

STUDY OF THE ^{14}C -CONTAMINATION POTENTIAL OF C-IMPURITIES IN CuO AND Fe

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ABSTRACT. The carbon concentration in CuO and iron was determined by isolating C. The values were in agreement with results reported in other studies. Contaminating carbon from CuO and Fe was transformed to AMS targets and measured for ^{14}C . C-traces in CuO were shown to be the major contribution to the ^{14}C sample processing blank. In addition, there is a significant variability in the ^{14}C content of CuO observed between different production batches. The combined contamination potential of CuO and Fe was found to be 4.47–8.92 μg recent carbon, whereas the more realistic estimate for AMS-target preparation conditions ranged between 1.63 and 3.24 μg recent carbon, depending on the ^{14}C level in CuO .

INTRODUCTION

After two decades of accelerator mass spectrometric (AMS) radiocarbon dating, most of the “early days” expectations have become reality. Tiny samples are now being dated with very good precision and most of the AMS facilities combine good accuracy with a very high throughput. However, in contrast with the expansion of AMS dating as such, little progress has been made regarding the dating limit of 40–50 ka (Wand *et al.* 1984; Vogel *et al.* 1984; Arnold *et al.* 1987; Gurfinkel 1987; Hedges *et al.* 1989; Klinedinst *et al.* 1994). In most AMS facilities, this background is caused mainly by contamination during chemical sample preparation. One of the most attractive features of AMS machines is their extremely low background counting rate, corresponding to ages of 100 ka or older. Some research groups have invested substantial effort in this particular aspect, but spectacular reduction of the background has not yet been reported.

On the other hand, the age of most of the materials to be dated is <20 ka, and therefore a contamination equivalent to a few μg Mod C does not introduce significant errors when a straightforward background correction procedure is applied. Of course, new horizons would open if better detection limits were achieved. This would not only be the case in archaeological applications but also in geochemistry and cosmochemistry (Jull *et al.* 1994). Also, in atmospherical applications, where small sample sizes are encountered, there is an urgent need to reduce contamination in order to achieve accurate and reliable data (Currie *et al.* 1994).

The need for a specific “all-in-one” approach to tackle the contamination problem is generally agreed upon. Contamination introduced during sample preparation and AMS-target production has very different origins. Suggested sources (Verkouteren *et al.* 1987; Vogel, Nelson and Southon 1987; Aerts-Bijma, Meijer and van der Plicht 1997) of contamination include: CO_2 adsorption on walls of gas handling units, CO_2 contamination in the H_2 gas used for graphitization, C traces in reagents and catalysts, diffusion of (pump) oil vapors in the oxidation unit, dust, sample handling in a “ ^{14}C -hot” atmosphere, and gas adsorption of the graphite. Measured backgrounds are, of course, the sum of all previous mentioned (and other unknown) sources of which very little is known about

their individual contributions to the total. Such knowledge, however, is a prerequisite to develop cleaner target preparation procedures.

As part of a larger background reduction project, we focused on the contamination potential of CuO and Fe. CuO is widely used as oxidizing agent for organic material and Fe is used as catalyst for the reduction of CO₂ to graphite according to the procedure first described by Vogel *et al.* (1984). In the past, interesting results were obtained in contamination source apportionment. All those studies had in common that background materials (anthracite, natural or spectroscopic graphite) were processed as real samples and that the measured, finite, ages were considered the result of contamination introduced during sample handling, neglecting any *in-situ* ¹⁴C possibly present in the background samples. A second problem is the evaluation of the different background contributions to the total. It was demonstrated by Vogel, Nelson and Southon (1987) and Verkouteren *et al.* (1987) that combustion with CuO and the reduction to graphite with a Fe-catalyst, although the latter to a lesser extent, introduced the major part of the observed contamination. In contrast, Beukens (1993) attributed the major part of the contamination to acetylene production while Gulliksen and Thomsen (1992) observed no measurable contamination during combustion but ascribed the background to the graphitization process. In contrast to previous studies, independent methods were applied to measure the C concentration in the materials and to assess the age of the contamination.

