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Application of supercritical carbon dioxide–co-solvent mixtures for removal of organic material from archeological artifacts for radiocarbon dating

Marvin W. Rowe[a], Jenny Phomakay[b], Jackson O. Lay[c], Oscar Guevara[d], Keerthi Srinivas[b], W. Kirk Hollis[e], Karen L. Steelman[f], Thomas Guilderson[g], Thomas W. Stafford Jr.[h], Sarah L. Chapman[i], Jerry W. King[b,*]

[a] *Texas A&M University, Doha, QATAR/Conservation Laboratory - Museum of New Mexico, Santa Fe, NM 87505, USA*
[b] *Department of Chemical Engineering, University of Arkansas, Fayetteville, AR 72701, USA*
[c] *Department of Chemistry, University of Arkansas, Fayetteville, AR 72701, USA*
[d] *Department of Biological and Agricultural Engineering, Fayetteville, AR 72701, USA*
[e] *Los Alamos National Laboratory, Los Alamos, NM 87544, USA*
[f] *Department of Chemistry, University of Central Arkansas, Conway, AR 72035, USA*
[g] *Center for AMS, Lawrence Livermore National Laboratory L-397, 7000 East Avenue, Livermore, CA 94551, USA*
[h] *Stafford Research Laboratories, Inc., 200 Acadia Avenue, Lafayette, CO 80026, USA*
[i] *Department of Anthropology, University of Arkansas, Fayetteville, AR 72701, USA*

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ABSTRACT

Archeological artifacts such as burial and embalmment materials are commonly dated by ^{14}C labeling using accelerator mass spectrometry (AMS). The presence of contaminant organic matter can interfere with the accurate determination of an object's age, hence sample preparation is a critical step before radiocarbon-based dating. Both harsh acid and base treatments have been applied to remove contamination, such as humic acids, resin-based adhesives, and plant oils. Additional removal of carbon-laden material can also be affected by applying such methods as plasma oxidation. In this study, SC-CO_2 with addition of a cosolvent has been applied to remove the above materials prior to plasma oxidation and subsequent dating via AMS. Initially, wood/charcoal samples were extracted using a modified-Isco SFX-2-10 extraction unit (Isco Inc., Lincoln, NE). Experiments were conducted using supercritical carbon dioxide/10% methanol at a pressure of 20.4 MPa (3000 psig) ($p_r = 2.80$) and 40 °C ($T_r = 1.36$), and carbon dioxide flow rates of $\sim 1.4 \pm 0.1$ ml/min. Comparison of the SC-CO_2–methanol cosolvent treatment with traditional acid–base–acid sample pretreatment on identical wood-charcoal samples showed comparable radiocarbon dating results encompassing a period of 10,000 years. In addition, both Russian and Egyptian mummy gauzes and Russian textiles were similarly treated and the extracts analyzed by MALDI-TOF-MS and GC/MS to determine the chemical identity of the extracted material. A polyglycerol-based polymer was positively identified in addition to fatty acid moieties as their fatty acid methyl ester derivatives (FAMES), which potentially formed from the in situ reaction of the triglycerides present in the embalment materials with the SC-fluid mixture. Model extractions from spiked-linen gauze samples have verified removal of such materials as beeswax, coconut oil, frankincense, glycerol, and humic acids in varying amounts. Application of supercritical fluid extraction (SFE) appears to be a promising method to pretreat small samples for ^{14}C radiocarbon dating where conservation of the archeological artifact is of importance. The SFE pretreatment has the potential to replace harsh acid–base pretreatment methods, and can be coupled with a non-destructive argon or oxygen plasma treatment for microgram carbon removal prior to accelerator MS isotope ratio age determination of the archeological artifact. This combination of techniques requires as little as 0.05 mg of carbon-equivalent weight for the age determination of the artifact while minimizing sample degradation.

