University
of Glasgow

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14C AMS AT SUERC: IMPROVING QA DATA WITH THE 5MV TANDEM AND 250kV SSAMS

P Naysmith[1,2] • G T Cook[1] • S P H T Freeman[1] • E M Scott[3] • R Anderson[1] • S Xu[1] • E Dunbar[1] • G K P Muir[1] • A Dougans[1] • K Wilcken[1] • C Schnabel[1] • N Russell[1] • P L Ascough[1] • C Maden[1]

ABSTRACT. In 2003, a National Electrostatics Corporation (NEC) 5MV tandem accelerator mass spectrometer was installed at SUERC, providing the radiocarbon laboratory with ^{14}C measurements to 4–5‰ repeatability. In 2007, a 250kV single-stage accelerator mass spectrometer (SSAMS) was added to provide additional ^{14}C capability and is now the preferred system for ^{14}C analysis. Changes to the technology and to our operations are evident in our copious quality assurance data: typically, we now use the 134-position MC-SNICS source, which is filled to capacity. Measurement of standards shows that spectrometer running without the complication of on-line $\delta^{13}C$ evaluation is a good operational compromise. Currently, 3‰ [14]C/^{13}C measurements are routinely achieved for samples up to nearly 3 half-lives old by consistent sample preparation and an automated data acquisition algorithm with sample random access for measurement repeats. Background and known-age standard data are presented for the period 2003–2008 for the 5MV system and 2007–2008 for the SSAMS, to demonstrate the improvements in data quality.

INTRODUCTION

In 1997, the Scottish Universities Environmental Research Centre (SUERC) Radiocarbon Laboratory started to prepare graphite for the analysis of ^{14}C by accelerator mass spectrometry (AMS). The prepared graphite was pressed into cathodes at SUERC and then sent to the NSF Facility at the University of Arizona for measurement. The cathodes, which included unknowns and secondary standards, together with primary standards prepared in Arizona, were loaded into wheels that had space for a total of 40 cathodes and then run on one of the two AMS systems. The results were then calculated using the method outlined by Donahue et al. (1990) and ^{14}C ages for all unknowns and standards sent back to SUERC. There are difficulties in being a satellite laboratory for an AMS facility such as: 1) working 1 or 2 months in arrears and not being able to address issues that might arise as quickly as we would have liked; 2) not running large numbers of secondary standards; and 3) having no control on when the cathodes are measured. However, this arrangement worked very well for over 5 yr and helped the SUERC Radiocarbon Laboratory staff gain very valuable experience in graphite production prior to the establishment of the SUERC AMS group.

Here, we consider retrospectively the quality assurance (QA) data generated by the partnership of the SUERC Radiocarbon and AMS groups. The data spans the period from the establishment of the latter group in 2003. Some ^{14}C group procedures, established when prepared samples were previously measured in Arizona, have subsequently been changed (e.g. sample graphite-ion ratios have been optimized for the local ion sources and the background correction reflects different views on sample contamination) and AMS Laboratory techniques have also developed over time. The AMS group now operates 2 accelerator mass spectrometers: the original tandem spectrometer based on a 5MV Pelletron is for multi-element AMS and a ^{14}C-only single-stage accelerator mass spectrometer (SSAMS) that was commissioned in 2007. The instruments have different ion optics, including source geometries (which have also varied), achieve different ion energies and differently remove molecular interferences, but produce essentially similar data (Freeman et al. 2010) except that the SSAMS cannot exceed 60 kyr BP. SSAMS ^{14}C detection is subject to both unresolved interferences

[1]SUERC, Scottish Enterprise Technology Park, Rankine Avenue, East Kilbride G75 0QF, Scotland, United Kingdom.
[2]Corresponding author. Email: P.Naysmith@suerc.gla.ac.uk.
[3]Statistics Department, University of Glasgow, Glasgow G12 8QQ, Scotland, United Kingdom.

and to a detector dark-count as ion energies are insufficient for multiple-electrode gating. In any case, sample chemistry is typically limiting to ~55 kyr.

The instruments are similarly used. Both are capable of simultaneous sample $\delta^{13}C$ measurement, but it is operationally expedient not to do this and instead to run with greater ion beams. $^{14}C/^{13}C$ accelerator measurements are instead normalized with $\delta^{13}C$ values generated off-line by isotope ratio mass spectrometry (typically using a VG SIRA 10) of subaliquots of CO_2. It follows that our ^{14}C measurements are potentially subject to additional on-line random fractionation, but the QA program shows that this is typically small. Instead, the large beams that are employed quickly reduce Poisson uncertainties, allowing a faster throughput of analyses. In any case, the standard deviation of results for different preparations of common materials, our secondary standards, serves as the minimum quoted measurement uncertainty.