METHODS

A direct and accurate determination of the ¹⁴C concentration in CuO and Fe is almost impossible. Earlier attempts were undertaken to insert pressed Fe-powder pellets in the ion source of the spectrometer but generally the C⁻ currents were too low and unstable to allow a reliable ¹⁴C concentration determination. Due to the lower C concentration and less favorable target characteristics the same approach for CuO is not applicable. We propose a two-step procedure to overcome this problem. First, an accurate determination of the C concentration is necessary, and second, enough contaminating C has to be isolated from the materials to make an AMS analysis possible. Once the C concentration is exactly known, one can afford to use a nonquantitative C-isolation method. This step is vulnerable to ¹⁴C-contamination, especially for CuO, due to the low C concentration. After C isolation, as CO₂ gas, further contamination is not to be feared during graphite target preparation if samples are large enough. The combination of the C concentration and the ¹⁴C levels of the carbon traces yields the contamination potential of Fe and CuO.

TABLE 1. Technical Details of the Materials Used in Radiocarbon Target Preparation and Their C Contaminations as Determined by CPAA

	Purchased from	Form	Metal purity	Total purity	C concentration	CPAA (ppm)	St. dev.
<i>Fe</i>	Johnson Matthey Karlsruhe (Germ.)	<325 mesh powder	99.9%	99.5%	< 0.3%	98	sd=37 n=6
	Johnson Matthey Karlsruhe (Germ.)	60 mesh powder	99.998%		Not specified	37.6	sd=2.7 n=3
<i>CuO</i>	UCB Brussels (Belgium)	Wires (0.7 × 6.0 mm)	p.a.	p.a.	< 0.01%	17.8	sd=3.5 n=3

Two different grades of Fe powder were thus far used as catalyst in the reduction process of CO₂. Full technical details of those materials are given in Table 1. Both types ensure a fast reduction of CO₂ in our systems and give good graphite target characteristics, although the 99.9% Fe is more

readily homogenized with graphite. Also, after pressing of the AMS target a slightly better surface is obtained resulting in better ion source performance.

CuO is purchased as the classical wire form (see Table 1) but for some applications the wires were crushed to powder ($<100\ \mu\text{m}$) and reoxidized before use. With ground CuO, better oxidation yields were obtained, allowing smaller quantities to be used for combustion.

Carbon Analysis

Several analytical techniques are appropriate for the analysis of C in a metal matrix. Most familiar are the combustion techniques where C is oxidized to CO_2 that is subsequently quantified manometrically or spectroscopically. In the low $\mu\text{g/g}$ range some difficulties may occur with those techniques. Nonquantitative oxidation of the carbon leads to negative errors, which, for this study, is a severe problem in the case of Fe because all the contaminating carbon, presumably present in reduced form, will be liberated in the Cs-sputtering process. In the case of CuO the C-concentration was expected to be in the range of the detection limits for the combustion techniques. Therefore, a sensitive nuclear analytical technique was applied, namely charged particle activation analysis (CPAA) (Strijkmans 1994). Charged particles bombarding a target (*ca.* 50 mg Fe or 100 mg CuO) induce nuclear reactions with the analyte element. Here we used the $^{12}\text{C}(\text{d},\text{n})^{13}\text{N}$ reaction. The radionuclides produced are short-lived positron emitters. Measurement of the annihilation radiation and standardization yields the C concentration in the matrix. Practical details of the analyses are reported in de Neve *et al.* (1997).

Carbon Isolation

We used a modified combustion unit for steel analysis for the isolation of carbon (Fig. 1). The unit is very similar to the dynamic-flow combustion systems for organic material. The central part of the furnace consists of a porcelain combustion tube wherein the samples are inserted in porcelain sample holders. Sample holders were prebaked at 950°C and each combustion tube was preconditioned by two blank combustions prior to use. Sample masses varied between 4–6 g for Fe and 8–12 g for CuO. Before heating, the system was evacuated and flushed with N_2 ($\text{CO}+\text{CO}_2+\text{C}_n\text{H}_m < 0.16\ \text{ppm}$) to avoid contamination. The gases formed by combustion were cryogenically trapped. This cold trap was indirectly cooled with liquid nitrogen. Since O_2 ($\text{CO}+\text{CO}_2+\text{CH}_4 < 0.9\ \text{ppm}$) condenses at liquid N_2 temperature, the trap was placed in a beaker filled with molecular sieve granules. By cooling the beaker with liquid N_2 the cold trap is at an optimum temperature for CO_2 condensation, while O_2 passes through. In this way, the system can be operated without any danger of explosion. At the end of combustion, the trapped gas was transported to a calibrated volume where it was manometrically quantified. A constant gasflow of $0.25\ \text{L min}^{-1}$ was maintained during combustion. Each combustion resulted in an amount of gas which was cryogenically distilled over a -80°C cold trap to remove water vapor prior to storage. Table 2 presents a detailed scheme of the combustion stages. The temperatures quoted in the table represent the value at the end of the specified sequence.

