^{14}C MEASUREMENTS OF SUB-MILLIGRAM CARBON SAMPLES FROM AEROSOLS

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ABSTRACT. Accelerator mass spectrometry (AMS) at the milligram level is routinely performed, but it is difficult to go substantially below 100 μg of carbon. We discuss various approaches for sample preparation, machine operation and data evaluation, to meet the special requirements of ^{14}C AMS measurements at the microgram-carbon level. Furthermore, we present first results obtained at the Vienna Environmental Research Accelerator (VERA) from ^{14}C measurements of a snow sample from Gaithersburg, Maryland, USA, prepared at the National Institute of Standards and Technology (NIST).

INTRODUCTION

The importance of carbonaceous aerosols in atmospheric chemistry and related phenomena (*e.g.*, air pollution, radiation budget, climate) has been stressed many times (*e.g.*, Andreae and Crutzen 1997; Finlayson-Pitts and Pitts 1997). In principle, the measurement of ^{14}C/^{12}C ratios with accelerator mass spectrometry (AMS) is well suited to understanding the origin of carbonaceous aerosols and to study their transport (Currie *et al.* 1994, 1996, 1998). For example, aerosols originating from the combustion of fossil fuel can be distinguished through their negligible ^{14}C content compared to that of biomass-burning aerosols. However, in most cases there is little aerosol material available, making ^{14}C measurements at the microgram-carbon level necessary. However, the AMS technique, which is established for milligram samples (Rom *et al.* 1998), cannot easily be extended down to 10 μg of carbon, necessary for aerosol studies. Good results are only possible through modifications in the sample preparation technique and in the operating conditions of the used AMS machine.

A collaboration between the Institut für Radiumforschung und Kernphysik of the University of Vienna, and of the National Institute of Standards and Technology (NIST) was started to develop the capability of measuring ^{14}C/^{12}C ratios in few-microgram-carbon samples. For that purpose we prepared small standard carbon samples (10–100 μg) at NIST utilizing a sample preparation method based upon a method developed by Verkouteren, Klinedinst and Currie (1997). Then, their ^{14}C/^{12}C isotopic ratios were measured with AMS at the University of Vienna.

We discuss here the sample preparation method, ^{14}C measurements, and data analysis and evaluation, with the goal of to assessing the conditions for measuring ^{14}C/^{12}C ratios in few-microgram carbonaceous aerosol samples.

METHODS

Sample Preparation

The common methods for the production of AMS targets (Slota *et al.* 1987; Verkouteren *et al.* 1987; Vogel *et al.* 1987) are useful for carbon samples >100 μg. Samples below this amount give in general smaller and less stable beam currents, and longer times are often required for the graphitization. Due to the small mass of carbon from the samples, relatively large "blank" contributions come from the

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CuO used for the combustion to CO_2. Other materials used in the sample preparation process (metals, gases) may also contribute to the chemistry blank (Verkouteren, Klinedinst and Currie 1997).

Therefore, a special method for the preparation of ^{14}C AMS targets in the range of 10 to 100 µg of carbon was developed by Verkouteren, Klinedinst and Currie (1997). The sample material is combusted to CO_2 with *ca.* 200 mg CuO (3 h at 950°C) in a sealed quartz tube. The CO_2 is cryo-transferred to an evacuated quartz tube containing *ca.* 2 mg Fe wool and 30–300 mg Mn chunks. The tube is flame-sealed and heated for 24 h at 500°C in a furnace. At this time, the CO_2 from the sample is first reduced to CO on the Mn surface and then to graphite on the Fe wool surface. After a magnetic separation of the Fe-C matrix from the Mn, the Fe-C targets are melted at 1575°C in a furnace and beads are formed because these beads provide more stable handling and beam conditions compared to graphitic targets. Since the reduction and pretreatment takes place in sealed quartz tubes, parallel processing of these time-intensive procedures can be performed.

By the method described above, we prepared AMS targets (see Table 1) from oxalic acid standards (HOxI and HOxII), from the aerosol Standard Reference Material (SRM 1648), collected in St. Louis, Missouri, USA, and from the ^{14}C-free Research Material (RM 21). The latter was used to provide isotopic blanks. Furthermore, we prepared tube blanks (carbon from CuO, without any sample material added), metal blanks (no CuO added, carbon essentially from the Fe wool, Mn and Al-target holder), and Al blanks (target holder with empty hole and without hole).

