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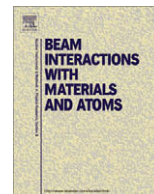
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Porous iron pellets for AMS ^{14}C analysis of small samples down to ultra-microscale size (10–25 μgC)

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ABSTRACT

We developed the use of a porous iron pellet as a catalyst for AMS ^{14}C analysis of small samples down to ultra-microscale size (10–25 μgC). It resulted in increased and more stable beam currents through our HVEE 4130 ^{14}C AMS system, which depend smoothly on the sample size. We find that both the expected decrease of oxalic acid standards and increase of backgrounds with decreasing sample size, due to increasing influence of contamination, are reproducible. Using a mass-dependent background correction for dead ($1.0 \pm 0.4 \mu\text{gC}$) and modern ($0.25 \pm 0.10 \mu\text{gC}$) contamination, we obtain reliable results for small samples down to 10 μgC and possibly smaller. Due to our low graphitization yield for ultra-small samples (increases from 40% to 80% on average with sample size), we measured graphite standards as small as 3 μgC . The standard deviation of the corrected activity is about 5% for a 10- μgC HOxII standard.

Here we report the iron pellet technique, which is new to the best of our knowledge. It is generally applicable for AMS ^{14}C laboratories that want to measure small samples down to ultra-microscale size. As an illustrative test-case, we analyze ^{14}C data for IAEA-C5, C7 and C8 samples with masses ranging from 15 to 300 μgC .

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1. Introduction

Since the development of the AMS technique in the 1980's, researchers have strived to analyze ever smaller samples. For ultra-small samples (10–25 μgC) various unwanted processes can lead to an unreliable target surface. Such as, sintering of the catalyst powder and inhomogeneous graphite production [1]. Nevertheless, the work of several AMS laboratories on sample size reduction has been impressive [2–4]. Our HVEE 4130 ^{14}C AMS system is not designed to analyze ultra-small samples [5,6]. These samples lead to low and unstable beam currents that are not reproducible, which result in unreliable ^{14}C activities or even total failure of the analysis. Therefore, we demonstrated earlier the alternative of sample dilution as a highly reliable means to analyze small samples [7,8], which we used to analyze samples <200 μgC . In addition, we developed a new way of dealing with the catalyst material to measure ultra-small samples. We press the iron powder into a porous iron pellet with a diameter that is slightly smaller than the hole in the target holder to produce a reliable target surface. It is generally applicable for AMS ^{14}C laboratories that want to measure small samples down to ultra-microscale size.

2. Experimental method

To demonstrate our new iron pellet technique, we performed a series of experiments. First, we measured 138 HOxII standards and 34 backgrounds in 5 different batches. We used a ^{14}C free natural CO_2 gas (Rommenhoeller) for the backgrounds. Their masses (before graphitization) ranged in between 10 μgC and 2.5 mgC. Then, we prepared one batch containing 16 backgrounds, 12 HOxII standards and about 10 samples each of IAEA-C5, C7 and C8. Their masses ranged in between 15 and 300 μgC . The sample materials were deliberately combusted in large quantities to CO_2 and used in small amounts.

The CO_2 was reduced to graphite at 500 °C with a hydrogen excess ($\text{H}_2:\text{CO}_2 = 2.5:1$). Peltier cooling elements cryogenically removed the water. We use reactor volumes of 2.5, 4 and 8 ml for mass ranges <500 μgC , 500–1000 μgC and >1000 μgC , respectively. For the ultra-small samples, the graphitization yield was relatively low. We define the graphitization yield, η , as follows:

$$\eta = \frac{p[\text{CO}_2]_{\text{initial}} + p[\text{H}_2]_{\text{initial}} - p[\text{CO}_2 + \text{H}_2]_{\text{final}}}{3 * p[\text{CO}_2]_{\text{initial}}} \cdot 100\%, \quad (1)$$

where $p[\text{CO}_2]_{\text{initial}}$ and $p[\text{H}_2]_{\text{initial}}$ are the initial pressures in the reactor of CO_2 only and H_2 only and $p[\text{CO}_2 + \text{H}_2]_{\text{final}}$ is the final pressure due to both CO_2 and H_2 . For a sample that contained 10 μgC in the form of CO_2 , the graphitization yield was 40% on average. As the

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CO₂ sample size increased to 25 µgC, the yield increased linearly to 80% on average. All the samples were measured and included in our results, regardless of their graphitization yield. Therefore, we measured the ultra-small samples as graphite samples that ranged in between 3 and 21 µgC. As the sample size increased from 25 to 300 µgC, the yield gradually increased from 80% to 93% (for our normal sized samples it is also 93%).

