THE EFFECT OF CYCLODODECANE ON CARBON-14 DATING OF ARCHAEOLOGICAL MATERIALS

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ABSTRACT—The impact of cyclododecane on the carbon-14 dating of archaeological materials was investigated using accelerator mass spectrometry. Two conservation-grade and two laboratory-grade cyclododecane samples were determined to be radiocarbon-free, indicating that the chemical is synthesized from petroleum-derived, rather than modern hydrocarbon sources. Radiocarbon dating of modern and archaeological gourd rind samples that were treated with cyclododecane produced the same results as for untreated samples. While the study does not demonstrate that residues are absent from cyclododecane-treated artifacts, it showed that the stringent sample cleaning protocols specifically designed to remove both burial and laboratory contaminants were sufficient to reduce cyclododecane residues to levels that would not interfere with radiocarbon dating.

TITRE—L'effet du cyclododécane sur la datation au carbone-14 du mobilier archéologique. RÉSUMÉ—L'impact du cyclododécane sur la datation au carbone-14 du mobilier archéologique a été étudié à l'aide de la spectrométrie de masse par accélérateur. L'analyse de deux échantillons de cyclododécane de qualité pour la conservation et de deux autres de qualité pour laboratoire a révélé qu'ils étaient exempts de radiocarbone, ce qui signifie qu'ils sont synthétisés d'une base de pétrole et non d'une source d'hydrocarbures modernes. La datation au radiocarbone d'échantillons modernes et de provenance archéologique de peaux de courge traitées avec du cyclododécane a produit le même résultat que pour des échantillons non traités. Cette étude ne démontre pas qu'aucun résidu ne demeure sur les artéfacts traités à l'aide de cyclododécane, mais elle indique que les protocoles rigoureux de préparation des échantillons élaborés pour éliminer les contaminants provenant du milieu d'enfouissement et de celui du laboratoire ont permis de réduire la quantité de cyclododécane à un niveau qui n'influence pas la datation au radiocarbone.

TITULO—El effecto del ciclododecano en el fechado por medio de carbono 14 de materiales arqueologicos. RESUMEN—Se investigó el impacto del ciclododecano en el fechado con carbono 14 de materiales arqueológicos, utilizando espectrometría de masas con acelerador. Se determinó que dos muestras de ciclododecano de calidad de conservación y dos muestras de calidad de laboratorio estaban libres de radiocarbono, lo que indica que el químico es sintetizado de derivados del petróleo, y no de fuentes modernas de hidrocarburo. El fechado con radiocarbono de muestras de cáscara de calabaza modernas y arqueológicas que fueron tratadas con ciclododecano dio lo mismos resultados que las muestras no tratadas. Siendo que el estudio no demuestra que no hay residuos en los artefactos tratados con ciclododecano, si demuestra que los rigurosos protocolos de limpieza diseñados específicamente para remover los contaminantes tanto de la excavación como del laboratorio, son suficientes para reducir los residuos del ciclododecano a niveles que no interfieren con el fechado con carbono 14.

TÍTULO—O efeito do cyclododecano em carbono-14 na datação de materiais arqueológicos. RESUMO—Investigou-se o efeito do ciclododecano em carbono-14 na datação de materiais arqueológicos usando-se o espectrometria de acelerador de massa. Duas amostras de ciclododecano (nível de conservaço e nível de laboratório) foram avaliadas livres de carbono, indicando que o elemento químico é sintetizado de um derivado de petróleo, ao invés de fontes de hidrocarbonetos modernos. A datação de amostras modernas e arqueológicas com o uso de radiocarbono, as quais foram tratadas com ciclododecano produziram os mesmos resultados das amostras não tratadas. Apesar do estudo não demonstrar que não se encontram resíduos em artefatos tratados com ciclododecano, ele mostrou que protocolos de limpeza especificamente estabelecidos para remover contaminantes intrínsicos e laboratoriais foram suficientes para reduzir os resíduos de ciclododecano a níveis que não interfeririam com a datação com radiocarbono.

