measured in the laboratory and are of sufficient size to provide multiple measurements over time. In each case, a subsample of the bone is taken and pretreated according to the modified Longin method used by the laboratory (Dunbar et al. 2016).

The original Known-Age Bone (lab code KAB), a horse femur previously measured to 2130 ± 60 yr BP provided by English Heritage, was in use between 2003 and 2011. This was eventually replaced in 2012 with a Scottish KAB (lab code SKAB), a human femur (430 ± 35 yr BP) from a site in Balumbie, Angus (thanks to Derek Hall).

Historic Environment Scotland have provided large bone samples as of 2018. The first (lab code HSKB) being an animal bone from an excavation at Edinburgh Castle. A second bone, a cattle scapula, also from the Edinburgh site (lab code ESKB) was introduced in 2022 to continue the series. While these last two bones had not been previously dated, they were selected from a context in the appropriate age range. Although not strictly "known-age" they continue to serve the same purpose, i.e., allow repeated measurements to be made on sub-samples of the same bone.

Cremated Bone

A large sample of cremated bone (lab code CBS) from a site near Dunragit, Dumfries and Galloway, Scotland is used as a check on the preparation of this sample type. A sample of the material is taken and processed according to the Groningen method (Lanting et al. 2001).

DISCUSSION AND CONCLUSIONS

This paper has presented information about the laboratory quality assurance program routinely operated in SUERC, comprising in any given year in several thousand additional measurements. A suite of different materials, of different ages have been used as working standards and routinely and frequently measured. In some cases more than 4000 measurements have been made, while for others, fewer measurements have been made because of their specialized nature. Using such samples supplements the information gained from participating in an intercomparison, specifically the continuous monitoring of performance and the checking for drifts, which can be identified and linked to particular stages in the dating process. Such

https://doi.org/10.1017/RDC.2023.45 Published online by Cambridge University Press

samples also allow laboratories to investigate the impacts of changes in laboratory procedures, e.g., a new pretreatment protocol. Further, the variation observed in such a series of results also allows the laboratory to explore whether there is any excess variation beyond what would be expected given the routinely quoted errors.

In addition to demonstrating the long-term stability of measurements in the lab (as shown in Figures 1–4) and general good agreement with published consensus values, quality assurance samples provide multiple more immediate benefits to the laboratory. The main intercomparison-derived samples (BC, HA, and BBM) are used to monitor AMS batch quality. This means being used not only to quantify the reportable error on a batch, but also to potentially reject data should the error be too high or the measured mean deviates significantly from consensus. Likewise, background samples are predominantly used for calculation purposes, but monitoring measured $F^{14}C$ values can identify any potential concerns before they become problematic. Data on these QA and background samples are also returned to the AMS Laboratory to help anticipate when maintenance (e.g., a source clean) may be required. Consistent results over the "in-house" standards give confidence in laboratory methodologies at a given time, while any deviation from the consensus will identify areas where procedures may need to be reviewed.

ACKNOWLEDGMENTS

Special thanks to Helen Kinch, Linzi Gustinelli, Kerrie-Anne Kelly, Euan Greig and all our former technical staff for sample preparation and analysis, and to AMS staff for measurement.

REFERENCES

Brown TA, Southon JR. 1997. Corrections for contamination background in AMS ^{14}C measurements. Nuclear Instruments and Methods in Physics Research B 123(1–4):208–123.

Cook GT, Higham TFG, Naysmith P, Brock F, Freeman SPHT, Bayliss A. 2012. Assessment of infinite-age bones from the Upper Thames Valley, UK, as ^{14}C background standards. Radiocarbon 54(3–4):845–853.

Cook GT, Dunbar E, Tripney BG, Fabel D. 2020. Using carbon isotopes to fight the rise in fraudulent whisky. Radiocarbon 62(1):51–62.

Dunbar E, Cook GT, Murdoch I, Xu S, Fabel D. 2018. Identification of fraudulent-age whiskies using accelerator mass spectrometry (AMS) radiocarbon (^{14}C) analyses. In: Proceedings of the Worldwide Distilled Spirits Conference 2017. Context, Packington. ISBN 9781899043781.

Dunbar E, Cook GT, Naysmith P, Tripney BG, Xu S. 2016. AMS ^{14}C Dating at the Scottish Universities Environmental Research Centre (SUERC) Radiocarbon dating laboratory Radiocarbon 58(1):9–23.

Dunbar E, Naysmith P, Cook GT, Scott EM, Xu S, Tripney BG. 2017. Investigation of the analytical $F^{14}C$ bone background value at SUERC. Radiocarbon 59(5):1463–1473.

Dunbar E, Scott E M, Tripney B. In review. Carbon isotope changes through the recent past: $F^{14}C$ and $\delta^{13}C$ values in single barley grain from 1852 to 2020. Radiocarbon.

Harkness DD, Cook GT, Miller BF, Scott EM, Baxter MS. 1989. Design and preparation of samples for the international collaborative study. Radiocarbon 31(3):407–413.

Hoper ST, McCormac FG, Hogg AG, Higham TFG, Head MJ. 1998. Evaluation of wood pretreatments on oak and cedar. Radiocarbon 40(1):45–50.

Lanting JN, Aerts-Bijma AT, van der Plicht J. 2001. Dating of cremated bones. Radiocarbon 43: 249–254.

Longin R. 1971. New method of collagen extraction for radiocarbon dating. Nature 230(5291):241–242.

Naysmith P, Dunbar E, Scott EM, Cook GT, Tripney BG. 2017. Preliminary results for estimating the bone background uncertainties at SUERC using statistical analysis. Radiocarbon 59(5):1579–1587.

Naysmith P, Scott EM, Dunbar E, Cook GT. 2019. Humics—their history in the radiocarbon inter-comparisons studies. Radiocarbon 61(5):1413–1422.

Scott EM, editor. 2003. The Third International Radiocarbon Inter-Comparison (TIRI) and the Fourth International Radiocarbon

https://doi.org/10.1017/RDC.2023.45 Published online by Cambridge University Press

Inter-Comparison (FIRI) 1990–2002: results, analyses, and conclusions. Radiocarbon 45(2): 135–408.

Scott EM, Aitchison TC, Harkness DD, Cook GT, Baxter MS. 1990. An overview of all three stages of the international radiocarbon intercomparison. Radiocarbon 32(3):309–319.

Scott EM, Cook GT, Naysmith P. 2010. The 5th International Radiocarbon Intercomparison (VIRI): an assessment of laboratory performance in Stage 3. Radiocarbon 52(2):859–866.

Scott E, Naysmith P, Cook G. 2017. Should Archaeologists Care about ^{14}C Intercomparisons? Why? A Summary Report on SIRI. Radiocarbon 59(5):1589–1596.

Scott EM, Naysmith P, Cook GT. 2018. Why do we need ^{14}C inter-comparisons?: The Glasgow ^{14}C inter-comparison series, a reflection over 30 years. Quaternary Geochronology 43:72–82.

Scott EM, Naysmith P, Dunbar E. In review. Preliminary results from Glasgow International Radiocarbon Intercomparison. Radiocarbon.

https://doi.org/10.1017/RDC.2023.45 Published online by Cambridge University Press