

RADIOCARBON LABORATORY AT THE NATIONAL AUTONOMOUS UNIVERSITY OF MEXICO: FIRST SET OF SAMPLES AND NEW ^{14}C INTERNAL REFERENCE MATERIAL

Laura E Beramendi-Orosco¹ • Galia Gonzalez-Hernandez • Jaime Urrutia-Fucugauchi • Ofelia Morton-Bermea

Laboratorio Universitario de Radiocarbono, Instituto de Geofísica, Universidad Nacional Autónoma de México, Ciudad Universitaria, México City 04510, México.

ABSTRACT. This contribution reports the first set of samples and the creation of an internal reference material at the recently opened Radiocarbon Laboratory at the National Autonomous University of Mexico (UNAM). Samples for the initial measurements were selected from archaeological and dating projects on Teotihuacán, one of the largest and best-studied Mesoamerican urban and ceremonial centers. The ^{14}C dates were compared to results obtained by 2 other laboratories in order to assess the results obtained at UNAM and validate the adopted methodology. As part of the quality assurance protocol, an internal reference material was created that consists of charred wood from the Teotihuacán site with a ^{14}C activity in the value range expected for samples from Mesoamerican archaeological sites. Results from 7 analyses have a mean of 1750 ± 16 BP (80.43 ± 0.16 pMC).

INTRODUCTION

The Radiocarbon Laboratory at the National Autonomous University of Mexico (UNAM) was created in February 2004. This lab incorporated some of the infrastructure that was part of the dating laboratory at the Institute of Anthropological Research at the same university, which closed in January 2003. The interest and demand for radiocarbon dating have been high since the first dates were reported in the early pioneering studies of Libby and coworkers on the Cuicuilco archaeological site in the Basin of Mexico (Arnold and Libby 1951; Libby 1955). The importance and need for a ^{14}C dating facility in Mexico dedicated to research projects on archaeology, anthropology, and earth sciences have been emphasized a number of times in diverse contexts, but only recently was a university project implemented. Taking into consideration the potential usefulness and role of the newly created laboratory, special attention was given to infrastructure, methodology, accuracy, precision of results, interlaboratory calibration exercises, and the implementation of internal reference material.

The counting system consists of a commercial benzene synthesizer (TASK, Inc.) and a Quantulus 1220TM ultra-low level liquid scintillation spectrometer. During the first year, our activities were focused on the reactivation of the laboratory and its infrastructure, specifically, to the benzene rig dating from the late 1970s, which was unused for some years. The Quantulus 1220, bought in February 2002, was already calibrated for determining ^{14}C before the dating laboratory at the Institute of Anthropological Research closed. The performance of the spectrometer was evaluated, confirming that the stability, background, and counting efficiency were in the manufacturer's recommended value range for the Quantulus 1220.

In order to evaluate the performance of a ^{14}C dating laboratory and detect any analytical problems (sources and magnitude), it is important to perform interlaboratory comparisons as well as regular analysis of standard reference materials (Long 1990). International interlaboratory comparisons are long processes involving several laboratories and different sets of samples, so for a new laboratory it is useful to make intercomparisons with other, well-established ^{14}C laboratories in order to assess the results. As part of the quality assurance protocol, it is also important to analyze reference mate-

¹Corresponding author. Email: laura@geofisica.unam.mx.

rials with certain periodicity (Long 1990; Le Clercq and van der Plicht 1998). There are 8 reference materials available through the IAEA (Le Clercq and van der Plicht 1998); however, the amount available is limited, making it necessary for laboratories to produce their own reference samples that are as similar as possible to the samples routinely analyzed.

We report the first set of dates from 7 samples of known archaeological contexts, checked against duplicates analyzed in 2 other laboratories. We also report on the creation of an internal reference material that will be used as part of the quality assurance program at the UNAM laboratory.