1. INTRODUCTION

Since the mid-1990s, volatile organic solids have been studied and tested for their applicability within the field of conservation, including uses such as hydrophobic protective coatings for water-sensitive objects, consolidants for fragile objects during transport, excavation, or handling, and as a sealant for surfaces during various working processes (Jägers and Jägers 1999). One of these volatile substances is cyclododecane (CDD), a cyclic hydrocarbon ($C_{12}H_{24}$) that sublimes in relatively short times. Among its applications in conservation, CDD has found use in stabilizing and lifting fragile archaeological materials. Because of its easy removal through eventual volatilization, it is considered an appealing alternative to conventional (nonsubliming) organic consolidants. Many of the latter are known to physically and chemically affect subsequent analyses, especially those targeting certain isotopes in organic materials such as carbon, oxygen, nitrogen, and strontium (e.g., Tuross et al. 1988; Katzenberg 1991; Johnson 1994; Katzenberg and Harrison 1997; Williams 1999). The physical and chemical effects of CDD on artifact materials and their subsequent testing, however, have not been studied. Although CDD is generally thought to sublime completely, there is mounting evidence that this may not be the case. Several studies have noted residues remaining on a substrate after sublimation of CDD (Caspi and Kaplan 2001; Maish and Risser 2002). Most batches are labeled as 99.0–99.5% pure, leaving 0.5–1.0% of the material unknown. Little information is provided by suppliers regarding CDD's composition and the presence of impurities. These uncertainties warrant the investigation of CDD's composition and the effect of its use on the analysis of organic archaeological materials. This paper focuses specifically on the impact of CDD on carbon-14 dating. Because carbon is an element shared by both an organic substrate and CDD, radiocarbon measurements obtained from CDD-treated organic materials could be compromised.

2. BACKGROUND

2.1 USE OF CDD IN CONSERVATION

Historically, methods for strengthening and protecting fragile objects and materials have involved the use of natural or synthetic adhesives and consolidants. Although such approaches typically are successful in increasing stability, most are irreversible from a practical standpoint and may permanently alter the chemical composition of a given object, especially porous organic materials. A new method of temporarily protecting objects and materials using CDD was introduced in 1995, emerging from an investigation of volatile binding media and their applicability in the field of conservation (Hangleiter et al. 1995; Hangleiter 1998). CDD is supplied in three different forms: a molten (or pure melt) form, a solution, and a solvent form in an aerosol spray. A substrate treated with pure melt CDD must be able to tolerate heating to the melting temperature without damage. For CDD applied as a solution, the substrate must be able to tolerate the solvent used. The rate of CDD sublimation can be manipulated to some extent by varying the ambient temperature and air circulation.

CDD has been found to be an effective sealant for surfaces, and its hydrophobic nature can be exploited to protect substrate surfaces against water. It also has been used as a barrier layer in conjunction with mold-making techniques, and as an effective temporary consolidant for a wide variety of materials. To date, published reports of substrates that have been treated with CDD or those involved in experimentation include: ceramics, stone, paper, textiles, marble, terracotta, limestone, mortar, paintings (oil and wall plaster), and fossils (e.g., Reidl and Hilbert 1998; Brückle et al. 1999; Jägers and Jägers 1999; Hangleiter 2000a, 2000b; Keynan and Eyb-Green 2000; Stein et al. 2000; Caspi and Kaplan 2001; Maish and Risser 2002; Arenstein et al. 2003; Arenstein et al. 2004; Larochette 2004; Muros and Hirx 2004; Hangleiter and Saltzmann 2005; Hangleiter 2006a, 2006b; Karas 2006; Pool 2006; Kremer Pigments 2007).

