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DIRECT BONE DATING IN A SMALL CO_2 COUNTER

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ABSTRACT. A small 200ml capacity CO_2 proportional counting system has been developed which uses only 100mg of carbon for complete filling. Thus, with respect to the small quantities needed, it compares favorably to dedicated accelerators at significantly lower cost. The performance of this equipment is demonstrated using a variety of samples including some human bone fragments from La Jolla which had been estimated to be 28,000 years old by aspartic acid racemization analysis.

INTRODUCTION

Direct dating of artifacts or bone is very valuable in archaeology inasmuch as association problems can be avoided. At Gypsum Cave (Harrington, 1933) atlatl shaft fragments and dung from giant sloths were found mixed together. The dung was dated to 10,455 ± 340 years (C-221, Libby, 1952) which led Harrington to believe that sloth and early man coexisted. However, direct dating of the atlatl shafts showed them to be only 2900 ± 80 years old (UCLA-1233) (Berger and Libby, 1967).

BONE DATING

Most bone samples recovered archaeologically tend to retain little native protein (collagen) on which to base a direct ^{14}C date when measured in conventionally-sized counters. Moreover, samples are often small or may be morphologically valuable so that only little can be sacrificed. Consequently, it became desirable to develop a special counting system which requires only small amounts of sample while yielding dates with acceptable standard deviations within reasonable counting time. Polach et al (1982) recently published a review of this approach.

In order to obtain the native organic fraction in bone, collagen is isolated by mild hydrochloric acid treatment followed by conversion to gelatin (Longin, 1971). This process eliminates most chemical contamination experienced in the field (Protsch, ms). However, when serious organic contamination is expected or outright asphalt impregnation is noticed, collagen is hydrolyzed completely into its component amino

acids which are then dated directly (Ho, Marcus, and Berger, 1969). Generally, the selection of the most suitable isolation technique for obtaining radiochemically pure amino acids or proteinaceous matter depends largely on the geochemistry and geomorphology of the recovery site. For example, dry cave deposits may not be chemically contaminated at all, while bone from the La Brea tar pits requires exhaustive decontamination, isolation, and characterization procedures.

In order to produce a clean CO_2 gas sample suitable for counting, the collagen fraction or amino acids are burned in a stream of pure oxygen. The CO_2 so generated is absorbed in carbonate-free 4N sodium hydroxide. This solution is flushed with oxygen gas to remove most radon dissolved in the solution. Then the original CO_2 is liberated by adding analytically pure hydrochloric acid. Subsequently, this CO_2 gas is cleaned in wash towers containing consecutively dilute silver nitrate and concentrated chromic acid. The next step involves passing the counting gas repeatedly over elementary copper at 500°C to remove such electro-negative impurities as oxygen or nitrogen oxides which interfere with CO_2 proportional counting. Finally, the counting gas is stored for about two weeks to permit complete radon decay.

The counter itself has a volume of 200ml equivalent to ca 8mM of CO_2 or 100mg of carbon all of which is used in the actual counting chamber. It is constructed of pure copper, epoxy-sealed, and fitted with a 1 mil anode wire at 3400V. The counter and separate anticoincidence system is located in a steel shield, 20cm thick, at the base of a five-story steel-reinforced concrete building. After preamplification the counter pulses are sorted into 3 anticoincidence and 3 coincidence channels for ultimate data reduction. With present shielding the dating range is ca 30,000 years but can be extended with additional modifications or made more accurate. Typically, a modern sample is counted for 2000 min to a standard deviation of 2%, a 3800-yr-old sample to 3% in 5000 min and a 18,000-yr-sample to 10% in one week. Thus this 200ml unit can produce about one date list/year when used for general archaeological/geological purposes.

TABLE 1. 200ml counter dates of bone samples

UCLA No.	Provenience	Counting time(min)	Age*(yr)
2380	Burial LAn717	2000	1125 ± 300
2384	La Jolla Shores W-2, #16755	4000	1930 ± 200
2347	Rancho La Brea	1000	Modern
2315A	Lake Taguatagua	5900	15,250 ± 910

*Age based on half-life 5568 ± 30; not calibrated or corrected

UCLA-2380 shows the kind of date to be expected from a relatively recent sample counted over a conventional period of 2000 min equivalent to 33.3 hours or ca 1 1/2 days. Such exploratory dates with an error on the order of ±300 years still permit archaeologic judgments, in many cases, on the chronologic period of a sample.

UCLA-2384 was analyzed to compare directly ^{14}C and aspartic acid racemization dates of the same human skeleton. The sample was composed of a few long bone fragments from site W-2, La Jolla Shores, California, where in 1926, Malcolm Rogers recovered a human skeleton without a cranium (SDM-16755). In 1973, bone fragments from this skeleton were dated by aspartic acid racemization and estimated to be 28,000 years old, using $K_{asp} = 1.08 \times 10^{-5}$ yr^{-1}. This date was used besides four others as new evidence for the antiquity of man in North America (Bada, Schroeder, and Carter 1974). The oldest racemization date in this suite of specimen was 48,000 years for SDM-16704, also called "The Del Mar Skeleton" which Spencer Rogers (1963) described earlier. Recently, Bischoff and Rosenbauer (1981) determined an age of 11,300 (+1300 -1200) years for the same skeleton (SDM-16704) by uranium series dating. If, indeed, the 48,000-year-old skeleton were actually 11,300 years old, then the 28,000-year-old specimen might also be more recent and datable by ^{14}C in the 200ml counter at UCLA.

For a direct bone ^{14}C date, ca 50g of bone were treated to isolate the gelatine fraction. After processing, the age was 1850 ± 200 yr. As a double check, a second set of bone fragments was treated similarly and dated at 1930 ± 200 yr. This compares with an age of 1770 ± 790 yr determined independently at the Riverside ^{14}C laboratory (UCR-1511D) and discussed in this volume by Taylor (1983). Consequently, SDM-16755 is actually < 2000 yr old. The discrepancy between ^{14}C and racemization dates may be caused by the need for a revised racemization rate based on a better localized environmental estimate for the Del Mar site. The ^{14}C age for SDM-16755 raises the question of whether the Del Mar skeleton (SDM-16704) also is really much more recent, in line with the uranium series date. However, it should be noted that elsewhere, good correspondence has been found between ^{14}C and racemization dates (Bada et al, 1974).

Another bone sample, UCLA-2347, from the tar pits of Rancho La Brea was dated to determine whether deer occupied the Rancho La Brean landscape of the Late Pleistocene. The amino acids native to bone were isolated according to the chromatographic procedure by Ho, Marcus and Berger (1969).

A 1000 minute count showed overnight that the deer bones were < 300 yr old and did not belong to the prehistoric fauna of the site.

Finally, to illustrate Late Pleistocene dating capability, a small bone sample from Lake Taguatagua, Chile was dated to assess the age of a large deposit of animal bones found in a former marsh environment near the perimeter of a lagoon. After collagen isolation and purification with dilute sodium hydroxide, the sample was assayed and calculated to be 15,210 ± 910 yr old (UCLA-2315A). Counting time for this sample was 5900 minutes or ca 4 days.

Ultimately, we hope that accelerator-based dates combining short measuring times and even smaller samples sizes with small standard deviations will become available. In the meantime, appropriately designed small gas counters can perform effectively many duties bridging the gap between liter-sized gas counters and accelerators.

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