"Not everything that counts can be counted, and not everything that can be counted counts."

A. Einstein

http://www.kluun.nl/files/Image/calimero.gif
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Abstract

In order to improve precision in AMS $^{14}$C ultra small (5-25 $\mu$g C) sample analysis two research aims were formulated. The first aims at reducing the background. The iron pellet, used as catalyst, was pre-treated in a hydrogen atmosphere at 400 °C. The second aims at improving the yields for small sample graphitization reactions.

For background reduction, we targeted the reduction of possibly present carbon in the catalyst material. This did not result in significant reduction. It did give us insight in mass effects for small samples and how to analyze these effects. There is a clear difference between a fixed amount of contamination background activity in a sample and contamination that gives a mass dependent activity. The turning point between these two lies around a sample size of 100 $\mu$g C.

We have managed to improve the graphitization yields of small samples. This was done by creating a smaller reactor (varying volume between 1.5-2.5 ml) than the conventional one (2.5 ml) and using magnesium perchlorate (Mg(ClO$_4$)$_2$) to trap the water. This reactor requires less reaction time (10-15 minutes, where the conventional Peltier method requires 2-3 hours). The graphitization yields found for small samples have gone up from approximately 40% to 70-90% and are now very similar to the yields found for graphitizing normal samples (> 200 $\mu$gC).

We can conclude that by increasing the graphitization yields for ultra-small (5-25 $\mu$g C) samples we have managed to increase the precision in AMS $^{14}$C ultra-small sample analysis.
1 Introduction

1.1) Introduction to the problem

The AMS (Accelerator Mass Spectrometry) technique for measuring $^{14}\text{C}$ has been developed in the 1980’s. This method has the advantage that it can measure small amounts (a few mg of carbon) of sample in a short time (about 45 minutes). Other methods (like $\beta$-counting) are much more time consuming (about 48 hours) and need more sample material (few grams of carbon). Therefore AMS is the most preferable method for $^{14}\text{C}$ dating nowadays.

Researchers are striving to measure and analyze ever smaller amounts of sample. Other AMS laboratories have already been working on small sample analysis [Santos et al, 2007][Brown and Southon, 1997]. For instance, small samples down to 20 µg C were graphitized with a graphitization yield up to 100%, using smaller reactors. The small samples (ranging down to 0.006 mgC) can be measured with accuracy and precision of a few percent [Santos et al, 2007]. For the Groningen HVEE 4130 $^{14}\text{C}$ AMS system the first steps in (ultra) small (5-25 µg C) sample analysis have been made by introducing iron pellets instead of iron powder as a catalyst for the graphitization reaction[de Rooij et al, 2008][de Rooij et al. 2009]. Further improvements are needed to optimize the small sample analysis.

1.2) Problem definition

Two problems for the AMS measurement arise when small samples (< 200 µg C) need to be measured.

At present the precision is comparable to the dilution method results [de Rooij et al. 2008]. We want to improve this precision.

The first problem arises in the preparation of the small AMS samples. After pretreatment, the sample gets completely converted into CO$_2$ (in a hot furnace) using pure O$_2$ [Wijma et al, 1996]. This CO$_2$ is catalytically reduced into graphite using an iron pellet as a catalyst and exposure to a surplus of H$_2$ gas at 500 ºC [de Rooij et al. 2009]. This process is called graphitization. The amount of CO$_2$ gas that is transformed into graphite depends on the yield of the graphitization reaction. For very small samples (< 100 µg C) the average graphitization yield in our common reactors is low and variable (20-85%). This causes the standard deviation (which is determined by the reference HOxII standards, the background, the mass of the sample and the number of counts) in the activity to be relatively large.

The second problem is contamination, which starts to play a bigger role for samples < 200 µg C. We can distinguish between modern contamination and dead contamination. Modern contamination means that the sample is contaminated with carbon that contains $^{14}\text{C}$ from other sources (presumably in most cases a leak) than the sample itself and therefore influences the outcome of a measurement. The modern contamination (0.25 ± 0.10 µg C [de Rooij et al, 2009]) causes the background to increase with decreasing sample size. Dead contamination is carbon that does not contain $^{14}\text{C}$ and therefore dilutes the sample in $^{14}\text{C}$. The relative contribution of this contamination becomes larger and larger.
as we reduce our sample size. The activity for the oxalic acids decreases with decreasing sample size due to the dead carbon contamination (1.0 ± 0.4 µg C [de Rooij et al, 2009]). Therefore, the activity for small samples needs to be corrected for modern and dead contamination [Santos et al, 2007]

The iron pellet used might contain some contamination (either dead or modern), so there lies a problem for the small samples as well. Furthermore all the steps in the whole process from the rough sample to graphite might contaminate a small sample since it is much more sensitive to contamination. The relatively large and variable amount of contaminant is another reason for the standard deviation in the activity to be relatively large.