We used the new iron pellet technique for the <500 µgC and 500–1000 µgC samples. The use of the iron pellet as a catalyst did not effect the graphitization yield for 200-µgC samples, nor did it have any influence on their reaction time. We expect the same for the ultra-small sample sizes. Using the iron pellet technique, the reaction time for ultra-small samples was 60–90 min. However, in our laboratory it is a standard procedure to run all the reactions overnight. Therefore, reaction time is neither an issue nor a subject of investigation.

The spherical iron powder (1.5 mg, <325 mesh, 99.5% pure) was pressed into a pellet with a diameter of 1.3 mm applying a force of 300 N. This gives the optimum pressure to guarantee a porous structure without the pellet falling apart. For 200-µgC samples, we found that a higher force (>400 N) results in a relatively high beam intensity at the beginning of the measurement, but it decreases rapidly in time. This is probably because the graphite is only allowed to grow on the iron pellet surface, since the iron pellet does not have a porous enough structure in this case.

We designed a small press to produce the iron pellets, which uses compressed air to reproduce the 300-N force (Fig. 1). The horizontal bar (A) contains 2 tempered bolts (B) with a hole of 1.3 mm in diameter. First, the holes are filled with 1.5 mg iron powder using a micropipette. Next, pins (D) are pressed down shortly using compressed air. Finally, with base C placed to the left, the pins are lowered again to release the pellets directly into the tubes (E). After graphitization, the pellet was pressed into 1.5 mm target holders from the back with a small silver pellet behind it. For the samples >1000 µgC, we used the iron powder in the conventional way [9].

The Groningen ¹⁴C AMS system simultaneously measures the ¹⁴C/¹²C and ¹³C/¹²C ratios [10]. The ¹⁴C/¹²C ratios of the sample

are reported relative to the HOxII standards and normalized for fractionation to δ¹³C = -25‰ [11]. The δ¹³C-normalized activity, ¹⁴a_N, is calculated as follows:

$${}^{14}a_N = 134.06 \cdot \frac{({}^{14}\text{C}/{}^{12}\text{C})_{\text{sample}} - ({}^{14}\text{C}/{}^{12}\text{C})_{\text{bg}}}{({}^{14}\text{C}/{}^{12}\text{C})_{\text{ref}} - ({}^{14}\text{C}/{}^{12}\text{C})_{\text{bg}}} \cdot \frac{\left(\frac{0.975}{1+\delta^{13}\text{C}_{\text{sample}}}\right)^2}{\left(\frac{0.975}{1-0.0177}\right)^2}, \quad (2)$$

where ¹⁴C/¹²C are the ratios of the sample, the batch mean background (bg) and the batch mean HOxII standard (ref). To calculate the batch mean ratios, we only use the backgrounds and HOxII standards that are over 200 µgC, because they do not show a mass dependence. The recommended ¹⁴C activity and δ¹³C value for HOxII are 134.06% and -17.7‰, respectively. The δ¹³C value for the sample (δ¹³C_{sample}) is found from the ¹³C/¹²C ratio of the sample according to

$$\delta^{13}\text{C}_{\text{sample}} = \frac{({}^{13}\text{C}/{}^{12}\text{C})_{\text{sample}}}{({}^{13}\text{C}/{}^{12}\text{C})_{\text{ref}}} \cdot (1 - 0.0177) - 1, \quad (3)$$

where (¹³C/¹²C)_{ref} is the batch mean ratio of the HOxII standards that are over 200 µgC.

3. Measurement results

Using the iron pellet technique, we obtain increased and more stable ¹²C³⁺ and ¹³C³⁺ currents for the 6 batches. They correlate with the sample size. For 10 µgC samples, the ¹³C³⁺ current is around 7 × 10⁻⁹ A (Fig. 2). The scatter is caused by differences in graphitization yield and/or cesium temperature. Note that we use the sample size before graphitization in all our graphs.

