

Supplemental Information for NBS/NIST SRM 4990x, Oxalic Acid, International Standard Reference Material for Contemporary Carbon-14

Introduction

From years of frequently asked questions about the production, characterization, and use of SRM 4990, NIST has collected and captured the history and knowledge to serve as a technical resource for users. This information is available below and can also be retrieved on the NIST Store at https://shop.nist.gov/ccrz_ProductDetails?sku=4990c&cclcl=en_US.

Clarifications

1. SRM 4990x is distributed by NIST as a service to the radiocarbon community. NIST does not certify this SRM in any way. Property values are those adopted by the International Radiocarbon Conference (IRC).
2. The properties of SRM 4990c, the current issue of SRM 4990x, were adopted by the 11th IRC in 1982 based upon measurements conducted in the late 1970s and early 1980s. The results of those measurements were published in *Radiocarbon* [1].
3. The terms SRM 4990, SRM 4990a, SRM 4990b, NBS Oxalic Acid I, NBS OxI, and OX have all been used to refer to the first batch of Oxalic Acid from 1957.
4. The terms NBS RM 49, SRM 4990c, NBS Oxalic Acid II, NBS OxII, and NOX have all been used to refer to the second batch of Oxalic Acid from 1977.

History of the Preparation and Distribution of NBS/NIST SRM 4990x

After agreeing that it would be beneficial to have an International Standard Reference Material for Radiocarbon Dating, the IRC arranged with Pfizer Chemical Company to produce 1000 pounds of oxalic acid by fermentation of beet sugar from the harvests of 1957. The U.S. National Bureau of Standards (NBS, now the National Institute of Standards and Technology, NIST) agreed to store, protect, and distribute the material. But NBS/NIST has never certified the material - that was done by the IRC. The first batch of oxalic acid was distributed as SRM 4990 (5 pounds or 2268 grams per unit), 4990a (1 pound or 454 grams per unit), and 4990b (0.5 pounds or 227 grams per unit).

The C-14 massic activity adopted by the IRC for this first batch is:

$$\text{SRMs 4990, 4990a, 4990b} = 14.27 \text{ DPM(C-14)} / \text{g(C)} \text{ at a reference time of 1950.}$$

By the early 1970s, the first batch of oxalic acid was almost depleted. Arrangements were made with Pfizer Chemical Company to produce another 1000 pounds of oxalic acid by fermentation of beet sugar from the harvests of 1977. This material has been rebottled as needed to produce SRM 4990c, which is distributed in 0.5 pound units. SRM 4990c was originally packaged as one 0.5 pound jar, but since 1994 it has been packaged as eight small jars, each jar containing one ounce or 28.5 grams. The units of SRM 4990c currently on sale were bottled in 2002 and have been sealed and stored in a controlled-temperature area ever since. The C-14 massic activity of this second batch (SRM 4990c) is about 30% higher than that of the first batch, mostly due to the atomic bomb tests.

The C-14 massic activity adopted by the IRC for this second batch is:

$$\text{SRM 4990c} = 18.36 \text{ DPM(C-14)} / \text{g(C)} \text{ at a reference time of 1980.}$$

Note that these massic activities are per gram of Carbon, not per gram of Oxalic Acid, and Note that no uncertainties were adopted for these C-14 massic activity values.

Supplemental Information for NBS/NIST SRM 4990x, Oxalic Acid, International Standard Reference Material for Contemporary Carbon-14

Uncertainties

Measurements of the C-14 massic activity ratio of the two batches were also made. Depending upon how the averages are computed, the ratio of the C-14 massic activities varies by up to 0.5 %. See the SRM 4990c Certificate and reference 1.

The C-14 massic activity ratio adopted by the 11th IRC in 1982 is:

$$\frac{\text{DPM(C-14)/g(C) SRM 4990c}}{\text{DPM(C-14)/g(C) SRM 4990}} = 1.2933 \pm 0.0004 (0.03 \%)$$

This is the weighted mean of the individual weighted-mean results and one standard deviation of the weighted mean. A later reevaluation, using a different weighting method, gives the ratio:

$$\frac{\text{DPM(C-14)/g(C) SRM 4990c}}{\text{DPM(C-14)/g(C) SRM 4990}} = 1.2931 \pm 0.0005 (0.04 \%)$$

This is a difference of 0.0002 (0.02 %). The same reevaluation gives the standard deviation of the mean between laboratories as 0.0008 (0.06 %).