Wheels of up to 134 samples, including standards, can be run on either machine. Since measurements of such large numbers of samples can last several days, our procedures have to cope with changes in measurement conditions. To this end, samples are measured to completion in groups of 10 in only a few hours, with OXII primary standards spanning groups for intergroup consistency. Each group of 10 samples contains 1 OXII primary standard, 1 wood secondary standard of just less than 1 half-life in age, either a modern secondary standard material or a background standard, and 7 unknowns. Such rapid analysis is relatively insensitive to longer-term drifts and changes are quickly apparent in the fast repeat measurements of individual samples, including primary and secondary standards. Operator intervention, to adjust the spectrometer or to change sample measurement parameters, can be immediate; each sample is automatically repeatedly measured in intragroup rotation until the sample total counting statistics and the scatter of the repeat $^{14}C/^{13}C$ measurements exceeds a quality threshold of typically 3‰, disregarding early inconsistent measurements as necessary. Finally, time trends remaining in the completed data sets can be compensated for in subsequent data reduction and normalization. Correlating trends in the various standards, and therefore in the measurements of all other samples, too, can be removed by normalizing measurements to measures of the primary standards made at a similar time only, essentially making variable the primary standard. In the event that a sample's repeat measurements pass a 95% chi-squared test of equivalence, then the total-counting-statistics uncertainty can be propagated, an approach that is borne out by our QA data; there is circularity to using secondary standards to both inform data production and estimate its quality, but our goal is the derivation of appropriate rather than the smallest estimates of analysis uncertainty.

RESULTS

To identify each system, they have been coded as S1–5MV tandem accelerator mass spectrometer and S3–250kV SSAMS. The Radiocarbon laboratory uses different types of natural materials as standards with the background standards employed depending on the form of the unknowns. Data are presented here for the 3 most commonly measured secondary standards.

The organic background standard is Heidelberg wood (code BK-HW), which is used in the latest ^{14}C intercomparison study where its code is VIRI K. This is an interglacial wood sample that has had the cellulose component purified from the raw bulk wood. The CO_2 is generated by individual sealed-quartz tube combustions in a furnace at 850 °C using copper oxide as the oxidant and silver wire to remove contaminants (Vandeputte et al. 1996). The CO_2 is cryogenically collected and converted to graphite using the zinc and iron reduction method of Slota et al. (1987). Duplicate graphite targets are prepared from a single combustion and run on different graphite units. Graphitization of the

background standard is rotated around all 16 of our graphite preparation units. In each wheel of samples run on the AMS, there are usually 6 or 7 background targets, 1 in every second group. The data are grouped together to calculate the mean background for the wheel. This number represents the background value for the whole process, including chemical pretreatment, graphitization, and measurement.

We use a Scots pine sample collected from the Garry Bog, Northern Ireland, as a secondary "known-age" standard. This has an in-house laboratory code of BC and has been dendrodated to 3299–3257 BC, with an average ^{14}C age of 4471 BP. This sample was used in the Fourth International Radiocarbon Intercomparison Study where its code was FIRI I. The results from the study gave a consensus value of 4485 ± 5 BP (Scott 2003). A large quantity of this material was pretreated to extract cellulose. The CO_2 is again generated by individual sealed-quartz tube combustions and then purified and graphitized as described above. Duplicate graphite targets are prepared from a single combustion and run on different graphite units each day. In each wheel, there are 13 BC coded samples, 1 in each group. The results from these samples are averaged and a standard deviation is calculated, which is used to limit the error to be applied to the unknowns in the wheel.

Approximately 20 kg of barley mash from a single year's growth was collected from Glengoyne Distillery and given the laboratory code BBM. The sample was used in the Third International Radiocarbon Intercomparison Study with a sample code of TIRI A; the consensus value from this study was 116.35 ± 0.41 pMC (Scott 2003). Sufficient barley mash is combusted to generate 2 L of CO_2, which is cryogenically collected and stored in a glass bulb. Aliquots of gas are then taken and converted into graphite. This sample is used to check the performance of the AMS as all the samples are from the same bulk gas.

