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CORRECTING FOR CONTAMINATION IN AMS ^{14}C DATING

Ken Mueller • Paul Muzikar[1]

Prime Lab, Department of Physics, Purdue University, West Lafayette, Indiana 47907 USA

ABSTRACT. When using accelerator mass spectrometry (AMS) for radiocarbon dating, it is important to correct for carbon contamination that is added to the sample and the standard during chemical processing. We derive an equation for making this correction that generalizes previous work in several ways. We treat the case in which contaminating carbon is added during both the combustion step and graphitization step. Taking this two-stage contamination process into account is particularly important when only a fraction of the CO_2 produced in the combustion is graphitized. We also allow for the fact that the ^{13}C fractions of the sample, the standard, and the contaminants may be different.

INTRODUCTION

The chemical processing of samples for accelerator mass spectrometry radiocarbon (AMS ^{14}C) dating inevitably introduces contamination by extraneous carbon. Correcting for this effect is important in obtaining accurate dates, especially for small samples (Vogel et al. 1987; Kirner et al. 1995). Donahue and coworkers (Donahue et al. 1990) derived a widely used formula for making this correction. More recently, Brown and Southon (Brown 1994; Brown and Southon 1997) derived a rather complex correction formula, which takes into account the fact that the contaminating carbon will in general not be modern, and that the standard will also be contaminated. (See also Currie et al. 1994, which presents a correction formula which allows for nonmodern extraneous carbon.)

In this paper we derive and discuss a correction formula that generalizes previous work in two ways. First, we allow for the fact that contamination may enter the sample at two different stages in the preparation process, and that these contaminants will in general have different properties. For specificity, we imagine that one contaminant enters during the combustion stage, and another enters during the graphitization stage; for carbonate samples, the first stage would be the hydrolysis which produces the CO_2. If, as is often the case, only a fraction of the CO_2 resulting from the combustion is graphitized, the two contaminants must be treated separately. Second, we allow for the fact that the sample, the standard, and the contaminants may have different ^{13}C contents.

DERIVATION

For our derivation, we will adopt the "constant contaminant mass" model, a model that has received justification from various experiments. We assume that, regardless of sample size, fixed masses of foreign carbon m_{c1} and m_{c2} are introduced into the sample during the chemical processing. We assume that m_{c1} enters during the combustion stage which produces CO_2, while m_{c2} enters during the graphitization stage. Finally, we assume that a fraction x of the CO_2 is graphitized. There are two reasons why x is often less than one: 1) an aliquot of CO_2 may be drawn off for a δ^{13}C determination, or 2) the amount of CO_2 may be too large for the graphitization tube.

In AMS dating, the ^{14}C/^{13}C ratio of the unknown sample is measured relative to that of a standard. This standard will also be chemically processed and have contamination introduced. In general this contamination of the standard must be taken into account. For simplicity we will assume that the all the CO_2 produced by the standard is graphitized.

To derive our formula, we first establish our notation. We let M denote the mass of carbon of the unknown sample (without the contaminants), x the fraction which is graphitized, m_{c1} the carbon

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[1] Corresponding author. Email: paul@physics.purdue.edu.

mass of the first contaminant, m_{c2} the carbon mass of the second contaminant, and M_{ox} the carbon mass of the standard; a commonly used standard is oxalic acid II. Let w denote the number of ^{14}C atoms per unit mass of the sample, and let w_{c1}, w_{c2}, and w_{ox} be the corresponding quantities for the contaminants and the standard. Finally, let v be the number of ^{13}C atoms per unit mass of the sample, with v_{c1}, v_{c2}, and v_{ox} the corresponding quantities for the contaminants and the standard. (Throughout this paper, the term "mass" can be taken to mean either grams or moles, with the corresponding interpretation of the w's and v's.)