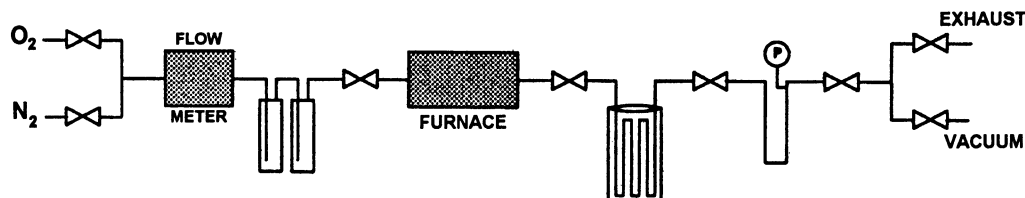


Fig. 1. Schematic diagram of the C-isolation unit

TABLE 2. Detailed Description of the Different Stages of the Combustion Method for the Isolation of C Traces in CuO and Fe

Sequence no.	Duration (min)	Temperature		Gas	Action
		Oven (°C)	Trap (°C)		
1	5	20	20	N ₂	Flushing
2	2	300	20	N ₂	Cleaning (removal adsorbed gases)
3	10	900	-150	N ₂	Heating
4	6	950	-150	O ₂	Combustion
5	5	850	-150	N ₂	Flushing
6	2	*	-150	*	Evacuation
7	*	*	20	*	Gas quantification

*Not relevant

¹⁴C Analysis

Before graphitization, the gas samples were treated with “sulfix” to remove S-containing contaminants which prohibit or slow down the graphitization reaction. Preliminary experiments had shown the necessity of this pretreatment. Graphitization and AMS measurements were performed at the Centre for Isotope Research in Groningen, the Netherlands, according to the standard procedures (Aerts-Bijma, Meijer and van der Plicht 1997). *Ca.* 1 mg Fe was used as catalyst and the ratio H₂/CO₂ was 2.5. Reactions were carried out at 600°C and took *ca.* 15 h to guarantee complete reduction. The ¹⁴C results were corrected for system background introduced during graphitization and AMS measurement. For each target δ¹³C was measured and used for isotope fractionation correction of ¹⁴C results.

RESULTS AND DISCUSSION

Carbon Concentration in Fe and CuO

The C concentration results obtained with charged particle activation analysis (CPAA) are shown in Table 1 for the different materials. The results are below the manufacturers' specifications. It should be emphasized that improved purity quoted for Fe reflects only a lower trace metal content and that for ¹⁴C purposes, both grades have a comparable contamination level. The general experience that high-purity Fe sometimes slows down the graphitization process is probably caused by the lower content. We believe that graphitization goes faster if more C nuclei are present in the Fe. For 99.5% Fe, the standard deviation on the mean is almost a factor of 10 higher than the standard deviation on an individual measurement, indicating C contamination is distributed inhomogeneously over the Fe-matrix.

Very few results of C concentrations in Fe have been published to date. Verkouteren, Klinedinst and Currie (1997) found comparable concentrations in Fe wool using a dynamic and a static combustion technique. Other data are results of direct ¹⁴C-measurements in Fe indicating “low” contamination levels.

For CuO, some data were published on C release from the matrix upon heating. Boutton (1991) found 3.6 μg g⁻¹ C in untreated CuO and after heating this amount was decreased by a factor of three. This agreed well with the results reported by Verkouteren *et al.* (1987) (*ca.* 1 ppm). However,

recent analyses by the same author showed higher contamination levels (Verkouteren, Klinedinst and Currie (1997)). Our results obtained by CPAA are somewhat higher, which is explained by the specific characteristics of the different analytical techniques. All previous studies made use of combustion techniques that may suffer from incomplete oxidation of the C contamination in the interior of the CuO matrix. The oxide layer around the Cu axis of the wires prohibits good penetration of the oxygen resulting in incomplete oxidation and C removal. This is also confirmed by the results given in the C isolation part of this discussion.