SUERC CALCULATIONS

In 2003, once the raw ratio data were produced, we calculated the final ^{14}C results using the method set out in Donahue et al. (1990). This method uses the raw 14/13 ratios and then applies a fractionation factor calculated from the off-line δ^{13}C value. We then calculated fraction modern (Fm) values for the samples before applying a contamination correction to calculate the final F values that were used to calculate ^{14}C ages. We used this method as it was consistent with the method employed when we sent samples to the NSF AMS facility in Arizona for measurement.

In 2007, the SUERC Radiocarbon Laboratory changed the way in which it calculates results. The method still uses the raw 14/13 ratios and then calculates an average background value for the wheel from all the backgrounds samples. However, the next step is to subtract this ratio from all the standards and unknowns in the wheel. Fractionation correction is then applied to all unknowns and standards (using the fractionation factor determined from the off-line δ^{13}C) to calculate F (F is Fm corrected for background). Once F is calculated, it can be used to determine ages for all the unknowns and standards. Age BP is used for the BC standards, but for BBM and BK-HW samples the F value is used.

From 2003 onwards, we have been measuring samples and standards on the 5MV machine. The data have now been collated and average values and standard deviations have been calculated for each of the standards (Table 1).

If we examine stability of the data over the 6-yr period, which will include data from both machines, we observe that for 2003 the standard deviations on the BC and BBM secondary standards were much higher than in subsequent years (Table 1). While it is not possible to identify the cause of the

Table 1 Summary data for standards run on both AMS machines since 2003.

Year	BBM (pMC)	Std dev (1 σ)	BC (yr BP)	Std dev (1 σ)	BK-HW (pMC)	Std dev (1 σ)
2003[a]	116.10	0.99	4540	57	0.0015	0.0008
2004[a]	116.61	0.53	4491	38	0.0019	0.0007
2005[a]	116.49	0.56	4493	45	0.0020	0.0011
2006[a]	116.50	0.46	4496	30	0.0022	0.0009
2007	116.38	0.51	4498	32	0.0018	0.0005
2008	116.34	0.46	4489	30	0.0019	0.0008

[a]5MV data only.

variability, there was a series of minor problems in setting up the machine and in obtaining the correct running conditions. There were also some small issues associated with pressing the samples into the aluminium cathodes, which were addressed towards the end of 2003. Also, there have been subsequent changes to our data reduction algorithms. All or some of these will be reflected in the higher standard deviations of the standards during this period.

Table 2 separates the 2007/2008 data into mean values obtained from the individual sources and indicates that the BBM and BC mean values for the SSAMS are closer to the consensus values, although the differences in means between the 2 sources are not significant. There is no significant difference between S1 and S3 for the background values.

Table 2 Summary data for all standards run on individual sources in 2007 to 2008.

Sample type	S1 (5MV AMS)	Std dev (1 σ)	S3 (SSAMS)	Std dev (1 σ)
BBM (pMC)	116.15	0.70	116.41	0.41
BC (yr BP)	4504	30	4489	31
BK-HW (pMC)	0.0017	0.0006	0.0019	0.0007

Table 3 gives a summary of the annual results and shows the number of standards run per year, indicating that the number has increased from 34 in 2003 to 285 in 2008. The FIRI consensus value for this sample is 4485 ± 5 BP (Scott 2003), and so even the preliminary data obtained in 2003 are, on average, within 1 σ of the consensus value. From 2004 onwards, the mean values are in excellent agreement with the consensus.

Table 3 Summary data in ^{14}C yr BP for Belfast cellulose from 2003 to 2008.

Year	Mean age (yr BP)	Std dev (1 σ)	Nr of analyses	Mean sigma on individual measurement
2003	4540	57	34	34
2004	4491	38	65	26
2005	4493	45	159	24
2006	4496	30	233	23
2007	4498	32	166	24
2008	4489	30	285	24

Figure 1 is a boxplot of the values in each of the 6 yr of operation. It also shows the consensus value of 4485 yr. This demonstrates that after 2003 the results are very consistent, showing only a small amount of scatter in the median around the consensus value and roughly the same annual variability; with each year also showing evidence of a very small (proportionately) number of outliers.