1.3) Aim of this research

Considering the problems mentioned in section (1-2) the following research aims can be formulated:

1) Reducing the background in the measurement of small samples by concentrating on reducing the contamination that might be present in the catalyst used.
2) Improving the graphitization yield of ultra small sample graphitization reactions.

These improvements should lead to a higher precision in the measurement of ultra small samples. Before treating these improvements in detail, some insight in the AMS method is needed. Therefore it will be outlined in the next chapters starting with the experimental method with the emphasis on the part of the method where the improvements have to be used. Then the results will be presented and discussed, and finally conclusions and recommendations for further research will be formulated.
2 Experimental Method

To improve the precision we do two experiments. In order to do the experiment for background reduction, the dead contamination and the modern contamination have to be determined. Therefore, we do tests with a $^{14}$C free natural CO$_2$ gas called Rommenhoeller (RH) and the HOxII standard (which has a high activity). The HOxII standard was deliberately combusted in a large quantity and used in small amounts. Experiments for graphitization yield improvement were done with the HOxII standard.

The strategy to reduce background contamination (both dead and modern) is to focus on the contamination possibly present in the catalyst used for the graphitization reaction. The catalyst used is iron powder (<325 mesh, 99.5 % pure) pressed into a pellet [de Rooij et al, 2009]. Pre-baking the pellet with an excess of H$_2$ gas is a way to try and reduce the carbon contamination present in the catalyst [Santos et al, 2007]. Exposing carbon to an excess of H$_2$ gas at high temperature ($\geq 400 ^\circ$C) results in:

$$C\ (s) + 2\ H_2\ (g) \rightarrow CH_4\ (g) \quad (2-1)$$

In order to test this method for the iron pellets, this experiment was set-up into 4 groups of pellets.

**Group I**
The pellets were pre-baked for 60 minutes within 1 bar of H$_2$ gas at a temperature of 400 $^\circ$C.

**Group II**
The iron powder was pre-baked for 60 minutes within 1 bar of H$_2$ gas at a temperature of 400 $^\circ$C. Afterwards the pellet was pressed out of the pre-baked iron powder.

**Group III (Control Group)**
The iron powder nor the pellets got any treatment before graphitizing the samples.

**Group IV (Reference Group)**
Large set of data [de Rooij et al, 2009] with normal pellets (so no treatment).

All pellets were pressed from 1.5 mg iron powder having a diameter of 1.3 mm applying a force of 300 N. For groups I to III, samples (both Rommenhoeller and HOxII) ranging from 10 $\mu$gC to 250 $\mu$g C were produced. All samples were graphitized in the conventional 2.5 ml reactors (figure 2-2).

The CO$_2$ gas was catalytically converted to graphite at 500$^\circ$C, according to the following nett (reaction produces CO (g) as an intermediate) equilibrium reaction:
CO₂ (g) + 2 H₂ (g) ↔ C (s) + 2 H₂O (g) \hspace{1cm} (2-2)

This reaction has a yield smaller than 100% because as long as there is just the smallest amount of water left in the reactor the reaction will reproduce CO₂ and not all the CO₂ can be converted into graphite. The formed C(s) can of course again result in CH₄ (g).

So, to get a high yield it is necessary to get rid of the water that forms during the reaction. For the background reduction experiment (and the conventional graphitization process) the water is cryogenically trapped using a Peltier element.

The graphitization yield is calculated using [Bakker, 2005]:

\[ \eta = \frac{P_{\text{initial}} - P_{\text{final}}}{3 \cdot P_{\text{CO}_2}} \times 100\% \] \hspace{1cm} (2-3)

Where \( P_{\text{initial}} = P_{\text{CO}_2} + P_{\text{H}_2} \) is the sum of the pressure of the CO₂ and H₂ present in the reactor before graphitization. \( P_{\text{final}} \) is the pressure in the reactor after the reaction has completed.

This results in low and varying yields (20-85%) for samples < 100 µg C (see figure 2-1). The sometimes rather low yields imply that not all the water is trapped with the current method or that a part of the CO₂ gas is converted into CO gas and part of the C is converted into CH₄.

Besides that, the reaction usually takes between 60 and 90 minutes (for small samples) to be completed.