The diameter of individual beads varied from 0.7 to 1.1 mm. For that purpose a special method was developed to guarantee a well-centered mount of each bead in an Al-target holder of the ion source. We first milled a hole with a diameter of 1.2 mm into a solid target holder with a depth of 0.5 mm to assure a geometry similar to the standard conditions (Rom *et al.* 1998). Then a deeper hole was drilled into each target holder, with the diameter and depth adjusted to the individual bead. The beads, having slightly irregular shapes, were finally pressed into these holes to fix them in a well-centered position.

TABLE 1a. Summary of Samples Used in the Present Investigation

Sample material	Carbon mass* (µg)	CuO mass* (mg)	Fe mass* (mg)	Mn mass* (mg)	Runs	$^{12}C^{3+}$ (nA)	$^{14}C^{3+}$ (counts)	^{14}C content (pMC)†	Nominal value (pMC)
HOxI	65.7	522	2.40	301	11	1646 ± 55	8789	reference	105.3
	35.8	195	2.17	92	15	252 ± 10	1520	--	
	15.3	185	1.90	30	18	50 ± 1	344	--	
HOxII	67.5	522	2.71	301	10	870 ± 21	4707	135.2 ± 4.0	136.0
	31.6	213	1.91	89	14	196 ± 6	1717	135.8 ± 6.6	
	14.9	297	1.77	31	18	215 ± 10	2171	148.1 ± 14.2	
SRM1648	88.2	510	1.95	301	10	2110 ± 89	6369	60.9 ± 1.7	60 ± 3‡
	34.0	179	2.70	89	14	183 ± 8	647	72.6 ± 4.1	
	15.5	172	2.03	30	18	84 ± 3	426	73.3 ± 6.7	
SRM21	116.2	465	2.49	301	10	1740 ± 90	380	2.2 ± 1.2	~0
	31.2	185	2.45	93	14	594 ± 26	623	14.8 ± 2.8	
	12.5	186	0.91	31	17	129 ± 8	278	16.7 ± 7.7	

*Standard deviations: C (<0.1 µg), CuO and Mn (<1 mg), Fe (<0.01 mg)
†pMC = percent Modern Carbon ■ 100 for 1950 AD
‡Beta counting (Currie *et al.* 1984)

TABLE 1b. Summary of Materials Used in the Present Investigation*

Sample material	Carbon mass (μg)	CuO mass (mg)	Fe mass (mg)	Mn mass (mg)	No. of Runs	$^{12}C^{3+}$ (nA)	$^{14}C^{3+}$ (counts)
Tube Blank	4.90	440	1.88	304	10	23 ± 2	70
	1.90	185	1.99	31	10	18 ± 2	33
Metal Blank	0	0	2.02	15	11	15 ± 2	31
	0	0	1.99	31	10	30 ± 3	32
	0	0	1.88	300	10	20 ± 3	37
	0	0	1.58	89	10	12 ± 1	22
Al Blank (no hole)	0	0	0	0	10	8 ± 1	11
	0	0	0	0	11	5 ± 1	9
Al Blank (with hole)	0	0	0	0	10	6 ± 1	14
	0	0	0	0	11	8 ± 1	20

*See footnotes for Table 1a.

^{14}C Measurements

VERA is an AMS facility designed for fast sequential injection of all three carbon isotopes ($^{12}C^-$, $^{13}C^-$, $^{14}C^-$). For a basic description of this new facility see Kutschera *et al.* (1997) and Priller *et al.* (1997). All AMS measurements were performed at a terminal voltage of 2.7 MV using Ar for stripping, the standard conditions for ^{14}C measurements (Rom *et al.* 1998; Wild *et al.* 1998).