Pressing the iron powder into a pellet did not increase our background. The ¹⁴C/¹²C ratio is still (2.4 ± 1.1) × 10⁻¹⁵ for backgrounds over 200 µgC. We observe the expected increase of the backgrounds with decreasing sample size, which is reproducible for the 6 batches. This effect is also observed by others and it is due to modern contamination [2,4,12]. We also observe that the ¹³C/¹²C ratio increases with decreasing sample size.

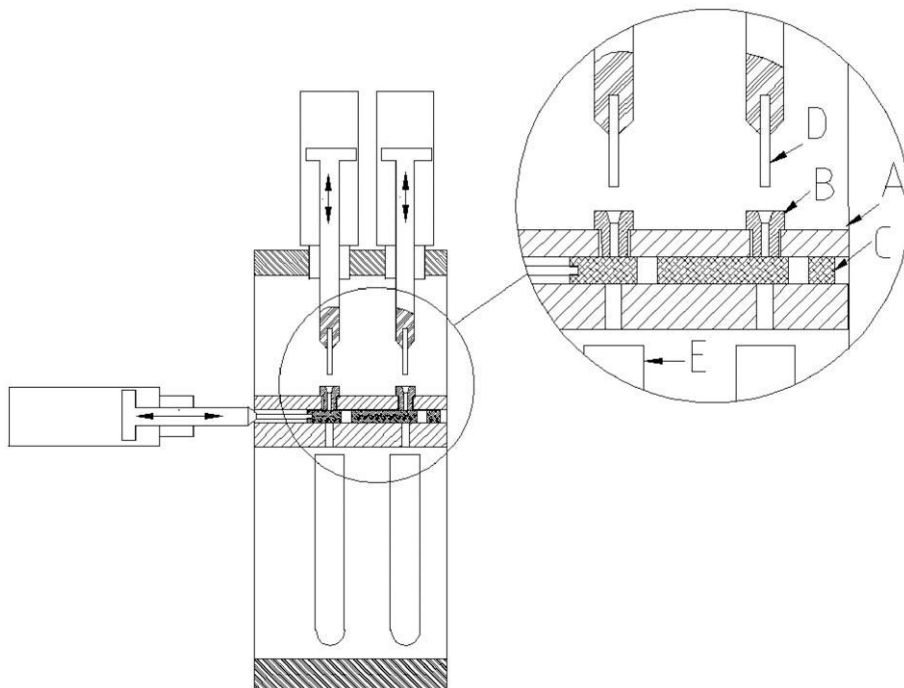


Fig. 1. The small press for the iron pellets that uses compressed air. The letters are explained in the text.

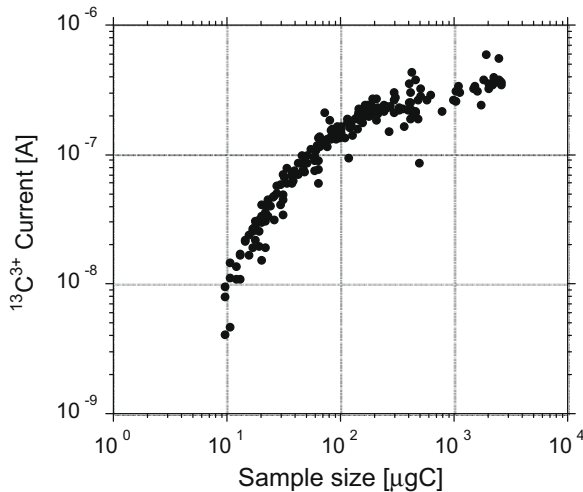


Fig. 2. The $^{13}\text{C}^{3+}$ current as a function of the sample size before graphitization, using the iron pellet technique. We observe a smooth mass dependence, which is reproducible.