To improve the graphitization yield, we do a second experiment with an alternative for the water trapping method. Instead of using a Peltier element, we use magnesium perchlorate (Mg(ClO₄)₂) as a water absorber [Santos et al, 2004]
A second factor that influences the yield of the reaction is the volume of the reactor. The current reactors have a volume of 2.5 ml (for samples < 500 µg C). So to achieve a higher yield we design a reactor that is both smaller and suited to carry Mg(ClO$_4$)$_2$ as an absorber. Therefore, the new reactor was made of individual parts instead of being made out of one part, like the current reactors are (see figure 2-2, left).

The design of the reactor starts with making a solid steel core. It is designed in a way that the quartz tubes can be pushed in directly (figure 2-2, right). The new reactor therefore has a variable volume.

All tests done in order to increase the graphitization yield were done with pellets that did not get pre-treatment.

Figure 2-2: Left the conventional reactor (2.5 ml) and at the right the reactor (variable volume) suited to carry Mg(ClO$_4$)$_2$. 
For both experiments the pellet, with the graphite on the surface and in the pores, is pressed into a target holder. The aluminum target holder has a diameter of 1.5 mm.

Besides, the target is pressed with a steel pin, this is done by an automatic target press. [Aerts-Bijma et al, 1997]. A silver pellet is pressed behind the iron pellet.

After the target pressing, the samples are placed in a wheel consisting of 59 targets ready to be measured with the Groningen HVEE 4130 $^{14}$C AMS system.

The AMS system simultaneously measures the $^{14}$C/$^{12}$C and $^{13}$C/$^{12}$C ratios [van der Plicht et al, 2000]. The $^{14}$C/$^{12}$C ratios of the sample are reported relative to the HOxII standards and normalized for fractionation to $\delta^{13}$C = -25 ‰ [Mook and van der Plicht, 1999]. The normalized activity $^{14}a_N$ is calculated as follows:

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

(2-4)

Where $\left(\frac{^{14}C}{^{12}C}\right)_{\text{ref}}$ and $\left(\frac{^{14}C}{^{12}C}\right)_{\text{bg}}$ are the ratios for the mean HOxII standard of the batch and the batch mean background respectively (for samples that are larger than 200 µg C and are assumed to show no mass dependence in their activity). The recommended values for $^{14}$C activity and $^{13}$C are 134.06% and -17.7‰.

The $\delta^{13}$C-value of the sample is found from the $^{13}$C/$^{12}$C ratio of the sample:

$$\delta^{13}C = \frac{\left(\frac{^{13}C}{^{12}C}\right)_{\text{sample}}}{\left(\frac{^{13}C}{^{12}C}\right)_{\text{ref}}} \cdot (1 - 0.0177) - 1$$

(2-5)

Where the $\left(\frac{^{13}C}{^{12}C}\right)_{\text{ref}}$ ratio is the batch mean ratio of the HOxII standard.

The modern carbon contamination is deduced using the results for the Rommenhoeller measurements.

We use the following assumption:

$$m_0 \cdot ^{14}a_N^{RH} = mcc \cdot 100\% + (m_0 - mcc)^{14}a_{N,cont}$$

(2-6)

Where $m_0$ is the mass of the sample and $^{14}a_{N,cont}$ is a constant contamination activity. The mcc activity is assumed to be 100%.

Equation (2-6) reduces to:

$$^{14}a_N^{RH} = \frac{mcc \cdot 100\%}{m_0} + \left(1 - \frac{mcc}{m_0}\right)^{14}a_{N,cont}$$

(2-7)

This equation is used to fit the RH results, where mcc and $^{14}a_{N,cont}$ are the fit parameters.
In order to determine the dead carbon contamination we use the following equation:

\[ m_0 \cdot ^{14}a_N^{OX} = (m_0 - mcc - dcc) \cdot 134.06\% + mcc \cdot 100\% \]  
(2-8)

Where the value for \( mcc \) is the one found with (2-6).

For our samples, the normalized activity is corrected with a mass-dependent contamination correction as follows [Santos et al, 2007]:

\[ ^{14}a_N = \frac{m \cdot ^{14}a_N - mcc \cdot 100\% - dcc \cdot 0\%}{m - mcc - dcc} \]  
(2-9)

Where \( mcc \) is modern carbon contamination and \( dcc \) is dead carbon contamination and \( m_0 \) is the sample mass (all in \( \mu g \) C). The \( ^{14}a_N \) value is taken as defined in (2-4).
3 Results and Discussion

3.1) Background reduction

For our background reduction experiment we will compare Group I and Group IV. Group I is the group where the pellets where pre-baked and Group IV is a large data set from de Rooij et al (2009) (see fig 3-1). These samples where made with normal iron pellets. At first Group I and Group IV are compared for modern carbon contamination.

