NEW ^{14}C REFERENCE MATERIALS WITH ACTIVITIES OF 15 AND 50 pMC

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ABSTRACT. Two new ^{14}C reference materials have been developed for international use, filling a gap in the present C1–C6 series available from the IAEA. By mixing a modern and a synthetic substance, 150 kg of C7 (*ca.* 50 pMC activity) and C8 (*ca.* 15 pMC activity), respectively, were obtained.

INTRODUCTION

As $^{14}C/C$ measurements are precise but not accurate, they are always measured and reported relative to a standard. The primary standards are HOxI and HOxII (formerly known as Oxalic Acid I and II) with activities of 103.98 and 134.06 pMC, respectively (Stuiver and Polach 1977; Stuiver 1983; Long 1995). Recently, an IAEA working group introduced six additional ^{14}C reference materials with values for $\delta^{13}C$ and ^{14}C as shown in Table 1 (Rozanski *et al.* 1992).

TABLE 1. Consensus Values of IAEA Reference Materials C1–C6

IAEA code	Material	^{14}C (pMC)	$\delta^{13}C$ (‰)
C-1	Marble	0.0	2.42 ± 0.33
C-2	Chalk	41.14 ± 0.03	−8.25 ± 0.31
C-3	Paper	129.41 ± 0.06	−24.91 ± 0.49
C-4	Wood	0.20–0.44	−23.96 ± 0.62
C-5	Wood	23.05 ± 0.02	−25.49 ± 0.72
C-6	Sucrose	150.61 ± 0.11	−10.80 ± 0.47

A reference material is most useful when it has a precisely known value, is completely homogeneous and is as similar as possible to a sample being measured. For this purpose, two new materials were developed with predetermined ^{14}C values that would complement the C1–C6 materials listed in Table 1.

By mixing two chemically identical substances, a modern one (*i.e.* natural in origin) and a fossil one (*i.e.,* synthesized from oil or natural gas), in principle materials can be fabricated in bulk quantities with any desired apparent age. It was decided to complement the list of C1–C6 materials by fabricating new substances, tuning the ^{14}C activities at 15 and 50 pMC.

METHODS

In order to make new reference materials with a desired ^{14}C activity, materials from both a natural and a synthetic source have to be mixed in a known ratio. The most thorough method of mixing two

solids is recrystallization. In order to undergo this process, the material has to meet a number of requirements:

1. It must be soluble and stable in water;
2. It must be available at a reasonable price from both a synthetic and a natural source;
3. It must be a solid with a low vapor pressure under room conditions;
4. It should not cause problems in a laboratory combustion system.

Ironically, the only compound that met these four criteria was oxalic acid, which has two industrial sources (Kroschwitz 1996).

The first production method is oxidation of carbohydrates such as sugar or sawdust with nitric acid:

$$C_2H_{12}O_6 + 4\,HNO_3 \xrightarrow{V_2O_5,\ 70\ ^\circ C} 3\,C_2O_4H_2 + 2N_2 + 5H_2O\ .$$

The alternative is a route from CO and water:

$$NaOH + CO \xrightarrow{\text{pressure}} HCOONa$$

$$2\,HCOONa \xrightarrow{\text{heat}} (COONa)_2 + H_2$$

$$(COONa)_2 + Ca(OH)_2 \longrightarrow (COO)_2Ca + 2NaOH$$

$$(COO)_2Ca + H_2SO_4 \longrightarrow (COOH)_2 + CaSO_4\ .$$

Both production methods are used in industry. The carbohydrate route is not used in Europe, however, due to environmental regulations (Hoechst, Inc., personal communication 1996). Therefore, natural oxalic acid was purchased in India from the Vaishali firm, Aurangabad. Synthetic oxalic acid was obtained from Rhône-Poulenc. The two were mixed by recrystallization at Chemie Uettikon GmbH, Lahr, Germany, a company specializing in the production of fine chemicals for pharmaceutical use.

A 150-kg mixture of the two oxalic acids was placed in a stainless steel container, and dissolved in 140 L deionized water. The solution was checked for clearness to ensure that no solid starting material was left. The solution was stirred vigorously for 1 h to ensure complete homogeneity. The solution was then cooled while being continuously stirred to a temperature of 4°C, during which the oxalic acid crystallized. The product was washed with deionized water and dried to the dihydrate. This was done for two batches with the desired activities of 15 and 50 pMC.

Results

The Groningen laboratory first measured these newly fabricated materials for ^{13}C and ^{14}C, in order to check homogeneity. Since oxalic acid is the primary standard, we avoided that name for the new reference materials and called them simply GS-36 (50 pMC) and GS-37 (15 pMC). Next, these materials were sent to several laboratories for measurement. Table 2 shows the values obtained for the two materials for the laboratories that submitted results.

Based on these results, the following values were assigned to the new reference materials:

GS 36 (IAEA-C7)	$\delta^{13}C = -14.48$ (‰)	$^{14}C = 49.53 \pm 0.12$ pMC
GS 37 (IAEA-C8)	$\delta^{13}C = -18.31$ (‰)	$^{14}C = 15.03 \pm 0.17$ pMC

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TABLE 2. Results of Measurements for the New IAEA Reference Materials C7 and C8

			GS36 (IAEAC7)		GS37 (IAEAC8)	
Code	Laboratory	Technique*	$\delta^{13}C$ (‰)	^{14}C (pMC)	$\delta^{13}C$ (‰)	^{14}C (pMC)
GrN	Groningen	PGC	−14.67	49.53	−18.00	14.73
GrA	Groningen	AMS	−14.49	49.53	−18.42	15.15
A	Tucson	LSC	−14.4	49.6	−18.7	15.23
Hd	Heidelberg	PGC	−14.41	49.6	−18.15	15.1
Q	Seattle	PGC	−14.63	49.35	−18.30	14.99
UB	Belfast	LSC	−14.36	49.74	−18.32	15.14
Wk	Waikato	LSC	−14.4	49.4	−18.2	14.9

*PGC = Proportional Gas Counting; LSC = Liquid Scintillation Spectrometry; AMS = Accelerator Mass Spectrometry

In addition, the measured results show that the new materials are also homogeneous.

In the near future the new reference materials GS-36 and GS-37 will be available *via* the IAEA in Vienna as C7 and C8, respectively.

CONCLUSION

By mixing a modern natural and a synthetic (fossil) oxalic acid, we produced new ^{14}C reference materials. These reference materials (C7 and C8) complement the present IAEA series. Their ^{14}C activities and $\delta^{13}C$ values were measured by several laboratories. Based on these measurements, we determined the values as follows: for C7, $\delta^{13}C = -14.48$‰ and $^{14}C = 49.53 \pm 0.12$ pMC; for C8, $\delta^{13}C = -18.31$‰ and $^{14}C = 15.03 \pm 0.17$ pMC.

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