After loading all targets in the 40-position target wheel (made of Al), we tuned VERA to obtain maximum transmission ($^{12}C^{3+}/^{12}C^-$). We then determined the mean $^{12}C^{3+}$ ion current after the high-energy analyzing magnet for each sample. The results of these runs were used for selecting the sensitivity of the fast current amplifiers, because the ion currents of the small samples were substantially lower than in the case of the 1-mg samples. Changing the sensitivities also requires offset calibration of the amplifiers. Since the current amplifiers have a longer rise time for higher sensitivities we had to lengthen the time periods of the sequential injection system to assure that the amplified cup currents were sampled after reaching a "plateau". We injected $^{12}C^-$ for *ca.* 2 ms followed by $^{13}C^-$ for *ca.* 127 ms and $^{14}C^-$ lasting *ca.* 860 ms. Including waiting periods, the total cycle time was 1 s, which was *ca.* 10 times longer than in the case of measurements on mg samples (Rom *et al.* 1998). For each run, 200 cycles were used. Since the beam currents ($^{12}C^{3+}$, $^{13}C^{3+}$) for different targets varied over a wide range, corresponding adjustments of the current amplifier sensitivities were necessary to obtain good results.

The overall measuring time was 2000–3600 s per sample; the typical $^{12}C^{3+}$-currents were stable within 2.0 to 6.2% during the total run time and ranged between 50 and 2110 nA (see Table 1a). The $^{12}C^{3+}$-currents of the Al target holders were substantially lower, with *ca.* 7 nA in both cases (drilled and solid). The collected total $^{14}C^{3+}$ counts ranged from 278 to 8789 (see Table 1a). This leads to a maximum Poisson statistical error of 6%. In the case of a modern sample at the mg level, we usually obtain a statistical error of <0.5% (Rom *et al.* 1998).

We noticed that the measured transmission decreased rapidly for targets with carbon masses of <15 μg (see Fig. 1). The drop in the $^{12}C^{3+}/^{12}C^-$ transmission is probably caused by a non-carbon beam component affecting the $^{12}C^-$ current reading but not the high-energy analyzed beam. Furthermore, we noticed that the measured $^{12}C^{3+}$ current was linearly correlated with the carbon mass, with a slope of (18 ± 2) nA/μg C (see Fig. 2).

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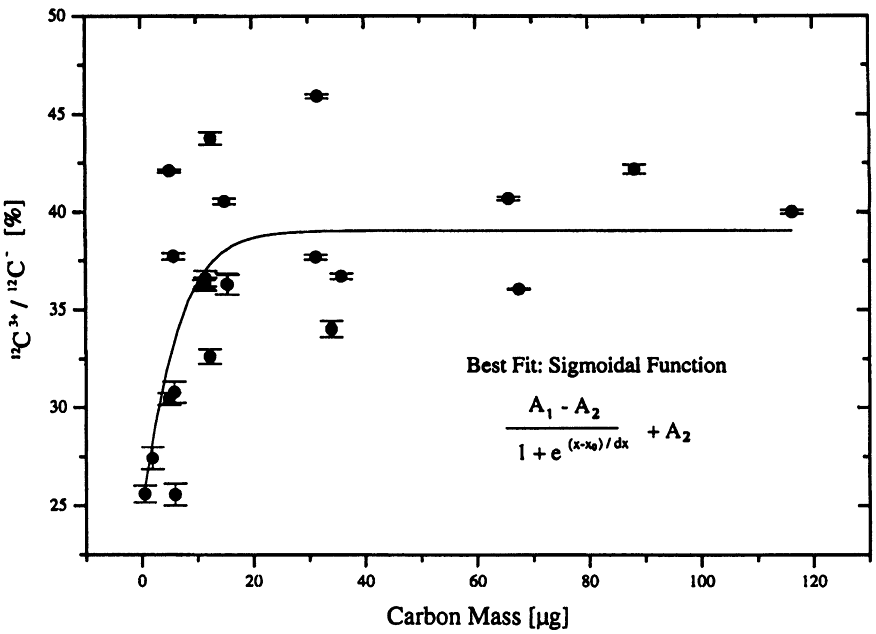

Fig. 1. Transmission measured through the $^{12}C^{3+}/^{12}C^-$ ratios for targets of different carbon masses. The solid curve is a sigmoidal fit to the data points.