2.2 EFFECTS OF CONSOLIDATION ON SUBSEQUENT CHEMICAL ANALYSES

Many organic polymers commonly used as consolidants in the field of conservation are difficult to remove completely and may permanently alter both inorganic and organic substrates. This is of particular concern when chemical analyses are required on consolidated material, particularly in the case of organic materials. Analytical techniques that may be affected by consolidation include trace element and isotopic analyses, measurements of specific gravity, and DNA and various other biochemical analyses (Johnson 1994). In the case of radiocarbon measurement, the presence of consolidant residues could lead to inaccurate radiocarbon dates.

2.3 RADIOCARBON DATING THEORY

Radiocarbon (carbon-14) is a naturally occurring, unstable isotope of carbon that is continuously generated in the earth's upper atmosphere. It is chemically indistinguishable from the stable carbon isotopes (carbon-12 and carbon-13), and, along with the stable carbon isotopes, becomes incorporated into all living things via photosynthesis and the food chain. Radiocarbon levels within living organisms are essentially the same as atmospheric levels, but after death, the amount of radiocarbon within organic remains drops at a predictable rate ($t_{1/2} = 5730$ years). Knowledge of the decay rate, combined with the precise measurement of radiocarbon levels within organic remains, is the basis of the dating method. Analysis involves extracting the total carbon from a sample of organic material and comparing its carbon isotope ($^{14}C/^{13}C$) ratio relative to that of a modern, known-age standard. Current instruments can measure radiocarbon levels through roughly 10 half lives of decay, (about 50,000 years). Beyond this, levels are indistinguishable from background (Taylor 1987). Results are expressed in years Before Present (BP), with January 1, 1950 being 0 BP.

2.4 EFFECT OF CONTAMINANTS ON RADIOCARBON MEASUREMENT

Sample preparation for radiocarbon dating assumes that all artifacts are contaminated with exogenous carbon that must be removed before measurement. Contamination can take the form of organic molecules from the burial environment, unintentional contamination arising from handling or the laboratory environment, and intentionally added carbon-based adhesives or consolidants associated with excavation, conservation treatments, or the storage and display of artifacts. Usually the exogenous carbon has a different radiocarbon content than the sample. If it is not removed, then contaminant and sample carbon are pooled during carbon extraction, and erroneous dates are the result.

In the modern environment, potential contaminants contain a wide range of radiocarbon contents. First, soil organic matter, which encompasses the diverse products of natural organic decay, can range in radiocarbon content from none to the artificially elevated levels found in the environment in the Post-Nuclear Age (i.e., after 1950). Second, large quantities of organic carbon derived from petroleum products have entered the environment. Because the carbon found in the multitude of plastics, adhesives, solvents, and coatings is predominantly derived from the carbon of plants that lived millions of years ago, these materials are generally radiocarbon free. Some of these materials are synthesized from a combination of Carboniferous Age hydrocarbons and modern (i.e., carbon-14 containing) organic molecules, thus generating materials of composite radiocarbon content.

The effect of contamination on a particular measurement is difficult to anticipate due to the range of potential contaminants in today's environment. Simply put, if the contaminant has a lower radiocarbon content than the sample, the measured age would be erroneously increased. If the opposite is true, then the measured age would be erroneously too young. This difficulty has been noted in the case of natural or synthetic resins found on museum artifacts such as preserved bone (Protsch 1986).

2.5 RADIOCARBON SAMPLE CLEANING

The wet chemical cleaning of materials destined for radiocarbon measurement is termed "pretreatment." Although a wide variety of pretreatment methods can be found in the literature, most routine radiocarbon pretreatment methods involve sequential washes with mineral acid/mineral base/mineral acid. This sequence is designed to dissolve inorganic carbonate salts and acid-soluble organic compounds with the first acid treatment, solubilize soil humic acids in mineral base washes, and reestablish a neutral or slighty acid pH within the sample to prevent the absorption of atmospheric carbon dioxide by the sample. Such treatments are often all that is required for artifacts recovered from undisturbed burial contexts that have received minimal sample handling.