![Graph of background reduction](image)

Figure 3-1) The normalized activity of the backgrounds as a function of the sample size before graphitization. The straight lines represent the amounts of modern carbon contamination (mass dependent activity, background activity is zero).

Data analysis gives a modern carbon contamination of $0.25 \pm 0.03 \, \mu g \, C$. This fit has an R-value (correlation) of 0.39. This analysis is based on the fact that the background activity is zero and the sample activity is mass dependent i.e.

$$14^a(N) = \frac{mcc \cdot 100\%}{m_0}.$$
The figure (3-1) indicates otherwise, namely that there is also a constant background activity. Therefore we should analyze it using equation (2-7).
Which gives:

![Graph](image)

Figure 3-2) Same graph as 3-1 but with a fit according to (2-7).

This fit gives two parameters. The modern carbon contamination which is \( \text{mcc} = 0.13 \pm 0.02 \, \mu\text{g C} \).
The background activity \( ^{14}\text{a}_{\text{N,cont}} = 0.13 \pm 0.01 \, \% \).
The fit as an R-value (correlation) of 0.76.
This fit is better than figure 3-1 because the data points have a higher correlation with the fit. The data shows two parts, a mass dependent one (0 -100 \( \mu\text{g C} \)) and a more constant part (>100 \( \mu\text{g C} \)). But still the fit is a little off. The value for \( \text{mcc} \) and \( ^{14}\text{a}_{\text{N,cont}} \) should be somewhat higher since the fit seems to cover the lower values of the data.
We will now compare these 2 graphs for Group IV with Group I.
Figure 3-3) The normalized activity of the backgrounds in Group I as a function of the sample size before graphitization. The straight lines represent the amounts of modern carbon contamination.

Data analysis of figure 3-3 gives a modern carbon contamination of $0.27 \pm 0.06 \, \mu\text{g C}$.

Applying the fit (2-7) on this Group gives:

Figure 3-4) Same graph as 3-6 but with a fit according to (2-7).
The modern carbon contamination is $mcc = 0.05 \pm 0.07 \mu g C$. The background contamination has an activity of $^{14}a_{N,cont} = 0.22 \pm 0.06 \%$. This fit has an R-value of 0.23.

Summarizing between Group IV and Group I:

<table>
<thead>
<tr>
<th></th>
<th>MCC1(^{(1)}) (µg C)</th>
<th>MCC2(^{(2)}) (µg C)</th>
<th>$^{14}a_{N,cont}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group IV</td>
<td>0.25 ± 0.03</td>
<td>0.13 ± 0.02</td>
<td>0.13 ± 0.01</td>
</tr>
<tr>
<td>Group I</td>
<td>0.27 ± 0.06</td>
<td>0.05 ± 0.07</td>
<td>0.22 ± 0.06</td>
</tr>
</tbody>
</table>

Table 3-1
(1) MCC1 is the modern carbon contamination found for the first fit (strictly background activity is zero).
(2) MCC2 is the modern carbon contamination found for the second fit with the extra background term, which should be considered to be more reliable since it gives a better fit.

As can be observed Group I has a higher modern contamination than Group IV (except for MCC2). But the contamination is not significantly higher. An explanation can be that pre-baking the sample contaminated the sample. This is however unlikely because the preparation (pre-baking the pellet with H\(_2\) excess at 400 °C) was integrated in the graphitization process without any special treatment that could contaminate the sample. Our observation that Group I has a higher contamination is not very strong since there are just a few interesting data points that show mass-dependence. The points at larger masses seem to have a more constant activity i.e. the activity shows no mass dependence as can be observed clearly for the higher masses in Group IV. So what the actual modern carbon contamination is for Group I is questionable since MCC2 is obviously too low because there are only 2 data points in the ultra small sample region that show mass dependence. Group I shows a larger error overall, this is simply because there are less data points in Group I than in Group IV.

The turning point where the constant contamination seems to ‘dominate’ the mass dependence lies around 100 µgC. So after this point the mass dependence plays a less important role for the backgrounds.

Our main focus however is on the dead contamination, since that is what is mainly expected to be reduced from the iron pellets after cleaning.

So, now Group I and IV are compared for dead carbon contamination (DCC). To determine the DCC values we use equation (2-8):

$$m_0^{14}a_N^{ox} = (m_0 - mcc - dcc) \cdot 134.06\% + mcc \cdot 100\%$$

Figure 3-8 shows the corrected activity minus the assigned value of 134.06 % for the HoxII standards.
Figure 3-5) The difference between the normalized and assigned activity of the HoXII samples as a function of sample size for Group IV.