Figure 1 Boxplot of Belfast cellulose results from 2003 to 2008 for both AMS systems

Figure 2 shows the boxplot of the 1-σ error quoted on each result (also summarized in Table 3 above). The mean tendency is an individual sigma between 20 and 30 yr, with a minimum of 15 yr. However, the error on the measurement is not the value that would be quoted on the reported age measurement. This would be limited by the standard deviation on the BC samples for the relevant batch, the additional uncertainty (typically around 2‰) being attributed to random processes (often referred to as random machine error). Since 2006, we have been quoting errors of ±30 to 35 yr on measurements <2 half-lives, and this is borne out by the mean and standard deviation values for those entire years. Also, in 2006 the Radiocarbon Laboratory changed from making graphite targets with 2 mL of CO_2 and 2 mg of Fe to targets with 3 mL of CO_2 and 3 mg of Fe. This was done to allow the targets to be sputtered for longer if necessary and to make the task of weighing such small quantities of Fe powder a little easier.

Figure 2 Boxplot of the 1-σ data for Belfast cellulose from 2003 to 2008

Figure 3 shows the batch data (i.e. summary data for the BC sample for each wheel). Control limits (upper control limit [UCL] and lower control limit [LCL]) are defined, which are based on the overall mean and the batch standard deviation. The upper chart shows how the batch mean age varies from batch to batch, with a small number (mainly in the early phase of operation) of batches being classed as lying beyond the control limits (and thus showing evidence of increased variability). The lower panel shows how the batch standard deviation is varying over time, again control limits are defined. If a batch standard deviation is greater than UCL or less than LCL, then this batch is flagged. The overall standard deviation is 33 yr.
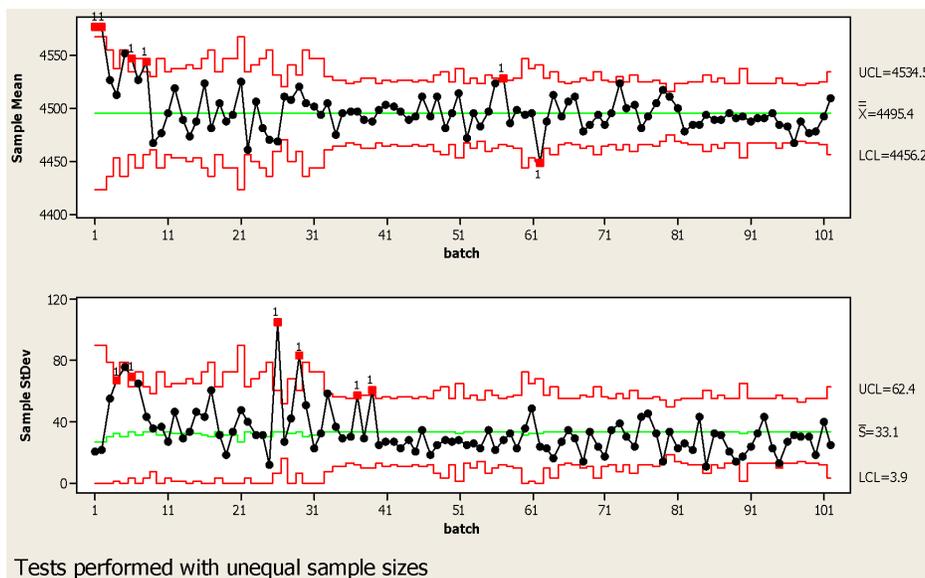
Figure 3 Control chart showing the data for each wheel run over the period from 2003 to 2008

Both panels show how the stability (and hence variability) is well controlled from around batch 26 for the age and around batch 40 for the standard deviation. Other fluctuations are well controlled and reflect a very well-behaved system, combining both chemistry and instrumental conditions. To confirm this latter point, Figure 4 shows the same quality control plot, but this time for the BK-HW sample. This confirms the stability of the system, but again also highlights occasional batches where either the mean or standard deviation exceeds the UCL.