For comparison, we compute the ratio of the 1980 and 1950 adopted C-14 massic activities, corrected to the same reference time using the current C-14 half-life of 5730 years. That calculated ratio is:

$$\frac{\text{DPM(C-14)/g(C) SRM 4990c}}{\text{DPM(C-14)/g(C) SRM 4990}} = 1.2913$$

(Using the old Libby half-life of 5568 years gives a ratio of 1.2914, an insignificant difference.)

This is a difference of 0.002 (0.15 %) from the C-14 massic activity ratio adopted by the IRC in 1982. The adopted C-14 massic activities and the adopted C-14 massic activity ratio are consistent to within 0.1 % to 0.2 %. Modern measurements of the C-14 massic activity, whether done by accelerator mass spectrometry (AMS), gas counting (GC), or liquid-scintillation counting (LSC), have a precision of 0.1 % to 0.2 %. Hence, the C-14 massic activity of a sample relative to the C-14 massic activity of the reference material can be determined with low uncertainty.

Accuracy

However, if the relative C-14 massic activity of a sample is to be used to estimate the value of some other property of the sample, such as the age (radiocarbon dating) or the fraction of contemporary carbon (ASTM D6866), large uncertainties in the value of that property may be introduced by the uncertainty in the necessary assumptions. For example, the calculation of the Radiocarbon Age of a sample depends upon assumptions about

- (a) the C-14 massic activity in the environment surrounding the sample at the time of formation,
- (b) the C-14/C-12 isotope fractionation in the formation of the sample,
- (c) the gain or loss of C-14 in the time between sample formation and sample measurement, and
- (d) corrections to the measured C-14 massic activity value, including uncertainties in the value of the reference material, which is usually SRM 4990x.

Supplemental Information for NBS/NIST SRM 4990x, Oxalic Acid, International Standard Reference Material for Contemporary Carbon-14

Improvements in sample measurement techniques (especially AMS) have made the uncertainties in (d) usually relatively negligible. Improvements in sample preparation have greatly reduced the uncertainties in (c). And the uncertainties in (b) are usually relatively small (with some exceptions).

What remains when comparing carefully measured radiocarbon ages with reliable calendar ages is a consistent and significant difference, with the radiocarbon ages being smaller. An International Calibration Committee was set up long ago to document these differences and to periodically publish “Radiocarbon Calibration Curves” for various environments, such as Northern Hemisphere Atmosphere, Southern Hemisphere Atmosphere, and Mixed Ocean Layer. Since 2004 this work has been overseen by the International Calibration Working Group and periodically the various Radiocarbon Calibration Curves are published in *Radiocarbon*. The latest such calibration curve for Northern Hemisphere Atmosphere, “IntCal20”, is discussed by Staff and Liu [2]. The ratio (radiocarbon age) / (calendar age) is approximately 0.9 for calendar ages from 50,000 years to 5,000 years. For calendar ages below 5000 years, the ratio increases to 1.0 at the present time. The ancient C-14 massic activity appears to have been higher than the contemporary C-14 massic activity, perhaps due to changes in the Earth’s magnetic field.

While there are significant differences between radiocarbon ages and calendar ages, the use of a stable, well-characterized Standard Reference Material for Contemporary Carbon-14 (SRM 4990x) reduces the uncertainty in the time difference between the radiocarbon ages of different samples. In turn, this reduces the uncertainty in the difference between the calculated calendar ages for those samples. This can be important in determining the sequence and/or time difference of historical events.

For questions or comments, contact:

Dr. Larry Lucas, Research Chemist
Radiation Physics Division
National Institute of Standards & Technology (NIST)
Gaithersburg, MD 20899-8462 USA
larry.lucas@nist.gov

References

- [1] *Radiocarbon* **25**, No.2 (1983).
- [2] *Science China Earth Sciences*, Vol. 64 No. 3: 507–510 (2021); available at <https://doi.org/10.1007/s11430-020-9722-x>