METHODS

Samples

The samples for the initial measurements were selected from archaeological projects from one of the largest and most intensely studied archaeological sites in Mesoamerica. Five samples of charred wood were provided from the Teotihuacán Archaeological Project of Dr Linda Manzanilla of the Institute of Anthropological Research, UNAM. Samples were collected in 2003 and 2004 during the excavation of a palace at the Xalla habitational complex, Teotihuacán. Another pair of charred wood samples was obtained from Dr Emily McClung de Tapia of the Institute of Anthropological Research, UNAM. These samples were collected in 1978 from a cave underneath the Pyramid of the Sun at Teotihuacán. A summary of sample provenance and characteristics is given in Table 1.

Table 1 Summary of samples included in the calibration process.

| Sample code | Site of collection and description | Date of collection | Supplier |
|-------------|---|--------------------|--|
| 64547 | Xalla Teotihuacán, Mexico. | 11/2003 | Linda Manzanilla (Inst. of Anthropological Research, UNAM) |
| 64908 | Charred wood from the fall of | 11/2003 | |
| 66799 | ceilings during the final fire of | 10/2004 | |
| 67418 | Teotihuacán. | 10/2004 | |
| 69668 | | 11/2004 | |
| TE28C41-5FW | Pyramid of the Sun, Teotihuacán, | 08/1978 | Emily McClung de Tapia (Inst. of Anthropological Research, UNAM) |
| TE28C29-3AE | Mexico. Charred wood from an offering or a fire. | 08/1978 | |

Samples were dried at 50 °C and divided into 2 fractions; one fraction was kept at the UNAM laboratory and the other sent either to the Institut für Bodenkunde, University of Hamburg, Germany, or, by the sample submitter, to Beta Analytic, Florida, USA.

Sample Pretreatment

Samples were dried at 50 °C, ground, and sieved before inspection under a microscope in order to remove rootlets and other non-sample material. Samples were then washed with distilled water at 40 °C for 24 hr or until the charred material settled, followed by acid/alkali/acid (AAA) pretreatment. The AAA method consisted of treating samples with 1M hydrochloric acid (HCl) at 50 °C for 24 hr, 0.1M sodium hydroxide (NaOH) at 50 °C for 24 hr, and 1M HCl at 50 °C for 24 hr. Samples were neutralized by washing with distilled water after each acid and alkali wash. Finally, samples were homogenized, dried at 50 °C, and stored in a desiccator until benzene synthesis.

Benzene Synthesis

Benzene synthesis was performed in the TASK Benzene Synthesizer via 4 major steps: 1) oxidation, 2) lithium carbide production, 3) acetylene production, and 4) trimerization of acetylene. The reaction conditions were established from the literature (Barker 1953; Tamers 1975; Noakes 1979; Becker-Heidmann et al. 1995), from communication with other laboratories (Randy Culp, CAIS, Georgia, USA; Peter Becker-Heidmann, University of Hamburg, Germany), and from our own experience in order to obtain yields >90%.

Briefly, 5 g of sample was combusted in an oxygen-rich atmosphere after the cryogenic removal of water with a trap of dry ice and isopropyl alcohol. The CO₂ obtained was trapped cryogenically with liquid nitrogen and sublimed to the storage tanks. The purified CO₂ was then pulsed into the reaction chamber to react with an excess of melted lithium metal at 800 °C, yielding lithium carbide (Li₂C₂). After complete reaction, the Li₂C₂ was heated and evacuated for 30 min in order to remove any radon present in the system. Once the reaction chamber was at room temperature, Li₂C₂ reacted with distilled water to produce acetylene (C₂H₂). The acetylene was purified when passed through a trap cooled with dry ice and isopropyl alcohol and through a tube containing ascarite and phosphorus pentoxide, after which C₂H₂ was frozen in a trap with liquid nitrogen. Trimerization was performed using the chromium-activated silica-alumina PKN/D1 catalyst, previously oxidized in a muffle furnace at 450 °C for more than 24 hr and activated in vacuum at 300 °C for 24 hr. The C₂H₂ was slowly passed (while still frozen, with the aid of a trap made of dry ice and isopropyl alcohol) into the catalyst column kept at ~200 °C. Finally, the benzene was removed from the catalyst by applying vacuum, heating to 150 °C, and freezing in a trap cooled by dry ice and isopropyl alcohol.