Then, the actually measured ratio is given by

$$F_m = \frac{({}^{14}\mathrm{C}/{}^{13}\mathrm{C})_{sample,\ measured}}{({}^{14}\mathrm{C}/{}^{13}\mathrm{C})_{ox,\ measured}} \tag{1}$$

or

$$F_m = \frac{\dfrac{x(Mw + m_{c1}w_{c1}) + m_{c2}w_{c2}}{x(Mv + m_{c1}v_{c1}) + m_{c2}v_{c2}}}{\dfrac{M_{ox}w_{ox} + m_{c1}w_{c1} + m_{c2}w_{c2}}{M_{ox}v_{ox} + m_{c1}v_{c1} + m_{c2}v_{c2}}} \tag{2}$$

The true value of F is given by

$$F = \frac{w/v}{w_{ox}/v_{ox}} \tag{3}$$

The goal is to obtain the value of F from the measured value F_m, assuming that by previous experiments we have determined the properties of the contaminating carbon; this point will be discussed later in this paper. We may rearrange the previous equations to obtain the following

$$F = \frac{\left(1 + \dfrac{m_{c1}w_{c1}}{M_{ox}w_{ox}} + \dfrac{m_{c2}w_{c2}}{M_{ox}w_{ox}}\right)\left(1 + \dfrac{m_{c1}v_{c1}}{Mv} + \dfrac{m_{c2}v_{c2}}{xMv}\right)}{\left(1 + \dfrac{m_{c1}v_{c1}}{M_{ox}v_{ox}} + \dfrac{m_{c2}v_{c2}}{M_{ox}v_{ox}}\right)} F_m - \frac{m_{c1}w_{c1}v_{ox}}{Mw_{ox}v} - \frac{m_{c2}w_{c2}v_{ox}}{xMw_{ox}v} \tag{4}$$

Equation (4) is the central result of this paper; it contains the two stage contamination effects, and the effects due to the different ^{13}C contents of the sample, contaminants, and standard. As it stands it is perhaps unusably complicated, and so in the following sections we discuss various physically motivated simplifications which are justified in appropriate circumstances.

ONE-STAGE CONTAMINATION MODEL

In this section show how our result simplifies if we set $x = 1$ and $m_{c2} = 0$, and thus adopt the more usual one-stage contamination model. Setting $m_{c2} = 0$ and $x = 1$ in the previous equation gives

$$F = \frac{\left(1+\frac{m_{c1}w_{c1}}{M_{ox}w_{ox}}\right)\left(1+\frac{m_{c1}v_{c1}}{Mv}\right)}{\left(1+\frac{m_{c1}v_{c1}}{M_{ox}v_{ox}}\right)}F_m - \frac{m_{c1}w_{c1}v_{ox}}{Mw_{ox}v} \tag{5}$$

Note that in three places, ^{13}C ratios appear (v_{c1}/v, v_{ox}/v, and v_{c1}/v_{ox}). This equation generalizes previous work on the one stage model, in that it incorporates the effects of these ^{13}C ratios. However, these three ratios will usually be very close to unity; in addition they always multiply m_{c1}, which presumably will always have an uncertainty in its precise value due to experimental error. Thus, in most cases it will be sufficiently accurate to set these three ratios equal to one, and so obtain the formula:

$$F = \frac{\left(1+\frac{m_{c1}w_{c1}}{M_{ox}w_{ox}}\right)\left(1+\frac{m_{c1}}{M}\right)}{\left(1+\frac{m_{c1}}{M_{ox}}\right)}F_m - \frac{m_{c1}w_{c1}}{Mw_{ox}} \tag{6}$$

Note that if the contaminant carbon had, for some reason, an unusual ^{13}C content, so that v_{c1}/v was not close to one, then the more accurate equation (5) would have to be used. Another situation in which equation (5) might have to be used would be in the case of a very old sample, for which F_m was much less than one. If F_m were small, then the last term in (5) could be a substantial correction effect, and the fact that v_{ox}/v differed from one could make a difference.

Several aspects of equation (6) deserve comment. First, note that structurally it is very similar to the formula derived by Donahue et al. (1990). In the special case that $w_{c1} = w_{ox}$, it reduces to

$$F \to \left(1+\frac{m_{c1}}{M}\right)F_m - \frac{m_{c1}}{M} \tag{7}$$

which parallels the Donahue et al. (1990) formula.