Objects from museums, on the other hand, are particularly challenging. Often they have experienced extensive handling and many have unknown conservation histories. Samples from such objects require additional pretreatments. These generally involve volatile solvent-series extractions using a Soxhlet apparatus. These pretreatments are designed to remove absorbed skin oils, surface dirt, and exogenous residues such as soap residues, coatings, adhesives, and consolidants. In a few studies, consolidant removal by Soxhlet extraction has been explicitly investigated (Johnson 1994; Bruhn et al. 2001). In some cases, polymers simply cannot be removed (Johnson 1994). Knowing the difficulties caused by many of the conventional consolidants used in conservation for elemental and isotopic studies, the effect of CDD treatment of samples on radiocarbon dating merits investigation.

3. EXPERIMENTAL

3.1 RESEARCH DESIGN

The goal of this study was to determine whether the use of cyclododecane as a temporary consolidant caused a shift in the carbon-14 age of a material, either directly after application or following partial or complete sublimation. The approach utilized the radiocarbon measurement of known-age samples that are either untreated or treated with CDD. In order to maximize sensitivity of detection, the experiments were designed to ensure the radiocarbon content of the sample and the contaminant (CDD) were as different as possible.

The first task in the experiment was to determine the radiocarbon content of CDD. Although it was probable the material was derived from fossil hydrocarbons, this could not be assumed. Some organic compounds are assembled from smaller molecules that can be derived from either petroleum or biological sources. Moreover, syntheses can occur via alternative pathways selected according to the economics of production. Thus substantial batch-to-batch variations in the radiocarbon content of a particular synthetic organic compound are possible.

As the radiocarbon content of synthetic organic materials is generally unrelated to their age it is meaningless to "radiocarbon date" them. Consequently, radiocarbon content is quantified in terms of Fraction Modern. This dimensionless unit is the ratio of sample radiocarbon content relative to the radiocarbon content of a theoretical modern standard from the year 1950. (Fraction Modern can also be used for natural materials. For example, an object that is 5730 radiocarbon years old, or precisely one half-life old, has a Fraction Modern (F) of 0.5 F. An object two half-lives old is 0.25 F.)

The research design involved first determining the radiocarbon content of four commercially available supplies of CDD. Samples of each batch of CDD, weighing approximately 100 mg, were allowed to sublime, then any remaining nonvolatile residues were quantified and their radiocarbon content was measured. Once the radiocarbon content was established and information about the composition or purity of the CDD was obtained from product literature, archaeological and modern gourd rinds were treated with one of the batches of consolidant and the carbon-14 age was measured at three stages during the treatment: directly after application, midway through the sublimation, and after sublimation was complete.

3.2 CARBON-14 ANALYSIS

3.2.1 Solid CDD Samples

To determine if solid cyclododecane contained carbon-14, four batches of CDD, two conservation-grade and two laboratory-grade, were selected from three different suppliers as follows: (A) Kremer Pigments (new in 2006), (B) Kremer Pigments (opened prior to 2006), (C) Lancaster Synthesis (opened prior to 2006), and (D) Chemical Service (opened prior to 2006). Samples weighing 100–400 mg were taken from each batch for accelerator mass spectrometry (AMS) dating; these were not put through any pretreatment protocol. Carbon was extracted from the solid CDD samples by combustion *in vacuo* in the presence of copper oxide. The resulting CO_2 was cryogenically purified on a gas distillation line and then converted to graphite using the method of Slota et al. (1987). The carbon-14 and carbon-13 in the CDD samples were measured by AMS and measurements were isotope fractionation corrected and background subtracted (Donahue et al. 1990). Ages were calculated by comparing the carbon-14 content of the samples to standards with known carbon-14 content.