The results for the HOxII standards are peculiar (Fig. 3). We only observe the expected decrease of the $^{14}\text{C}/^{12}\text{C}$ ratio with decreasing sample size for 3 out of the 6 batches (black dots). Compared with each other, these 3 batches have similar results. Their $^{14}\text{C}/^{12}\text{C}$ ratio decreases for sample sizes below 200 μgC . The corresponding $^{13}\text{C}/^{12}\text{C}$ ratio as a function of sample size is more or less constant, but has a peak value at around 20 μgC . This first set of 3 batches indeed suggests the expected dilution of the HOxII standards with ^{14}C -free carbon. The peak value for the $^{13}\text{C}/^{12}\text{C}$ ratio around 20 μgC appears to correspond to relatively high values for the $^{14}\text{C}/^{12}\text{C}$ ratio. The fractionation correction compensates for this effect and the $\delta^{13}\text{C}$ -normalized ^{14}C activity ($^{14}a_N$) as a function of sample size shows a smooth decrease with decreasing sample size. Therefore, the peak value is likely to be a machine-effect.

The other 3 batches contained a smaller amount of samples. However, we can still observe that the results amongst these 3 batches are also similar. Their $^{14}\text{C}/^{12}\text{C}$ ratio remains more or less constant, except for the significantly higher values in between 20 and 100 μgC (open circles). The corresponding $^{13}\text{C}/^{12}\text{C}$ ratio increases rapidly with decreasing sample size below 200 μgC . We do not fully understand the difference between the two sets of batches at this point. Fortunately, however, for this second set of 3 batches, $^{14}a_N$ as a function of sample size is the same as for the first set of 3 batches. Since all the samples were prepared under identical conditions, the difference between the two sets of batches is also likely to be a machine-effect. It might be due to small geometrical differences that occur after placing a new batch in the ion source and/or cleaning of the ionizer. We found that smaller samples are more sensitive to geometrical differences.

For around 5 HOxII standards, the activity is relatively low. This is probably due to improper pressing of the target. We need to make sure the iron pellet with the graphite is in a horizontal position with the silver pellet on top of it before bringing the press down. Otherwise, an inhomogeneous graphite/silver mixture will cause extreme variations in the beam current through the accelerator. Relatively low currents that occur during the sputtering of silver result in $^{14}\text{C}/^{12}\text{C}$ and $^{13}\text{C}/^{12}\text{C}$ ratios that deviate strongly from the true value. The presence of Ag powder amongst the graphite is known to lead to erroneous $\delta^{13}\text{C}_{\text{tot}}$ values (Nadeau, personal communication). That is, $\delta^{13}\text{C}_{\text{tot}}$ values that do not represent a ^{14}C -fractionation that is twice the ^{13}C fractionation. An excess of iron powder can have the same effect. This results in activities that are either too low or too high. It is also the reason why the outlier