Benzene synthesis from the oxalic acid II standard reference material (SRM 4990C) was obtained at the same reaction conditions, changing only the oxidation step. Instead of combusting the sample, 18.5 g of oxalic acid was oxidized with 200 mL of 6% potassium permanganate acid solution. Quantities were adjusted to obtain 10 L of CO₂ at room temperature and at Mexico City's atmospheric pressure (585 mmHg). The benzene volume analyzed was 3 mL plus 0.5 mL of scintillation cocktail (0.5 g of PPO + 0.02 g of POPOP dissolved in 100 g of dead spectrophotometric-grade benzene).

Analysis of Benzene Purity

After the rehabilitation of the benzene synthesizer and determination of the reaction conditions, the purity of the benzene obtained was evaluated. Benzene samples synthesized from oxalic acid SRM4990C and from the charred wood sample 69668 were analyzed by gas chromatography-mass spectrometry (GC/MS) using a gas chromatograph (model 6890, Agilent Technologies) coupled to a mass spectrometer (model 5973N, Agilent Technologies) with an automated injector and a quadrupole mass detector. The GC was fitted with a capillary column (Zebron, 28 m × 0.25 mm ID, coated with a 0.25-μm film of 5% diphenyl/95% polydimethylsiloxane). Samples (0.2 μL) were injected at 250 °C in split mode in a 1:300 proportion, with 1.2 mL/min of helium as carrier gas and at temperatures from 40 °C (held for 5 min) up to 190 °C by increasing the temperature 10 °C per min. The transfer line between the GC and the MS was at 280 °C. The mass spectrometer was operated in electron impact mode with a mass range of m/z 35–200 (2.26 scans per second), with a source and analyzer temperature of 250 and 130 °C, respectively.

Analysis by Liquid Scintillation Spectrometry

Samples were analyzed using 20-mL and 7-mL low-⁴⁰K glass scintillation vials. First, the geometry of the vials was chosen because the Quantulus 1220 has holders for 20-mL vials, but since the vol-

ume of benzene analyzed is 3 mL, the 7-mL vials were considered more appropriate (Pawlyta et al. 1998). Analysis was performed in a Quantulus 1220 ultra-low level liquid scintillation spectrometer. Each sample was analyzed for 2500 min, in 50 cycles of 50 min each, alternating sample vials with 4990C standard and background vials. The counting window was set to optimize the figure of merit (FM) with a ^{14}C counting efficiency of ~60%.

Analysis of $^{13}\text{C}/^{12}\text{C}$ Ratio

Stable ^{13}C isotope analyses were performed by the Stable Isotopes Laboratory at the Institute of Geology, UNAM. Results are reported relative to the Vienna Pee-Dee Belemnite (VPDB) standard with a precision of $\pm 0.2\%$.

RESULTS AND DISCUSSION

Benzene Purity

The partial chromatograms of the total ion current (TIC) for benzene synthesized from SRM 4990C and from the charred wood sample 69668 showed a major peak, comprising more than 95% of total area, which corresponds to benzene, and other smaller peaks corresponding to other aromatic hydrocarbons. Product identifications and concentrations are given in Table 2.

Table 2 Impurities in benzene samples synthesized from SRM 4990-C and charred wood sample 69668.

| Sample | Peak | Identification | Concentration (%) |
|-----------|------|---------------------|-------------------|
| SRM 4990C | 1 | Benzene | 99.05 |
| | 2 | Toluene | 0.95 |
| 69668 | 1 | Benzene | 96.30 |
| | 2 | Toluene | 3.53 |
| | 3 | Ethylbenzene | 0.11 |
| | 4 | Methylethylbenzene | 0.03 |
| | 5 | Methylpropylbenzene | 0.03 |

Both benzene samples have as impurities aromatic hydrocarbons ranging from toluene to 1-methylpropylbenzene, but the impurities differ in concentration and purity. The benzene sample obtained from SRM 4990C was purer than the benzene sample obtained from the charred wood sample 69668. The reason for this difference is unknown, although it may be due to the different nature of the original sample materials (Switsur and Waterhouse 1989). However, for both samples the benzene purity is >95%, and these compounds reportedly do not cause quench effects in low concentrations (Becker-Heidmann et al. 1995). These results indicate that the benzene synthesizer is operating correctly and with the proper reaction conditions, resulting in high yields and benzene purity.