3.2.2 CDD Sublimation Residues

To determine the carbon-14 date of the sublimation residues and how these may differ from those of the bulk CDD, samples of the four CDD batches (weighing approximately 100 mg), were placed in 9mm quartz combustion tubes that were open on one end. Glass wool was then inserted into the tube opening to prevent contamination of the sample from dust and other particulates. To speed up the sublimation rate, the four tubes were placed in a heat block at 60°C and placed in a fume cupboard. To avoid crystallization of the CDD on the inside of the combustion tube, the exposed portions of the tubes were covered with aluminum foil. This allowed the entire length of the tubes to achieve 60°C. Sublimation occurred with this experimental set-up at an extremely slow rate, less than 1.00 mg after six months. Due to time limitations, the glass wool was eventually removed from the tops of the tubes and they were placed in an oven set to 70°C until the CDD samples sublimed completely. The same methods and procedures for carbon-14 dating, described in section 3.1, were followed for the residue samples in an attempt to detect carbon-containing contaminants with a potential carbon-14 signature. The tubes were purged with nitrogen to remove any particulates, then filled with 200 mg of CuO and combusted. Any resulting carbon dioxide was assumed to be residue-derived.

3.2.3 Archaeological and Modern Gourd Rind

Gourd rind was selected as the organic substrate to be treated with CDD and carbon-14 dated in this part of the experiment; both archaeological and modern samples were used. Bone and wood were initially considered; however, these materials can be some of the more problematic organics to carbon-14 date in terms of uniformity, porosity, and in the case of ancient bone, sufficient collagen remaining to be able to get a carbon-14 reading. Conversely, gourds (a short-lived cultigen) produce a rind matrix with fewer variables, being relatively uniform, nonporous, and with comparable surface areas. The archaeological gourd rind samples were excavated in the 1870s from Mammoth Cave in Kentucky (fig. 1); the seven gourd fragments used for the experiment came from the same archaeological context and object.[1] These had been previously radiocarbon dated to 2,750 BP ± 40 (Smith 2007). The modern samples were from a gourd rind (*Crescentia alata*) collected in El Salvador in the early 1990s.[2]

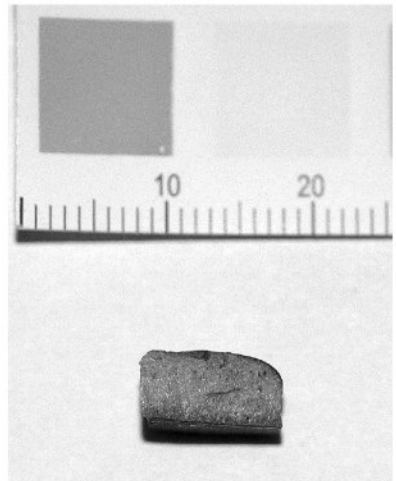

Fig. 1. Archaeological gourd rind fragment from Mammoth Cave, Kentucky that was used in the CDD and carbon-14 dating experiments.

The archaeological and modern gourd samples were cut, weighed and treated with a new batch of CDD acquired from Kremer Pigments (batch A), and then carbon-14 dated at various stages: after CDD application, after partial sublimation, and after complete sublimation. In order to account for any differences in porosity, CDD application, and uniformity, two samples of each gourd type were prepared for each of the three stages, indicated by (1) and (2) in table 1. Ancient gourd samples of approximately the same size were cut from the dated fragments, and samples of similar size were cut from the modern gourd rind. Including the untreated controls, the total number of samples was 14, as listed in table 1.

Gourds 3–14 were immersed in pure-melt CDD until each sample was 3 times its original weight. Gourds 3–6 were wrapped in aluminum foil before being sealed into glass vials to prevent sublimation. Gourds 7–14 were weighed regularly until their respective target weights were reached, indicating that partial or full sublimation of the CDD had been achieved. These were packaged to maintain their respective states, and all were submitted for carbon-14 dating. The ancient gourds were prepared for AMS in one session, and all of the modern gourds were prepared in a second session, to simplify sample