The fact that we have 2 instruments provides us with the opportunity to do a comparison of the results for the BBM and BK-HW samples (a modern and background sample, respectively) from the 2 ion sources. Table 4 summarizes the results (mean and standard deviation) for BBM and BK-HW run from 2007 to 2008 and categorizes them by the source used (S1–5MV tandem, S3–SSAMS). Figures 5 and 6 show the distribution of the results in the form of cumulative distribution function plots. If the data lie along a straight line, then the assumption of a Gaussian distribution for the data is justified. Figure 5 shows that for both sources, the data for BBM generally follow a straight line but with a slightly different slope (mean value) and the confidence limits for S1 are slightly wider than those for S3, indicating more variability in S1. Figure 6 shows for BK-HW that the results do not follow a straight line, there being evidence of curvature and therefore that the assumption of a Gaussian distribution is not tenable. The BBM results also show good agreement with the previously published consensus value of 116.35 ± 0.41 pMC (Scott 2003).
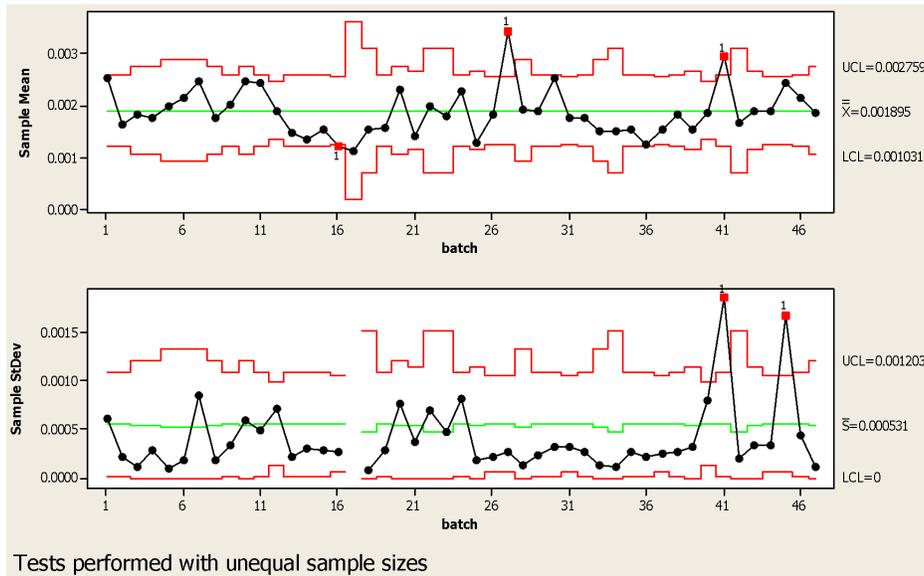
Figure 4 Control chart for wheels run on both machines showing results for a background standard (BK-HW)

Table 4 Comparison of BBM and BK-HW samples on both instruments during 2007 to 2008.

	BBM			BK-HW		
Source	Mean F	Std dev	*n*	Mean F	Std dev	*n*
S1 (5MV)	1.1615	0.0070	66	0.0017	0.0006	60
S3 (SSAMS)	1.1641	0.0041	156	0.0019	0.0007	179
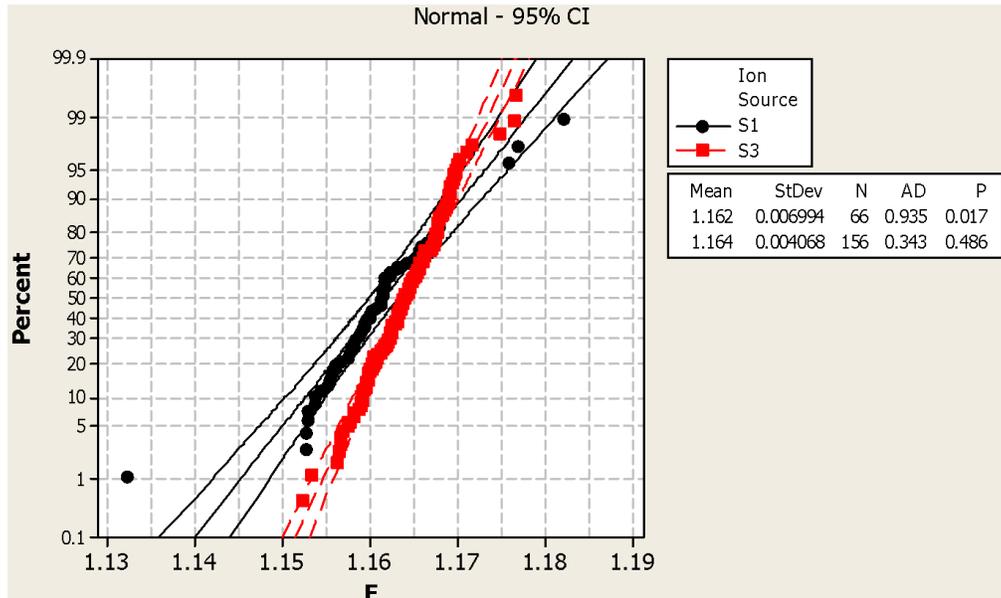
Figure 5 Gaussian plot for BBM for 2007 to 2008 on separate sources
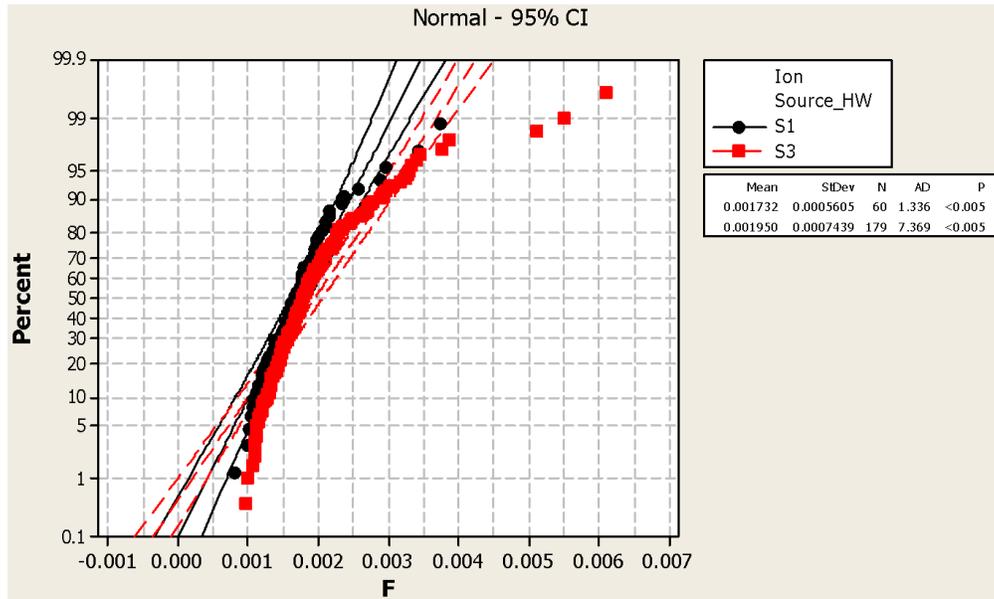
Figure 6 Gaussian plot for BK-HW for 2007 to 2008 on separate sources