Comparison with Other Laboratories

Two samples (64547 and 64908) were sent to the Institut für Bodenkunde, University of Hamburg, Germany. A comparison of the results is presented in Table 3. Results are in very good agreement: sample 64908 differs by only 60 ^{14}C yr, while sample 64547 differs by 120 ^{14}C yr. In both cases, the difference is less than 2 σ .

Table 3 Results of comparison between UNAM and University of Hamburg.

| Sample code | UNAM | | | Hamburg | | |
|-------------|------------|---------------------------|--|----------|---------------------------|--|
| | Lab code | $\delta^{13}\text{C}$ (‰) | Conventional age BP ($\pm 1 \sigma$) | Lab code | $\delta^{13}\text{C}$ (‰) | Conventional age BP ($\pm 1 \sigma$) |
| 64908 | UNAM-04-01 | -24.13 | 1920 \pm 60 | HAM-3807 | -23.8 | 1980 \pm 60 |
| 64547 | UNAM-04-04 | n.a. ^a | 2160 \pm 50 | HAM-3804 | -25.1 | 2040 \pm 45 |

^aNot analyzed.

In a second stage of calibration, 5 samples were sent to Beta Analytic (see Table 4). For 3 samples (67418, 69668, and TE28C41-5FW), the results are in very good agreement, differing by <40 ¹⁴C yr. For samples 66799 and TE28C29-3AE, the difference is greater, but the results are still in good agreement, differing by 130 and 200 ¹⁴C yr, respectively.

Table 4 Results of comparison between UNAM and Beta Analytic.

| Sample code | UNAM | | | Beta Analytic | | |
|-------------|------------------|---------------------------|---------------------------------------|------------------|---------------------------|---------------------------------------|
| | Lab code (UNAM-) | $\delta^{13}\text{C}$ (‰) | Conventional age (BP $\pm 1 \sigma$) | Lab code (Beta-) | $\delta^{13}\text{C}$ (‰) | Conventional age (BP $\pm 1 \sigma$) |
| 66799 | 05-18 | -23.87 | 1640 \pm 60 | 204319 | -23.8 | 1770 \pm 40 |
| 67418 | 05-16 | -25.48 | 1720 \pm 50 | 204317 | -24.5 | 1680 \pm 60 |
| 69668 | 05-19 | -22.61 | 1720 \pm 60 | 204318 | -22.1 | 1720 \pm 40 |
| TE28C41-5FW | 05-32 | n.a. ^a | 1850 \pm 60 | 208985 | -24.2 | 1840 \pm 50 |
| TE28C29-3AE | 05-33 | n.a. ^a | 1720 \pm 70 | 208984 | -24.1 | 1920 \pm 60 |

^aNot analyzed.

Internal Reference Material

A high percentage of the samples that will be analyzed in the laboratory are charred wood from archaeological excavations in Mexico with ¹⁴C activities similar to this first set of samples. This makes sample 69668 a possible internal reference material due to its characteristics and abundance (~500 g).

Results for the 8 different analyses are shown in Table 5 and Figure 1. Separate benzene syntheses were performed for each determination, and an aliquot of the sample, without pretreatment, was analyzed by Beta Analytic as part of the intercomparison. The results are consistent with a mean of 1750 \pm 16 BP (80.43 \pm 0.16 pMC), with only 2 samples falling outside the $\pm 2\text{-}\sigma$ error of the mean band: sample UNAM-06-05 by 56 ¹⁴C yr (0.56 pMC) and sample UNAM-05-20 by 28 ¹⁴C yr (0.28 pMC).