Table 1. Gourd Samples Used for the Experiment

Gourd #	Description of gourd sample treatment
Gourd # 1:	Ancient gourd control
Gourd # 2:	Modern gourd control
Gourd # 3:	Ancient gourd w/CDD after application (1)
Gourd # 4:	Ancient gourd w/CDD after application (2)
Gourd # 5:	Modern gourd w/CDD after application (1)
Gourd # 6:	Modern gourd w/CDD after application (2)
Gourd # 7:	Ancient gourd w/CDD mid-way through sublimation (1)
Gourd # 8:	Ancient gourd w/CDD mid-way through sublimation (2)
Gourd # 9:	Modern gourd w/CDD mid-way through sublimation (1)
Gourd # 10:	Modern gourd w/CDD mid-way through sublimation (2)
Gourd # 11:	Ancient gourd w/CDD after sublimation (1)
Gourd # 12:	Ancient gourd w/CDD after sublimation (2)
Gourd # 13:	Modern gourd w/CDD after sublimation (1)
Gourd # 14:	Modern gourd w/CDD after sublimation (2)

tracking. All of the samples, except for the two untreated controls, received the extended radiocarbon sample treatment involving extraction with hexane, ethanol, and methanol using the Soxhlet apparatus, and the standard acid-base-acid treatment. All samples were then combusted into CO_2 and converted to graphite.

4. RESULTS

4.1 SOLID CDD SAMPLES

All four bulk CDD samples were found to contain very low levels of carbon-14, and can be essentially considered radiocarbon-free (table 2).

All of the measurements were at the limits of detecting a carbon-14 age, indicated by the > symbol; the upper limit at the University of Arizona's AMS Facility is approximately 48,000 years BP. Background-level measurements obtained during the AMS process are responsible for the minimal variation between the dates, and sample D also can be considered at the limit of carbon-14 detection even though it registered a ± carbon-14 age of a 2 sigma value (95%).

4.2 CDD SUBLIMATION RESIDUES

Table 3 summarizes the results of the four CDD samples that were analyzed for nonvolatile, or nonsubliming, carbon-containing residues with potential carbon-14 signatures.

No carbon-containing residues were detected for sample A and only trace residues were detected for CDD samples from batches B and C. With samples B and C, microgram quantities of gas registered on the pressure transducers after combustion and isolation of carbon dioxide, but because transducer sensitivity was ± 0.1 torr, (equivalent to ± 20 micrograms of carbon) these measurements can be considered questionable. CDD sample D was contaminated during the dating process and was subsequently discarded.

4.3 ARCHAEOLOGICAL AND MODERN GOURD RIND

Table 4 summarizes the results of analysis of the ancient gourd samples from Mammoth Cave used for this part of the experiment. The results for the ancient gourd samples show margin of error values at 1 sigma (68%).

Table 5 details the results of the carbon-14 dates obtained for the modern gourd samples. The results for the modern samples show values within the post-bomb range after AD 1950 (Taylor 1987), and so radiocarbon measurements are expressed as a fraction (F) of modern values.

5. DISCUSSION OF RESULTS AND CONCLUSIONS

In order to understand the origin of any shift in the carbon-14 content of an organic archaeological substrate treated with CDD, it was necessary to determine the carbon-14 content of both the solid and any nonvolatile residues. Any carbon-containing residues left behind after sublimation of the solid CDD samples could potentially have carbon-14 dates of their own that differ from that of the CDD and, further, were likely to differ by batch. AMS dating of the solid form found that all four batches, from three

Table 2. Carbon-14 Age of the Solid CDD Samples

Lab # (U of A)	Sample	AMS Suite	$\Delta^{13}C$ value	F	±ΔF	^{14}C age (BP)	$\pm^{14}C$ age (BP)
x6980	CDD A	1 of 4	−25.2	<0.0020		>49,900	
x6981A	CDD B	2 of 4	−24.8	<0.0020		>49,900	
x6982	CDD C	3 of 4	−25.5	<0.0030		>46,700	
x6983	CDD D	4 of 4	−23.4	0.0026	0.0010	47,900	3,200

$\Delta^{13}C$: Change in the carbon-13 content of the sample during the dating process
F: Fraction Modern (ratio of sample radiocarbon content relative to the radiocarbon content of a theoretical modern standard from the year 1950)
±ΔF: Margin of error of Fraction Modern