If the mass of the standard is very large so that $\frac{m_{c1}}{M_{ox}} \to 0$, equation (6) reduces to a slightly different formula

$$F \to F_m + \frac{m_{c1}}{M}\left(F_m - \frac{w_{c1}}{w_{ox}}\right) \tag{8}$$

In this limit, whether F is greater than or less than F_m depends in a simple way on the ^{14}C content of the contaminating carbon. Note that (8) is equivalent to the Currie et al. (1994) formula.

Finally, we can see that equation (6) is equivalent to the Brown Southon (1997) result by making the following identifications

$$\frac{R_s^A}{R_{ox1}^A} = F \qquad \frac{R_s}{R_{ox1}} = F_m \tag{9}$$

$$C_{ox1}h_{box1} = \frac{m_{c1}}{M_{ox} + m_{c1}} \qquad C_s h_{bs} = \frac{m_{c1}}{M + m_{c1}} \tag{10}$$

$$h_{bs} = \frac{w_{c1}}{w_{ox}} \frac{m_{c1}}{M + m_{c1}} \qquad h_{box1} = \frac{w_{c1}}{w_{ox}} \frac{m_{c1}}{M_{ox} + m_{c1}} \tag{11}$$

In order to use equation (6) in analyzing data, it is necessary to determine both m_{c1} and w_{c1}/w_{ox}; this is not a trivial task, since many experiments yield only the product $m_{c1}w_{c1}/w_{ox}$. However, Brown and Southon (1997) were able to determine the needed quantites by a well-designed series of measurements.

Note that if $x = 1$ and all the ^{13}C ratios in (4) are set equal to one, we also arrive at version of the one stage model, even without setting m_{c2} equal to zero. In a sense this point is obvious, since if all the CO_2 is graphitized, the two contaminants may be combined into one effective contaminant. To see this, start with (4) and set $x = 1$, along with all the ^{13}C ratios. This gives

$$F = \frac{\left(1 + \frac{m_c w_c}{M_{ox} w_{ox}}\right)\left(1 + \frac{m_c}{M}\right)}{\left(1 + \frac{m_c}{M_{ox}}\right)} F_m - \frac{m_c w_c}{M w_{ox}} \tag{12}$$

where we have defined the properties of an average contaminant (m_c, w_c) as follows:

$$m_c = m_{c1} + m_{c2} \qquad m_c w_c = m_{c1} w_{c1} + m_{c2} w_{c2} \tag{13}$$

TWO-STAGE CONTAMINATION MODEL

When x is not equal to one, we must resort to the two-stage model. As argued in the previous section, it will usually be sufficiently accurate to set all the ^{13}C ratios in (4) equal to one. Doing this produces the following equation

$$F = \frac{\left(1 + \frac{m_{c1} w_{c1}}{M_{ox} w_{ox}} + \frac{m_{c2} w_{c2}}{M_{ox} w_{ox}}\right)\left(1 + \frac{m_{c1}}{M} + \frac{m_{c2}}{xM}\right)}{\left(1 + \frac{m_{c1}}{M_{ox}} + \frac{m_{c2}}{M_{ox}}\right)} F_m - \frac{m_{c1} w_{c1}}{M w_{ox}} - \frac{m_{c2} w_{c2}}{x M w_{ox}} \tag{14}$$

So we can see that when $x < 1$, the correction formula is more complicated, and cannot be reduced to an effective single contaminant model; we need to know the values of m_{c1}, m_{c2}, $m_{c1}w_{c1}/w_{ox}$, and $m_{c2}w_{c2}/w_{ox}$.

We note that the paper by Vogel et al. (1987) does address this issue. They were able to separately determine the contamination added during combustion and during graphitization. In our notation, they were able to measure $m_{c1}w_{c1}$ and $m_{c2}w_{c2}$. In a more recent paper Schleicher et al. (1998) were able to determine the contamination introduced during different steps in their procedure.

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