The average dead carbon contamination is 0.86 ± 0.02 μg C. The fit has correlation R=0.92.
The value for the modern carbon contamination was fixed at 0.25 μg C. This is the value found for an assumed background activity of zero percent. According to our second fit (MCC2) this value is lower. Therefore, we investigate the DCC values for different MCC values for this fit. Varying the MCC value between 0.10 - 0.25 μg C gives DCC = 0.88 ± 0.04 μg C. The error in this result seems to be small.
For Group I:

![Graph](image)

Figure 3-6) The difference between the normalized and assigned activity of the HoXII samples as a function of sample size for Group I.

One outlier at mass 34 µg C was excluded due to analysis problems. Probably, during the target pressing, the silver was pressed before the graphite, the average number of counts becomes very low, because silver shows little or no activity. Averaged the sample has a very low activity. Data of this sample shows that this is what probably went wrong.

These 36 datapoints give a dead carbon contamination of $1.01 \pm 0.07$ µg C. The fit has correlation $R = 0.86$.

If we vary our MCC value between 0.05 - 0.27 µg C we find $DCC = 1.04 \pm 0.10$ µg C.

Group I ($1.04 \pm 0.10$ µg C) has a higher contamination than Group IV ($0.88 \pm 0.04$ µg C). Considering the error in the result the contamination is close for both groups. The error for Group I is by definition larger since there are less datapoints in Group I than in Group IV.

Fact is, that the contamination for Group I is not lower than that of Group IV contrary to what was hoped for, because the pellet was cleaned.

A point of discussion is the correlation of the fit. Since we focus on the small samples we should pay extra attention to the points close to the range of 10 µg C, which clearly don’t
get covered well by our fit. Considering these points our mass-dependent contamination might even be higher and more variable.

Comparison between Group II and Group III

Group II and Group III where both measured in the same wheel. For some reason the measured background (Roemenholler) was higher (5-10 times higher activity than in Group I) than it should be normally. At this point, it is not clear why this has happened. A lot of factors can be excluded. Two different wheels where measured in the same week. Both wheels had very high backgrounds. This only happened in that particular week. Both wheels where prepared in different weeks, so, presumably, it can’t be something that has happened in the lab. The same gases where used as before and after these high backgrounds occured (when the backgrounds had their normal, lower values) Because of these high backgrounds Group II and Group III can not be compared with Group I and Group IV. Therefore we will strictly compare Group II with Group III.

If we compare both Group II and Group III for modern carbon contamination (MCC):

![Graph](image)

Figure 3-7) The normalized activity of the backgrounds in Group II as a function of the sample size before graphitization. The straight line represents the amounts of modern carbon contamination (background activity is zero).

This fit results in $\text{MCC} = 1.57 \pm 0.29 \mu g C$. 

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With the other fit:

![Graph](image)

Figure 3-8) Same graph as 3-7 but with a different fit according to (2-7).

The modern carbon contamination is $mcc = 1.48 \pm 0.43 \, \mu g \, C$.

The background contamination has an activity of $^{14}a_{N,cont} = 0.11 \pm 0.41 \%$. 
For Group III:

Figure 3-9) The normalized activity of the backgrounds in Group III as a function of the sample size before graphitization. The straight lines represent the amounts of modern carbon contamination (background activity taken to be zero).

This fit results in $\text{MCC} = 0.79 \pm 0.30 \ \mu\text{g C}$. The fit has a correlation $R = 0.49$. 
The modern carbon contamination is $mcc = 0.32 \pm 0.38 \, \mu g \, C$. The background contamination has an activity of $^{14}a_{N,cont} = 0.85 \pm 0.47 \%$. The fit has a correlation of $R = 0.25$.

Summarizing between Group II and Group III:

<table>
<thead>
<tr>
<th></th>
<th>MCC1 (µg C)</th>
<th>MCC2 (µg C)</th>
<th>$^{14}a_{N,cont}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group II</td>
<td>1.57 ± 0.29</td>
<td>1.48 ± 0.43</td>
<td>0.11 ± 0.41</td>
</tr>
<tr>
<td>Group III</td>
<td>0.79 ± 0.30</td>
<td>0.32 ± 0.38</td>
<td>0.85 ± 0.47</td>
</tr>
</tbody>
</table>

Table 3-2) MCC values for Group II and Group III.