The results obtained thus far agree with the general idea that contamination originating from CuO is much worse than from Fe. Using 0.5 g CuO and 2 mg Fe for a classical 1-mg target produces a total contamination potential of *ca.* 9 µg C, of which 8.9 µg originates from CuO, and 0.1–0.2 µg from Fe. Most laboratories indicate lower total contamination due to non-quantitative release of the contamination and the probable sub-Modern level of the contamination.

¹⁴C Analysis of the Carbon Contamination

Large amounts of CuO (8–12 g) and Fe (4–6 g) were combusted in the system (Fig. 1) described previously. Only Fe powder with the highest C concentration was analyzed with this method. Considering the lower C concentration in the low C grade Fe, the expensive price of that product and the necessity for a duplicate ¹⁴C analysis, we believe there is no need to isolate C from both types of Fe at this stage of the project. In the future, when AMS sample preparation backgrounds are reduced, this aspect of the problem should be considered. Before the materials were combusted we ran also 2 blanks (3.1 and 3.4 µg C) to correct the results for contemporary contamination in this apparatus. Due to space limitations, we were obliged to perform at least 3 (Fe) or 7 (CuO) combustions in order to obtain enough carbon for a robust AMS target. After each combustion the CO₂ pressure was measured and each individual CO₂ aliquot was flame-sealed in a Pyrex[®] tube. In Table 3, the mean C concentration data determined with the isolation method are presented for Fe and CuO.

TABLE 3. Overview of Stable Carbon Isotope and Radiocarbon Results for the Different Targets Prepared After Collection of Individual CO₂ Aliquots Extracted from the Fe and CuO Matrices*

	Fe				CuO	
C concentration (ppm)	21.7				6.44	
Standard deviation	3.8				0.95	
No. of runs	4	4	3	7	7	8
Lab no. (GrA-)	3541	4391	4392	3565	4393	4394
Mass (µg)	477	505	424	320	317	315
δ ¹³ C (‰ _{vs VPDB})	-26.6	-32.5	-37.5	-3.8	-32.6	-23.1
¹⁴ a (%)	20.34	9.7	12.4	104.1	73.4	64.5
¹⁴ a _{corr} (%)	17.1	7.1	10.1	104.1	66.2	56.2

*Result of blank runs: 3.1 and 3.4 µg C per combustion

For both materials, the concentration is a factor 3 to 4 lower than determined by CPAA. One of the main explanations for this observation is incomplete cryogenic trapping of CO₂ during combustion, and as already mentioned, inefficient O₂ penetration in the materials resulting in incomplete oxidation. Our C concentration results in CuO are in good agreement with the already published values using similar detection circumstances. For ¹⁴C contamination assessment, we believe that C concen-

trations obtained with the combustion method reflect the best real sample preparation conditions for ^{14}C dating. This is in contrast to the results for Fe, where all the carbon present is potentially dangerous for contamination during sputtering in the AMS ion source. These results allow, in combination with the ^{14}C results, a better assessment of the contamination potential of the reagents used in AMS sample preparation.

The results of the ^{14}C analyses are also reported in Table 3. Measured values and blank-corrected values are tabulated. The blank correction was applied assuming contamination was of contemporary origin (*i.e.*, 100 pMC). We believe this assumption is reasonable because a significant part of the blank consists of C species originating from N_2 and O_2 . In addition, stable carbon isotope results (measured with AMS) are given as the per mil deviation from the international PDB limestone standard (IAEA 1993). The stable carbon isotope and ^{14}C results for Fe confirm the general belief that contamination is mainly of fossil origin, introduced in the Fe-ore reduction process.

Vogel, Nelson and Southon (1987) determined ^{14}C in Fe with a direct approach and obtained lower contamination levels, 1.5 pMC, also indicating fossil origin. Direct measurement of our Fe-targets yielded low C^- currents in the machine. An average ^{12}C current of only 150 pA for 99.5% Fe and 80 pA for 99.998% Fe was observed. Over the whole time frame of these measurements, only 10–40 ^{14}C counts were registered for each target, which was too low for an accurate and reliable ^{14}C determination in the materials. However, the C current reflects the purity of those materials. Fossil origin of C contamination in Fe is recently confirmed by the low stable carbon isotope results. Verkouteren, Klinedinst and Currie (1997) report the same stable isotope values for contaminating C in Fe wool. However, a significant contemporary contribution must have been added. In the ironmaking process, different C-containing materials are used: reducing agents (*e.g.*, coke, CO, CH_4 , hydrocarbons), limestone and hot air. This makes interpretation of the $\delta^{13}\text{C}$ values complicated. Taking into account the possibility of a small isotope fractionation (of some ‰) effect of the graphitization and the relative contributions of the different C sources, stable carbon isotope results confirm the measured contribution of a modern compound.