1. Introduction

The radiocarbon dating of many archeological artifacts, such as Egyptian mummies, can be inaccurate due to contamination from soil organic matter. Traditional decontamination methods require the use of harsh acid–base pretreatment methods, which can be

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* Corresponding author. Tel.: +1 479 575 3835; fax: +1 479 575 7926.
E-mail addresses: jwking1@uark.edu, kingjw100@hotmail.com (J.W. King).

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destructive to these delicate ancient artifacts [1], as well as introduce inaccuracies prior to accelerator mass spectrometry (AMS) isotope ratio determinations [2]. The goal of this research is to develop a nondestructive radiocarbon dating technique for fragile archeological artifacts. Currently, radiocarbon dating utilizes two destructive steps. Organic-containing artifacts are pre-cleaned with serial strong acid, base, and acid (ABA) treatments, usually at elevated temperatures (~323 K) to eliminate commonly occurring humic acid, carbonate and oxalate contaminants, followed by high temperature combustion (>1023 K) of the organic carbon collected from the samples. Unfortunately samples can be highly degraded using these chemical washes, and a more benign cleaning method is desired.

A method has already been developed that renders the second step virtually nondestructive for many organic materials: plasma-chemical extraction of organic carbon [3–5]. In the course of conducting that research, the technique developed for dating rock paintings [6–9] – plasma-chemical extraction – also eliminated the need for the two acid steps required in step (1) [10,11]. Plasma oxidation may also be preferable for any type of sample containing significant amounts of oxalate-containing minerals. Two previous studies found that in unusual circumstances, acid treatment is insufficient to remove offending calcium oxalate minerals [12,13]. Thus, to be able to obtain nondestructive radiocarbon dating requires only a nondestructive substitution for the strong base wash used to extract the contaminating humic acids. Here we report on the possibility of using a supercritical fluid-based cleaning technique to extract soil organic matter (SOM) containing humic acids from organic-containing archeological artifacts.

Our approach employs supercritical CO_2 (SC-CO_2), which has been found to be benign enough to be used by other conservators (Sousa et al. [14], Kaye and Cole-Hamilton [15,16], Saleh et al. [17]) as well in the commercial dry cleaning industry [18]. For example, Sousa et al. [14] cleaned silk garments from an 18th century Virgin and Child from Palácio das Necessidades in Lisbon using SC-CO_2, SC-CO_2 + isopropanol, and SC-CO_2 + isopropanol + water. The gentle nature of SC-CO_2 was highlighted in this work as the silk was fragile and the fibers could easily suffer disintegration by simple handling. Sousa et al. [14] also looked at the loss of textile material, color variation, and dirt removal using gravimetry, spectroscopy, and optical microscopy. They observed removal of dirt particles, while the textile structure was not physically damaged even under high magnification.

Additional studies focusing on pesticide contamination migration on artifacts in museum collections have been reported by Tello and Unger [19], Werner et al. [20], and Zimmt et al. [21] in MCI workshop proceedings published by the Smithsonian Institute. In these studies, removal of dust, grease, DDT, diazinon, mercury, lindane, linseed oil, and water from the artifacts using both SC-CO_2 and liquid CO_2 (LCO_2) with various cosolvent additives were cited. The cleaning or extraction process is dependent upon the solvent characteristics of the supercritical fluid and/or its cosolvent. In addition, the use of SC-CO_2 – aside from its adjustable solvent properties – facilitates removal of contaminants from artifacts by improving their mass transport out of the sample matrix due to SC-CO_2's low viscosity and surface tension. As with critical point drying [22], SFE using SC-CO_2 plus cosolvent when properly applied, eliminates any physicochemical perturbation of the sample matrix and hence morphological distortion of the artifact – which has been nicely demonstrated on woods and textiles treated with SC-CO_2 [19,23].