Especially the datapoints of Group III show low correlation with the fit. Therefore the fit becomes unreliable, but Group II has a significantly higher contamination than Group III. Possibly the cleaning steps that had to be done to create the powder-cleaned pellets of Group II contaminated the pellets, and therefore the method makes the results worse instead of reducing the background. But again, the correlation is low, the results are very unreliable, more datapoints for these groups would give a better and more reliable result.
Compared for dead carbon contamination (DCC):

Group II:

Figure 3-11) The difference between the normalized and assigned activity of the HoXII samples as a function of sample size for Group II.

This fit results in $DCC = 0.49 \pm 0.17 \mu g \text{C}$. The correlation of the fit is $R = 0.75$.

If we vary our MCC value between 1.10 and 1.90 $\mu g \text{C}$ we get $DCC = 0.51 \pm 0.22 \mu g \text{C}$. 
For Group III:

**Figure 3-12** The difference between the normalized and assigned activity of the HoXII samples as a function of sample size for Group III.

This fit results in $DCC = 0.80 \pm 0.19 \, \mu g \, C$. The fit has correlation $R = 0.74$.

If we vary our MCC value between 0.30 and 0.90 $\mu g \, C$ we get $DCC = 0.85 \pm 0.27 \, \mu g \, C$.

These results look much better than the ones for Group I and Group IV. But since the backgrounds for Group II and III are so high these DCC values can’t be taken too serious since there is a direct relation between both of them (2-8). If the backgrounds were low (as they should be) the DCC values for Group II and III were much higher and more realistic one would say, but the shape of the curve is more or less the same as that of Group I and Group IV.

Comparing the graphs for the DCC of Group II and III to Group I and IV shows that Group II shows a little improvement compared to Group III, but also here more data-points should give a better insight in the actual results.

**3.2) Background correction**

Having calculated the modern and dead carbon contamination we can calculate the corrected activities for the 4 groups according to equation (2-9).
Figure 3-13) The corrected activity, $^{14}\text{a}_N^\text{c}$, for the HOxII standards of Group I.

The assigned value for the HOxII standard is 134.06 %. Most of the points are in range with that value if we account for the (large) propagated errors, based on statistics we expect two-third of the datapoints to be in range with the assigned value. The outliers are in the mass range of 10 - 20 $\mu$g C. These points also have the largest errors. This is because the error contribution of the dead carbon contamination is high for small masses. Because the activities are large the $^{14}\text{a}_N$ and mcc terms are less important. The error in the mass is negligible [de Rooij et al, 2009]. The error bars are also large because of the large DCC variability (see fig. 3-6).

Since the error bars are large for the points in the lower mass (10 - 20 $\mu$g C) region these points should be in range with the assigned value but most of them are not. So we might conclude that the error bars are still too small, so the error should be taken larger.
For Group II half of the points are in range of the consensus value. The backgrounds were very high for this Group. Since the mass correction depends on the MCC value, which is too high for this group, it is not a surprise that the corrected results are not optimal.
Just like for Group II, Group III shows a large spread in the corrected results. For this Group two-third of the points are not in range with the consensus value. This is again a confirmation of the incorrect values for the modern contamination. It is noteworthy that the 2 points with the largest mass are out of range. This shows that the mass correction is most likely incorrect, which is again probably due to the high MCC value. Another explanation might be that the error bars are again taken too small.
Figure 3-16) The corrected activity, $^{14}a'_N$, for the HOxII standards of Group IV.

This is a large data set where most of the points are expected to be in agreement with the consensus value. Most outliers are in the ultra small sample range (10 - 20 µg C) as expected but some are also in the higher mass regions (500-600 µg C). A critical look at the curve shows that the small samples ($< 30$ µg C) are overcorrected. Regarding (2-9), the value for dcc might be taken too large compared to the value for mcc (resulting in a too high value for $^{14}a'_N$). So either (2-9) is not optimal as a correction for ultra small samples or the error bars are again too small. All in all the uncertainty in the results can be explained by the high variability in the dead and modern carbon contamination values.
3.3) Graphitization yield improvements

After a few tests we can compare the yields of the new reactor (kept at approximately 2.5 ml, Mg(ClO₄)₂ as absorber, later on we will vary the volume of the reactor) with the yields resulting from the original reactors using the original ‘Peltier’ (water trapping) method. All yield calculations are based on equation (2-3).

![Graph showing yield as a function of sample size before graphitization for both methods for 2.5 ml reactors](image

Figure 3-17) shows that the average yield for the new reactor is not significantly different. The average for Mg(ClO₄)₂ is (59.2 ± 3.4) % and for the conventional water trapping method (50.8 ± 3.3) % (taken over respectively 5 and 15 points). Regarding these numbers there is room for more improvement and higher yields. An important observation made during these measurements is that the reactions with Mg(ClO₄)₂ as absorber have a very low reaction time (order of 5-10 minutes) compared to the Peltier method (order of 60-90 minutes). This means that the Mg(ClO₄)₂ absorbs water very quickly and makes reaction (2-2) go very fast.