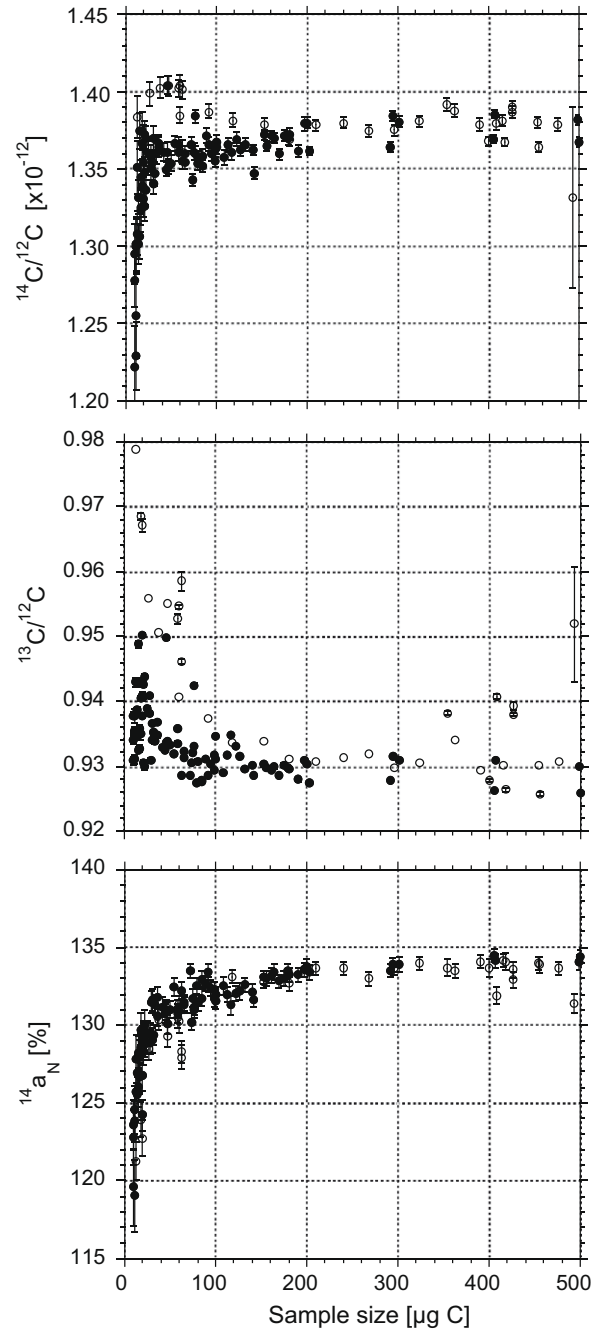


Fig. 3. The $^{14}\text{C}/^{12}\text{C}$ ratio (upper), $^{13}\text{C}/^{12}\text{C}$ ratio (middle) and the $\delta^{13}\text{C}$ -normalized ^{14}C activity (lower) of the HOxII standards as a function of the sample size before graphitization. The difference between two sets of batches (black dots and open circles) is likely to be a machine-effect. The fractionation correction compensates for this effect, such that it is not observable for $^{14}a_N$.

close to 500 μgC has a huge error bar. The $^{13}\text{C}^{3+}$ current during the measurement of this sample was extremely low (Fig. 2). In the future, we will press the iron pellets without the Ag pellet to avoid this problem. For the properly pressed targets, we observe the expected decrease of the HOxII standards with decreasing sample size for samples below 200 μgC , which is reproducible for the 6 batches. This effect is also observed by others and it is associated with dead contamination, mostly due to the presence of ^{14}C -free carbon in the graphitizing catalyst [4].

We did not observe any memory effect from our graphitization reactors. Still, we think the possibility of a memory effect is worth a detailed study.

4. Background correction

The increase of the backgrounds and the decrease of the HOxII standards, with decreasing sample size are due to modern and dead contamination, respectively. These effects are reproducible. Therefore, we can find the ^{14}C activity of the samples by using a mass-dependent background correction. We quantify the modern and dead carbon amount using the approach of Santos et al. [4]. Fig. 4 shows the normalized activity, $^{14}a_N$, as a function of sample size for the backgrounds (upper). The normalized activity was calculated from (2) and (3) with $(^{14}\text{C}/^{12}\text{C})_{\text{bg}} = 0$. The straight lines represent amounts of modern carbon contamination. With the present set-up our modern carbon contamination (mcc) is in between 0.15 and 0.35 μgC . We use $\text{mcc} = 0.25 \pm 0.10 \mu\text{gC}$. Fig. 4 also shows the deviation of the normalized activity, $^{14}a_N$, from the recommended value ($=134.06\%$) as a function of sample size for the HOxII standards (lower). Without pre-cleaning the iron pellet, e.g. reduction of the iron pellet at 400°C in 1 atmosphere of hydrogen [1], our dead carbon contamination (dcc) is in between 0.5 and 2 μgC . For samples $<40 \mu\text{gC}$ it is around 0.75 μgC , whereas for larger samples it seems to increase to 1.5 μgC . This phenomenon requires further study. At this point, we use $\text{dcc} = 1.0 \pm 0.4 \mu\text{gC}$. The normalized activity ($^{14}a_N$) is corrected with the mass-dependent background correction of Santos et al. [4]:

$$^{14}a'_N = \frac{m \cdot ^{14}a_N - \text{mcc} \cdot 100\% - \text{dcc} \cdot 0\%}{m - \text{mcc} - \text{dcc}}, \tag{4}$$