Table 3. Analyses of CDD Residues

Sample	Suite	Mass of tube (mg)	Starting mass of CDD (mg)	Total mass (mg)	Combustion yield (torr)	Carbon yield on combustion (mg)	Mass percent of non-volatiles
CDD A	1 of 4	6805.16	104.30	6909.46	0.0	0.00	0.00
CDD B	2 of 4	6649.84	105.82	6755.66	0.1	0.0045	0.0043
CDD C	3 of 4	7292.30	108.91	7401.21	0.1	0.0045	0.0041
CDD D	4 of 4	6484.70	150.55	6635.25	Sample lost	0.0045	Sample lost

different suppliers, were essentially radiocarbon-free and at the limits of carbon-14 detection (47,000–60,000 BP), with only minimal differences in the carbon-14 content. That age suggests that CDD, from all suppliers tested, is derived from petroleum.

Following the radiocarbon dating of the bulk cyclododecane, the sublimation residues of the CDD were measured. In all cases, only trace amounts of residue were obtained from the samples. From samples of approximately 100 mg, residues of 0.0041–0.0043 mass percent were obtained. These results are within the range of routine contamination; even with 100 mg samples, it is not uncommon for a few micrograms of carbon-14-containing contaminants to be acquired during the dating process. It appears from these results that the cyclododecane does not contain nonvolatile, carbon-containing residues. This should be confirmed with further experiments using a larger sample size and an experimental protocol to produce more rapid sublimation.

Determining how CDD treatment affects the carbon-14 dates of an organic material was tracked by analyzing both ancient and modern gourd rind samples at three different stages: after CDD application, after partial sublimation, and after complete sublimation. The rationale for evaluation at these three stages was that any trend in a carbon-14 age shift of the organic substrate would be revealed. Of these,

Table 4. Results of Ancient Gourd Samples

Sample	$\Delta^{13}C$ value	F value	±ΔF	^{14}C age (BP)	$\pm^{14}C$ age (BP)
Gourd # 1: ancient control	−26.1	0.7207	0.0031	2,631	34
Gourd # 3: after CDD application (1)	−26.2	0.7332	0.0058	2,493	64
Gourd # 4: after CDD application (2)	−26.9	0.7204	0.0031	2,634	34
Gourd # 7: mid-way through sublimation (1)	−26.5	0.7313	0.0031	2,514	34
Gourd # 8: mid-way through sublimation (2)	−26.6	0.7260	0.0031	2,572	34
Gourd # 11: after complete sublimation (1)	−26.5	0.7298	0.0033	2,530	37
Gourd # 12: after complete sublimation (2)	−26.1	0.7317	0.0036	2,509	40

$\Delta^{13}C$: Change in the carbon-13 content of the sample during the dating process
F: Fraction Modern (ratio of sample radiocarbon content relative to the radiocarbon content of a theoretical modern standard from the year 1950)
±ΔF: Margin of error of Fraction Modern

Table 5. Results of Modern Gourd Samples

Sample	$\Delta^{13}C$ value	F value	$\pm\Delta F$	^{14}C age (BP)	$\pm^{14}C$ age (BP)
Gourd # 2: modern control	−26.8	1.1644	0.0045	Post-bomb	n.a
Gourd # 5: after CDD application (1)	−27.3	1.1539	0.0044	Post-bomb	n.a
Gourd # 6: after CDD application (2)	−27.1	1.1565	0.0044	Post-bomb	n.a
Gourd # 9: mid-way through sublimation (1)	−26.7	1.1445	0.0044	Post-bomb	n.a
Gourd # 10: mid-way through sublimation (2)	−28.2	1.1292	0.0045	Post-bomb	n.a
Gourd # 13: after complete sublimation (1)	−26.6	1.1641	0.0045	Post-bomb	n.a
Gourd # 14: after complete sublimation (2)	−26.8	1.1642	0.0046	Post-bomb	n.a

$\Delta^{13}C$: Change in the carbon-13 content of the sample during the dating process
F: Fraction Modern (ratio of sample radiocarbon content relative to the radiocarbon content of a theoretical modern standard from the year 1950)
$\pm\Delta F$: Margin of error of Fraction Modern

the most dramatic effect was anticipated with the sample group that was treated but not allowed to sublime.