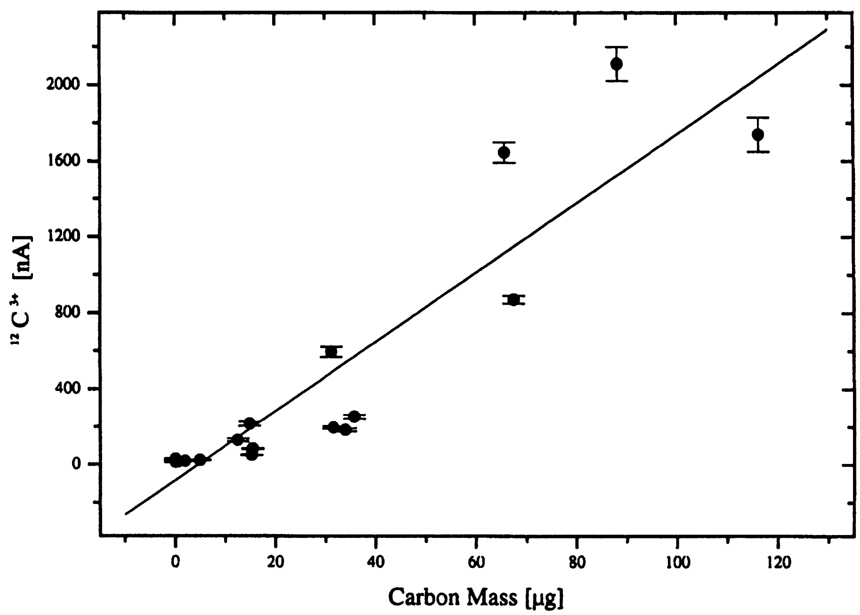

Fig. 2. Analyzed $^{12}C^{3+}$ current as a function of the target carbon mass. The solid line is a linear fit to the data points.

Data Analysis

First, we calculated the $^{12}C^{3+}/^{12}C^{-}$, $^{13}C^{3+}/^{12}C^{3+}$ and $^{14}C^{3+}/^{12}C^{3+}$ ratios of the individual targets. Then the raw data of each target were used to calculate the mean values, $\bar{x}$, and standard deviations of the mean, σ, whereby n was the number of runs ($10 \leq n \leq 18$).

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i \tag{1}$$

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n(n-1)}} \tag{2}$$

The $^{14}C^{3+}/^{12}C^{3+}$ ratios of the individual targets were normalized to $\delta^{13}C = -25‰$ (Stuiver and Polach 1977).

$$\left(\frac{^{14}C}{^{12}C}\right)_{S,-25} = \left(\frac{^{14}C}{^{12}C}\right)_{S,\,meas}\left[1 - \frac{2(25 + \delta^{13}C_S)}{1000}\right]$$

(S denotes the individual sample, called "target" in the text.) (3)

The $\delta^{13}C_S$ values were determined from the measured $^{13}C^{3+}/^{12}C^{3+}$ ratios of individual targets by the following formula, which is designed for use on the PDB scale (Rom *et al.* 1998):

$$\delta^{13}C_s = \frac{\frac{1000 + \delta^{13}C_{HOxI}}{1000}\left(\frac{^{13}C}{^{12}C}\right)_{S,\,meas} - \left(\frac{^{13}C}{^{12}C}\right)_{HOxI,\,meas}}{\left(\frac{^{13}C}{^{12}C}\right)_{HOxI,\,meas}}\ 1000‰ \tag{4}$$

$(\delta^{13}C_{HOxI} = -19‰)$.

We assumed that the total carbon mass, m_{meas} (measured as CO_2 with the calibrated volume of the sample preparation gas system), is the sum of a "true" carbon mass, m_{true}, and a contamination carbon mass, m_{con}.

$$m_{meas} = m_{true} + m_{con} \tag{5}$$

Assuming that the tube blank represents the major contribution to m_{con}, it is possible to calculate the $^{14}C/^{12}C$ ratios of each individual target according to

$$\left[\left(\frac{^{14}C}{^{12}C}\right)_{S,-25}\right]_{true} = \frac{\left(\frac{^{14}C}{^{12}C}\right)_{S,-25} m_{meas} - \left(\frac{^{14}C}{^{12}C}\right)_{TB,-25} m_{con}}{m_{true}}, \tag{6}$$

(TB = Tube Blank).

The weighted average of $^{14}C/^{12}C$ ratios for several tube blanks was $(7.33 \pm 1.53) \times 10^{-13}$. The m_{con} values for each individual target were calculated by using Figure 3. The error is the larger of the internal and external error calculated according to Priller *et al.* (1997).