With the new reactor it is possible to vary the volume of the reactor. By cutting the quartz tubes it is easy to decrease the volume of the new reactor. Varying the volume of the new reactor between 1.5 ml and 2.5 ml gives significantly higher yields for a smaller volume (see figure 3-2). The points at volume higher than 2.5 ml are from a different (larger) reactor that also makes use of Mg(ClO₄)₂ as an absorber. This was done just to test if the Mg(ClO₄)₂ method was also applicable and profitable for larger samples. For completeness a few small samples where graphitized with this reactor.
Figure 3-18: Graphitization yield as a function of reactor volume, the sample masses range from 6 to 22 µg C. The closed points at 2.5 ml are samples graphitized with the Peltier type reactor.

Figure 3-18 clearly shows that a smaller reactor volume results in a higher graphitization yield. The mass range of the samples is not very clear in figure 3-18. For better insight figure 3-18 is subdivided for different mass ranges:
For mass range 5-10 µg C:

Figure 3-19) Graphitization yield as a function of reactor volume, the sample masses range from 5 to 10 µg C.

These are all samples smaller than 10 µg C. They have a much higher yield and smaller yield spread in smaller volume than they have in the conventional 2.5 ml reactor. Note that all these samples were produced in the new reactor.
For mass range 10-15 µg C:

Figure 3-20) Graphitization yield as a function of reactor volume, the sample masses range from 10 to 15 µg C.

This figure gives a clear difference in graphitization yield for the new reactor and the conventional 2.5 ml reactor.
For mass range 15-21 µg C:

For the somewhat larger samples (> 20 µg C) the yield starts to become lower. The 2 samples graphitized in the 3.4 ml reactor show no higher yield than with the Peltier water trapping method. This can be an indication that the Mg(ClO$_4$)$_2$ is not the main reason for higher yields.

Decreasing the volume, in combination with the Mg(ClO$_4$)$_2$ as absorber, yields are achieved that are of the same order as the yields for ‘normal’ large samples. The average yield using the new reactor (with smaller volume) is (74.9 ± 3.9) % and for the conventional reactor the average yield is (50.8 ± 3.3) %.

Considering these results it seems that the decreased volume plays the major role in improving the yields. To be sure, we would have to study the Peltier method by varying the volume of the conventional reactor. This is rather difficult to do technically. First of all the conventional 2.5 ml reactors are made out of one piece. It might be possible to try it for the new reactor, but then the lower tube can’t be shortened because it’s full length is needed in order to trap the water with the Peltier element. However, the role of the Mg(ClO$_4$)$_2$ in increasing the yield is not shown to be of significant importance. This is
demonstrated by the few samples that were graphitized in the larger reactor of 3.4 ml, which have a normal (low) yield for small samples (> 20 µg C). So it can not be stated with certainty that the Mg(ClO$_4$)$_2$ increases the yield significantly. Again, what can be stated with certainty is that the Mg(ClO$_4$)$_2$ speeds up the reaction. Small samples where graphitized within 10 minutes, which can become of importance in mass production of small samples. Also the Mg(ClO$_4$)$_2$ method is preferred for the smaller reactors, because it is easier to work with Mg(ClO$_4$)$_2$ as a water trapping method (Peltier method requires the use of an external Peltier element, Mg(ClO$_4$)$_2$ is integrated in the reactor) and might even be used to graphitize more than one sample. It is however, not known so far if the Mg(ClO$_4$)$_2$ causes a memory effect which might contaminate the sample. This requires further study. Other labs are suspicious that Mg(ClO$_4$)$_2$ might influence the precision of the measurements of small samples [Santos et al, 2004]
4 Conclusions

Our experiments on pre-baking the iron pellets for background reduction were inconclusive. The small datasets for especially Group II and Group III gave no reliable results. If we compare Group II and Group III, which where measured in the same wheel, we can see a large difference in modern carbon contamination. Group II (roughly $1.50 \pm 0.35 \mu g$ C) shows a much higher MCC than Group III (roughly $0.55 \pm 0.35 \mu g$ C), while it was expected the other way around. Possibly, the steps taken to reduce the iron powder (pre-baking the powder and use it to press a pellet) caused contamination instead of reducing it. But this can not be concluded using the data, since it is very unreliable. There is a high variability in both MCC and DCC values. For DCC Group II ($0.51 \pm 0.22 \mu g$ C) and Group III ($0.85 \pm 0.27 \mu g$ C) do give expected values (i.e. Group III has higher DCC than Group II). We can however not be sure, since something went wrong with the measurement of these samples. So, a clear answer requires to re-do the experiment.