Finally, Figure 7 illustrates how the number of standards we produce and measure has increased since 2003.
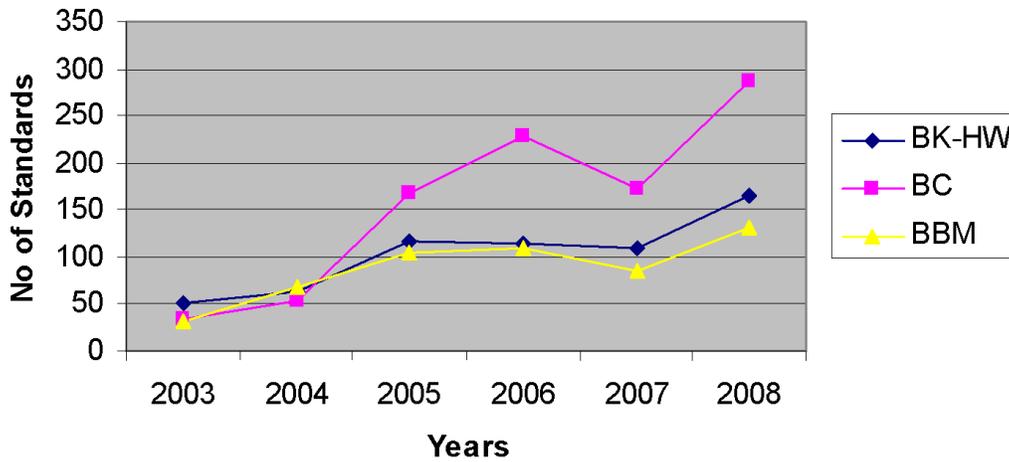

Figure 7 Plot of the numbers of standards prepared on an annual basis

CONCLUSIONS

Despite the fact that the laboratory has seen a massive increase in the numbers of standards and unknowns prepared and measured since the commissioning of the 5MV AMS in 2003, we have not observed any decrease in the quality of the results produced. In fact, the best quality data have been produced from 2006 onward. The 250kV SSAMS instrument, which was commissioned in 2007, is performing as well as (and perhaps even slightly better than) the 5MV tandem and is now the pre-

ferred instrument for the majority of the routine ^{14}C measurements. This can be explained by the fact that the SSAMS is dedicated to measuring ^{14}C and does not require the setup changes imposed upon the 5MV instrument to measure the various other nuclides in our cosmogenic program.

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