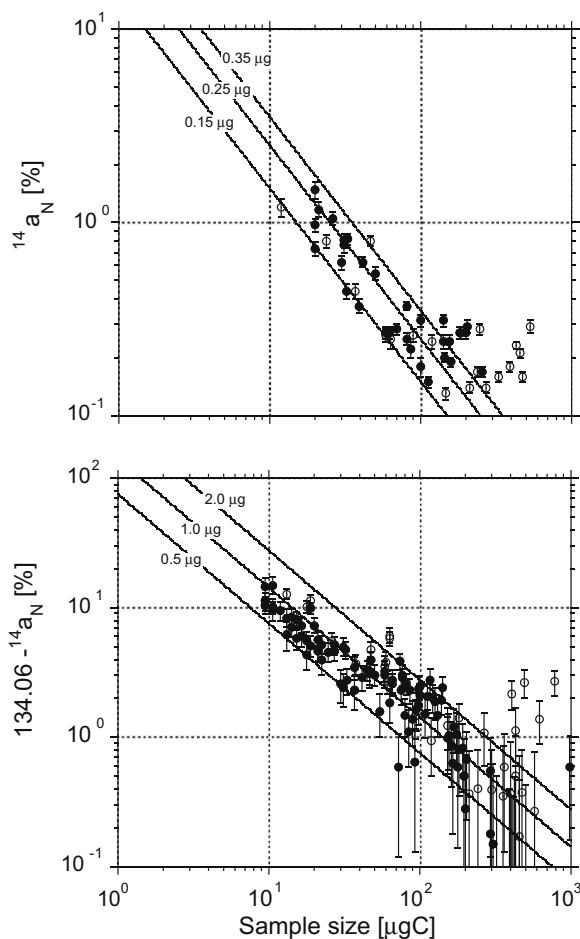


Fig. 4. The normalized activity, $^{14}a_N$, of the backgrounds (upper) and the deviation of the normalized activity from the recommended value, $134.06 - ^{14}a_N$, of the HOxII standards (lower) as a function of the sample size before graphitization. The straight lines represent amounts of modern (upper) and dead (lower) carbon contamination.

where $^{14}a'_N$ is the corrected activity and m is the sample mass in μgC .

5. Corrected results

The corrected activity (i.e. corrected for dead and modern carbon contamination) is shown for the series of HOxII standards and IAEA-C5, C7 and C8 samples with masses ranging in between 15 and 300 μgC (Fig. 5). The error bars represent propagated errors. The C7 samples show only fair agreement with the consensus value. For one C7 sample ($m = 15 \mu\text{gC}$) we found an outlier of $55.8 \pm 1.8\%$, which is beyond the range of the figure. Presumably, this sample suffered from contamination. All the other samples show excellent agreement with the consensus values. As the sample size becomes smaller, the spread in the results increases. This corresponds with the increase of the error that consists of the dcc term (dominant for relatively high activities), the $^{14}a_N$ and mcc terms (more important for lower activities). The contribution of the m term error is negligible.

6. Discussion

We demonstrated our novel catalyst technique for the AMS ^{14}C analysis of small samples down to 10 μgC . For the analysis, we used a mass-dependent background correction that is based on the sample size before graphitization. However, our graphitization yield for ultra-small samples is relatively low. For a sample that contains 10 μgC in the form of CO_2 , the graphitization yield is 40% on average. As the CO_2 sample size increases to 25 μgC , the