A key feature of the methodologies described herein is their applicability to small archeological samples with minimal destruction of the sample matrix. Plasma oxidation [1] after SFE-treatment of an artifact supplements the SC-fluid mixture based extraction method, thereby yielding a non-destructive protocol for prepared samples prior to ^{14}C dating. As indicated previously, sample contamination with respect to ^{14}C can arise from a number of sources, most notably, soil organic matter. It is essential that a pretreatment prior to plasma oxidation be employed to yield accurate ^{14}C dating results. Traditionally, sequential acid–base treatment of the sample has been applied to remove both inorganic and organic contaminants [2]. We believe that SFE with SC-CO_2–co-solvent mixtures can be utilized to eliminate naturally occurring matter prior to plasma oxidation.

2. Materials and methods

The actual archeological samples used in this study came from diverse sources. The fiber, charcoal, macro flora, and wood "SR" samples were obtained from the Stafford Research Laboratories in Lafayette, Colorado, and were of interest due to their known humic acid content. The Egyptian mummy samples consisted of wrappings of a Late Period Egyptian child mummy as well as a bovine mummy from the same time period – both enrobed in a linen gauze covered with some type of resin. Their respective ages determined by radiocarbon ^{14}C dating were between AD 137 and 227 for the child mummy and between BC 365 and 167 for the bovine mummy. The Russian textile sample was from the 4th International Radiocarbon Interlaboratory comparison standards. The Canopic jar contents were obtained from the collection at the Mabee-Gerrer Museum of Art in Shawnee, Oklahoma.

In our initial studies, wood/charcoal samples were selected to provide samples that were known to be heavily contaminated with humic acid. A modified-Isco SFX-2-10 extraction unit (Isco Inc., Lincoln, NE) was used for the reported experiments. We conducted experiments on four samples using supercritical carbon dioxide/10% methanol solvent mixture at a pressure of 20.4 MPa ($p_r = 2.80$) and 313 K ($T_r = 1.36$). The gas flow rate used was ~1.4 ± 0.1 mL/min. For the standard reference material, SR 5994, the extraction was run using a total volume of SC-CO_2 of 84 mL; for SR 5960, 108 mL; for SR 6097, 117 mL; and for SR 6101, 84 mL. As aliquots of these samples had already been treated by ABA, combusted, and radiocarbon dated, they were useful to compare to the SC-CO_2 results. After SFE, samples were oxidized using a plasma discharge at 20 W for 30 min. The collected CO_2 from the organic material in the artifact was sent to the Center for Accelerator Mass Spectrometry at the Lawrence Livermore National Laboratory (CAMS-LLNL) for graphitization and radiocarbon measurement.

The solubility parameter for a mixture of 10% methanol in SC-CO_2 at 20.4 MPa (3000 psig) and 313 K from theoretical calculations [24] is as follows: dispersion solubility parameter contribution is 10.59 $\text{MPa}^{1/2}$, the polar solubility parameter contribution is 5.31 $\text{MPa}^{1/2}$ and the hydrogen-bonding solubility parameter is 25.4 $\text{MPa}^{1/2}$, yielding an overall (total) solubility parameter of 17.16 $\text{MPa}^{1/2}$ or 8.56 $\text{cal}^{1/2}/\text{cc}^{3/2}$. This is similar in solvent strength to a non-polar solvent.

In a second series of experiments, an Isco SFX-2-10 (Isco, Lincoln, NE) extraction unit was employed. The extractor consisted of two Isco Model 100 DX pumps and a heated module for containing the stainless steel restrictor calibrated to deliver approximately 1.5 mL/min CO_2 (see Fig. 1). The extraction fluid consisted of 99.995% pure CO_2 from Air Gas–Specialty Gases (Tulsa, OK) used in conjunction with HPLC-Grade methanol from EMD Chemicals, Inc., Gibbstown, NJ. The capillary tubing serving as a restrictor was enclosed in a restrictor heater module set at 60 °C (333 K) to prevent precipitation of the extracted contaminants in the capillary as the temperature fell to ambient conditions. The Isco SFX-2-10 unit was consistently cleaned with the SC-fluid mixture between experiments in order to prevent cross contamination between samples as they were extracted.