In the case of CuO, the measured ^{14}C level of the C contamination is unexpectedly high and at first sight quite difficult to explain. Further, there is a significant difference in ^{14}C content between fabrication batches. Sample GrA-3565 was prepared from a different batch of CuO than samples GrA-4393 and GrA-4394. The suppliers provided us with production details indicating different production times of the two CuO lots. The observed difference jeopardizes general conclusions regarding the contamination potential of CuO. Nevertheless, both results indicate a higher modern contribution than in Fe. This is presumably due to a slightly different production and purification process compared to Fe. After melting of copper sulfide ores, the resultant products are mixed with limestone in a converter and hot air is forced under high pressure through the mass. Thereafter, pure copper is produced through electrolysis. Fine copper wires are reoxidized at high temperatures in ambient air. It seems very reasonable that indeed a modern C-contamination component in CuO originates from the different steps in the production process.

Implications For Radiocarbon Dating

The significance of our results as shown in Table 4 will be discussed here. Combined absolute and estimated contamination figures are summarized and translated into the corresponding dating limits. All results are calculated supposing practical laboratory conditions, *i.e.*, 500 mg CuO and 2 mg Fe-catalyst per mg C in the sample. Note that those conditions determine the relative importance of the contaminants. In general, Fe contributes only *ca.* 1% to the total contamination. The results of this independent study are in good agreement with combustion blanks reported previously. Different

groups reported absolute blank values in the 0.5–4 μg modern carbon range (Gurfinkel 1987; Klinedinst *et al.* 1994; Verkouteren *et al.* 1987; Vogel, Nelson and Southon 1987; Verkouteren, Klinedinst and Currie 1997; Donahue, Jull and Toolin 1990).

TABLE 4. Summary of Absolute and Estimated Contamination Potential of C Traces in CuO and Fe (in μg) and Their Implications for the ¹⁴C Dating Limit

¹⁴ C in CuO	Contamination	
	Absolute	Estimate
50 pMC	4.47	1.63
	43,500	51,600
100 pMC	8.92	3.24
	38,000	46,000

The C concentration results obtained with CPAA combined with the ¹⁴C values for the isolated C were used to determine the absolute contamination contributions due to CuO and Fe. C concentration results from the combustion experiments combined with ¹⁴C values yield the more realistic contamination estimate. This was done for the minimum and maximum estimate of ¹⁴C level in CuO, 50 and 100 pMC. Summarizing, an observed dating limit >46 ka is caused mainly by ¹⁴C contamination of CuO. For a lower ¹⁴C content of the contaminating C in CuO, this value can increase to 51.6 ka. Those results obtained with our independent approach indicate a larger contribution of CuO to the total background than previously assumed. Certainly, other less-characterized C sources contribute to the total background. If this were not the case, more laboratories should, with a minimum of effort, routinely obtain dating limits *ca.* 50 ka.

According to these blank values, any dating limit <38 ka has surely other background contributions that are worse than the mentioned materials. And in the range 38–46 ka, it is very likely that other, equally important, contaminants contribute to the total background. Dating limits better than 51.6 ka are probably entirely determined by impurities in the CuO. This is in disagreement with the studies by Beukens (1993) and Gulliksen and Thomson (1992), who reported negligible combustion backgrounds.

CONCLUSION

Future developments in ¹⁴C dating of very old samples with AMS requires the identification of all important individual contamination sources during sample preparation. The independent method for isolation of C traces in Fe and CuO is a valuable tool to assess the importance of those materials in relation to background research. Our study confirmed the relative importance of CuO (combustion) compared to Fe with respect to contamination potential. Moreover, contamination in CuO seems to vary between different batches, urging for regular quality control. The results also strengthen the idea that observed dating limits are quite fundamental and new target preparation approaches have to be accomplished to explore new ¹⁴C-dating horizons.

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