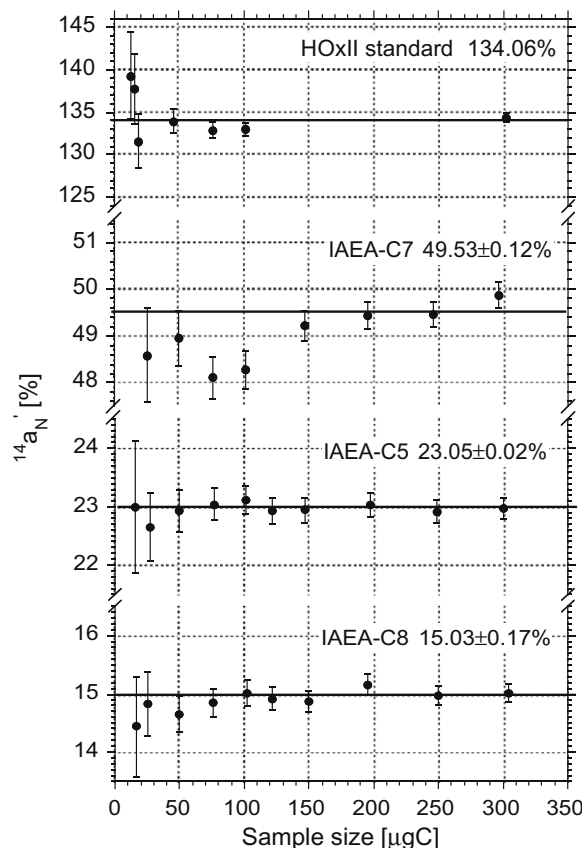


Fig. 5. The corrected activity, $^{14}a'_N$, for the series of HOxII standards and IAEA-C5, C7 and C8 samples as a function of the sample size before graphitization. For most of the measurements, we find agreement with the consensus values within the error bars.

yield increases linearly to 80% on average. Therefore, the sample size before graphitization does not represent the true sample size that was measured. The true sample size is relevant in the correction for dead carbon contamination, since this is most likely caused by ^{14}C -free carbon in the iron powder. Still, we obtain reliable results for the ultra-small samples. Our graphitization yield shows a smooth mass dependence, which is reproducible. Therefore, the graphitization yield is incorporated in the shape of $^{14}a_N$ as a function of sample size (Fig. 3). The use of the true sample size that was measured would change this shape somewhat (especially for the ultra-small masses), as well as the value of the best fit for dcc as a function of sample size (Fig. 4). However, this would be within the error of $\pm 0.4 \mu\text{gC}$ that we use.

We found relatively low values with our definition of the graphitization yield. Amongst other variables, we use the initial pressures in the reactor of CO_2 only and H_2 only. According to a definition that uses the initial pressure due to both CO_2 and H_2 instead [15], the graphitization yield is a factor 1.2 larger. This could be due to the non-linearity of the pressure sensor. Therefore, we use our definition to keep the pressure range as small as possible. It is not unlikely that the sample size before graphitization is in fact a little closer to the true sample size than we expect. In addition, the dead carbon contamination requires further study. For samples $< 40 \mu\text{gC}$, it is around $0.75 \mu\text{gC}$, whereas for larger samples it seems to increase to $1.5 \mu\text{gC}$. At this point, we use an average value with a large error bar.

7. Conclusion

Our novel catalyst technique for the AMS ^{14}C analysis of small samples down to $10 \mu\text{gC}$ is successful. We press the iron powder into a porous iron pellet with a diameter that is slightly smaller than the hole in the target holder. The use of the iron pellet technique results in a homogeneous graphite and target surface. We have increased and more stable beam currents through our HVEE 4130 ^{14}C AMS system that show a smooth sample size dependence. The reproducible dependence of the $\delta^{13}\text{C}$ normalized ^{14}C activity on the sample size is associated with a combination of dead and modern contamination. Therefore, we can find the ^{14}C activity of the ultra-small samples by using a mass-dependent background correction.

As an illustrative test-case, we presented the successful ^{14}C analysis of 10 samples each of IAEA-C5, C7 and C8, with masses ranging from 15 to $300 \mu\text{gC}$, using the new iron pellet technique.

The standard deviation of the corrected activity is about 5% for a $10\text{-}\mu\text{gC}$ HOxII standard. Mainly due to the relatively high levels of contamination, the precision is comparable to the dilution method alternative. Using the new iron pellet technique, however, we can work systematically on the reduction of the background. We will try to achieve this by pre-cleaning the iron pellet, e.g. reduction of the iron pellet at 400°C in 1 atmosphere of hydrogen [1].

We will also try to increase the graphitization yield, which is only 40% on average for a $10\text{-}\mu\text{gC}$ sample. This would enable us to analyze even smaller samples (at least down to $3 \mu\text{gC}$) and improve our precision. The use of magnesium perchlorate [13,14] to remove water is a good alternative for the Peltier element. It allows us to make smaller graphitization reactors to increase the graphitization yield. Tests in our newly designed test reactor ($\sim 1.8 \text{ ml}$) indicate that the average graphitization yield for a $10\text{-}\mu\text{gC}$ sample increases to over 80%. All in all, we expect to improve the precision for ultra-small samples considerably in the near future.

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