All of the ancient and modern gourd rinds, aside from the two untreated controls, were subjected to the extended chemical pretreatment procedures. The carbon-14 dates obtained from the treated samples were not altered in comparison to the ancient and modern gourd controls. The one ambiguous result from this sample set is that of gourd 3, which was found to be younger than the untreated ancient gourd control (gourd 1). Whatever the reason for this variation, it is unlikely to have resulted from the presence of CDD, which would have skewed the measurement to older than the untreated control.

Because the treated gourd samples initially contained substantial amounts of CDD, the results suggest that the extended chemical pretreatment and extraction methods used in the carbon-14 dating successfully removed the CDD from the substrate. When such sample preparation procedures are used, the CDD treatment does not alter the carbon-14 dating process, regardless of the age of the sample material (archaeological or modern). These interpretations were supported by the carbon-14 results obtained from samples that had been allowed to sublime completely (gourds 7–14), when compared to the untreated controls. There is some evidence in the results shown in table 5 that traces of CDD remained in gourds 5, 6, 9, and 10. The radiocarbon content of these was lower than the untreated control (gourd 2). However, this interpretation is equivocal, as CDD contamination should have depleted the Δ carbon-13 values and it did not in three out of four cases. Importantly, gourds 13 and 14 had radiocarbon content that were the same as the untreated control, indicating that in circumstances mimicking the way CDD is actually used in conservation treatments, the radiocarbon dating sample cleaning protocols are sufficient to remove any traces of CDD contamination. Based on these findings, one can conclude either that CDD does not contain residues that affect the radiocarbon dating, or that any residues it leaves behind are subsequently removed by the chemical cleaning protocols preceding carbon-14 measurement. This research did not attempt to distinguish between these possibilities. Further tests would be required to determine if the standard acid-base-acid pretreatment alone would successfully remove CDD from a treated sample and result in unchanged carbon-14 dates in comparison to the control. The authors have discussed a second phase of study using a more complex substrate for CDD treatment such as bone or wood. These substrates would be more likely to retain larger amounts of the consolidant in the pores and would also be more resistant to solvent extraction during the pretreatment phase.

Results of the research support the following: that CDD does not contain a notable amount of carbon-14; that either it does not leave behind carbon-containing contaminants with carbon-14 signatures, or these contaminants are removed by the chemical pretreatments; and that CDD–present at any stage of sublimation–does not alter the carbon-14 date of archaeological or modern gourd samples which have undergone the extended chemical pretreatments. Impurities detected in minimal quantities by carbon-14 dating warrant further investigation. However, in terms of its use in archaeological conservation and on organic substrates, CDD remains an appealing alternative to conventional (nonsubliming) organic consolidants and can now be used with more confidence with regard to its effect on future carbon-14 studies.

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NOTES

1. The archaeological gourd rind fragments were donated by Bruce Smith, Curator of North American Archaeology, Department of Anthropology, National Museum of Natural History, Smithsonian Institution.
2. The modern gourd rind fragments were collected by Harriet F. Beaubien from Joya de Cerén, El Salvador.

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SOURCES OF MATERIALS

Cyclododecane batches A and B
Kremer Pigments, Inc.
247 West 29th Street
New York, NY. 10001
(800) 995-5501
www.kremer-pigmente.com

THE EFFECT OF CYCLODODECANE ON CARBON-14 DATING OF ARCHAEOLOGICAL MATERIALS

Cyclododecane batch C
Lancaster Synthesis, Inc.
P.O. Box 1000
Windham, NH 03087-9977
(800) 238-2324
andyb@lancaster-us.com

Cyclododecane batch D
Chem Service, Inc.
P.O. Box 599
West Chester, PA 19381-0599
(610) 692-3026

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