CONCLUSIONS

From the benzene purity analysis, it can be concluded that the benzene synthesizer has been rehabilitated and is operating properly, producing benzene in high yields and with purity >95%. The 2 laboratory intercomparisons helped to assess the performance of the counting system at the new UNAM Radiocarbon Laboratory. The results obtained are in very good agreement with results from 2 other laboratories, validating the pretreatment, synthesis, and counting methodology adopted.

Table 5 Results of measurements for the internal reference material. Result obtained by Beta Analytic for an aliquot of the same sample is shown for comparison.

| Lab code | Conventional age BP ($\pm 1 \sigma$) | pMC % ($\pm 1 \sigma$) |
|-------------------------|---|------------------------------------|
| UNAM-05-05 | 1760 \pm 60 | 80.32 \pm 0.6 |
| UNAM-05-19 | 1720 \pm 60 | 80.73 \pm 0.6 |
| UNAM-05-20 | 1690 \pm 60 | 81.03 \pm 0.6 |
| UNAM-05-24 | 1730 \pm 50 | 80.62 \pm 0.5 |
| UNAM-06-05 | 1840 \pm 50 | 79.55 \pm 0.5 |
| UNAM-06-06 | 1770 \pm 50 | 80.25 \pm 0.5 |
| UNAM-06-07 | 1770 \pm 50 | 80.20 \pm 0.5 |
| Beta-204318 | 1720 \pm 40 | 80.73 \pm 0.4 |
| <i>Mean^a</i> | <i>1750 \pm 16</i> | <i>80.43 \pm 0.16</i> |

^aStandard error of the mean calculated as $se = sd / \sqrt{n}$; $n = 8$.

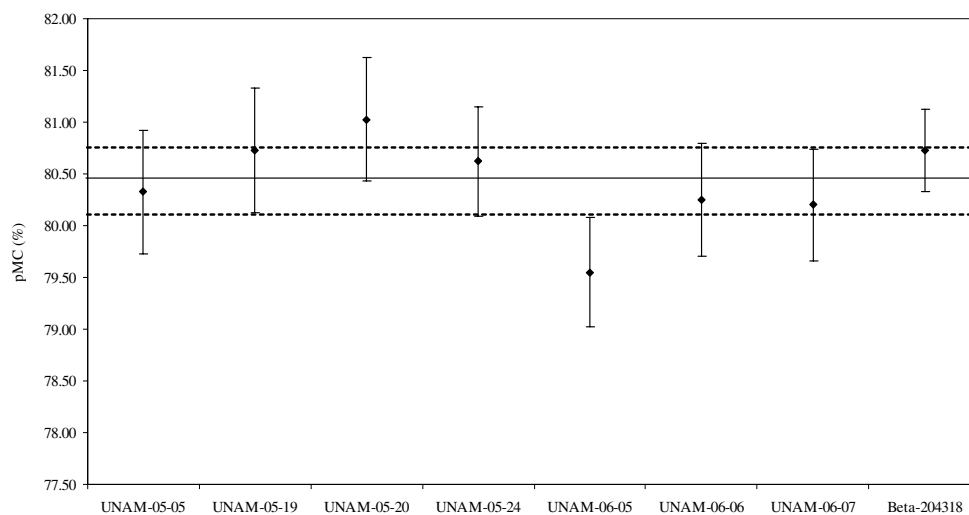


Figure 1 pMC results for the internal reference material obtained for 8 different analyses, including the result obtained by Beta Analytic. Solid line corresponds to the mean and dotted lines correspond to $\pm 2 \sigma$ of the mean.

Sample 69668 can work as an internal reference material, since the results obtained from 8 analyses are consistent, indicating that the sample is homogeneous. This new reference material, with a ^{14}C activity in the value range expected for samples from archaeological sites in Mexico, will help the lab to continuously assess the counting system and methodology and also aid in the early detection of analytical problems.

From the results presented, it can be concluded that the Radiocarbon Laboratory at the National Autonomous University of Mexico is now in operation, with analytical capabilities for generating reliable results. We would thereafter like to present this new lab with the laboratory code UNAM. To further assess the performance of the UNAM Radiocarbon Laboratory, we are currently participating in the Fifth International Radiocarbon Intercomparison (VIRI).

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