Comparing Group I (where the pellets where pre-baked instead of the powder, so there where less steps that might have contaminated the sample) with Group IV gave no improvement in the modern carbon contamination (Group I: $0.27 \pm 0.06 \mu g$ C, Group IV: $0.25 \pm 0.03 \mu g$ C). These numbers are not very reliable. For Group I for instance, there were only 2 interesting data points showing a mass dependent background activity. More data points might give more insight in the real contamination numbers. For the dead carbon contamination Group I gave a larger contamination than Group IV (resp. $1.04 \pm 0.10 \mu g$ C and $0.88 \pm 0.04 \mu g$ C).

Again, more data points, with a better spread in the masses might give a better result. There are a few possible explanations why the method did not gave the desired effect:

1) The reduction method could have only reduced the carbon present at the outer side of the pellet, contamination present in the core is not reduced with this method, but still the contamination should not have increased.
2) The reactors where contaminated by samples graphitized earlier.
3) The contamination finds its origin elsewhere in the preparation process.
4) There is simply not a significant amount of contamination present in the iron pellets.

All in all, the main reason for the contamination is debatable.

We did find a clear difference between a mass dependent activity (background = 0%) and a constant contamination activity. For the Rommenhoeffer backgrounds the turning point for these two lies around a sample size of approximately $100 \mu g$ C. So there seems to be a sample contamination and a fixed amount of contamination, both having different origins. The fixed amounts of contamination could very well be present in the iron powder, the glasswork used or like mentioned earlier, originate somewhere else in the whole sample preparation process. This requires further research.
We have succeeded in improving the graphitization yield for small samples. The yields for small samples (10 µg C) with the new reactor are comparable to the normal yields (70-90%) of large samples graphitized in the conventional reactors. The main reason for this improvement seems to be the decreased volume of the reactor (from 2.5 ml to 1.5 ml). A smaller reactor seems to give a higher yield. The role of the Mg(ClO$_4$)$_2$, which is used as a water absorber is not clear at this point. What is sure is that the reaction time has been decreased from 1-2 hours to 10-15 minutes with the use of Mg(ClO$_4$)$_2$. Initial tests show that a smaller reactor allows graphitization of smaller samples (< 10 µg C) because most of the sample will be converted into graphite.
5 Recommendations

For future research improvements can be made in small sample radiocarbon analysis. Most of the results obtained in this report need some more thorough investigation. The yield improvements with the new reactor deserve some more attention. The role of Mg(ClO$_4$)$_2$ in this needs to be investigated independently from volume changes. Furthermore samples graphitized with this new method need to be measured with the HVEE 4130 AMS in order to determine if there is any discrepancy or contamination compared to the samples graphitized using the conventional reactor.

For the background reduction the experiment for Group II and Group III needs to be repeated since these groups had very high backgrounds. The results obtained for these groups in our experiment do not give a good indication if the reduction method works or not. Therefore it needs to be repeated with more data points.

The other experiment done (comparison between Group I and Group IV) can be optimized as well. More data points (especially small Rommenhoellers) for Group I might give a better fit and smaller error, and therefore a more reliable result. If however the whole process is variable, this large spread of datapoints remains.

The samples made for studying the dead carbon contamination should be made with a reference material with an activity close to the present day $^{14}$C content of atmospheric CO$_2$ (approximately 100%), as this is the most likely cause of MCC contamination, instead of the HOxII standard used in this experiment. HOxI has a natural activity of 100%, which corresponds to the activity of the modern carbon contamination. This will make it much easier to make a good fit of the results and will give better and more reliable results.

A series of small sample antracites should be made in order to do a better analysis on the samples. This is still hard to do in practice nowadays.
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References


M.de Rooij, J. van der Plicht, H.A.J. Meijer, 2008, Sample dilution for AMS $^{14}$C analysis of small samples (30 – 150 µgC), Radiocarbon 50 nr. 3 (2008), 413


M. de Rooij, J. van der Plicht, H.A.J. Meijer, 2009, Porous iron pellets for AMS $^{14}$C analysis of small samples down to ultra-microscale size (5-25 µgC). (2009)


I. Bakker, Improving the measurement of small radiocarbon samples with the AMS, 2005, Training Thesis, Master Programme Energy and Environmental Sciences