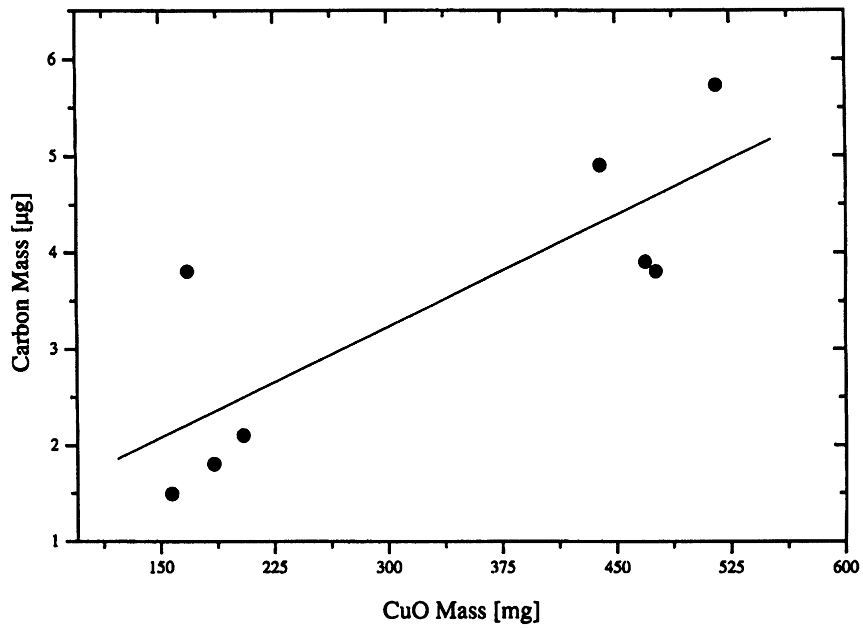

Fig. 3. Residual carbon background derived from CuO and from the quartz tube (measured as CO_2). The solid line is a linear fit to the data points.

Finally, we calculated the relative ^{14}C content $^{14}C_{rel.}$ expressed in percent Modern Carbon (pMC).

$$^{14}C_{rel.} = \frac{\left[\left(\frac{^{14}C}{^{12}C}\right)_{S,-25}\right]_{true}}{0.95\left[\left(\frac{^{14}C}{^{12}C}\right)_{HOxI,-19}\right]_{true}} 100\ \text{pMC} \tag{7}$$

Results

The present investigation shows that it is possible to measure $^{14}C/^{12}C$ ratios of samples containing 10–100 μg carbon at VERA. Referenced to the particular HOxI samples, we obtained results which were close to the nominal values, but with substantial scattering (see Table 1a).

Furthermore, we measured ^{14}C originating from a snow aerosol sample (148 µg carbon) collected in 1996 at Gaithersburg, Maryland, USA. This sample was processed at NIST utilizing the sublimation method developed by Biegalski *et al.* (1997). This method allows the preparation of carbon targets from small snow and ice samples, resulting in low contamination and modest mass loss. The ^{14}C content, (130 ± 9) pMC, was quite high, but may have been due to collecting the snow during a large snow storm. At that time, the fossil-fuel combustion emissions from vehicles was likely minimal and the residential wood burning was very high.

Conclusion and Outlook

In this paper, we demonstrated that it is possible to measure the ^{14}C content of sub-milligram carbon targets at VERA. However, substantial improvements are required to decrease the uncertainties of ^{14}C measurements at the few-microgram level.

In the near future we want to push the limits to <10 μg by using highly purified CuO, extra-pure metals (Fe, Mn, Al) and a stable isotope mass spectrometer (to be acquired in the near future). This will allow us to measure $\delta^{13}C$ values (from CO_2) with much higher precision than currently by using AMS. Furthermore, we know now that part of the observed scatter of data was probably due the overall running conditions for the present experiment, which were somewhat less favorable as compared to our standard conditions reported in Rom *et al.* (1998). This was due to a small misalignment of the Cs-beam focussing electrode in the sputter source, leading to a slight off-center position of the Cs-spot on the targets. This problem can be eliminated in future experiments.

Consequently, we expect that it will be possible to measure ^{14}C in carbonaceous aerosol samples, extracted from snow from the Austrian Alps collected at the high altitude research station "Sonnblick" (3105 m), where *ca.* 50 μg carbon per sample should be available. In addition, aerosol samples from ice cores may be investigated in the future, where we expect only a few micrograms carbon per sample.

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