

ABSTRACT

Sophia L. Carman. **THE EFFECT OF CONSERVATION TREATMENTS ON ORGANIC RESIDUES IN ARCHAEOLOGICAL CERAMICS.**

(Under the direction of Dr. Laura Mazow) East Carolina University, Department of Anthropology, May 2015.

Conservation treatments, while focused on preserving the physical form of a ceramic vessel, may inadvertently have a negative impact on other information stored in preserved organic residues that may remain on or in the object. This research investigates the effect of common conservation treatments on the preservation of organic residues in order to better understand how conservation treatments commonly used in the field and laboratory can affect the integrity of organic residues in archaeological ceramic sherds. Olive oil, an organic residue that is frequently found in the archaeological record of the Near East, was applied in an experimental setting to the surface of archaeological ceramic sherds. The sherds then underwent various conservation treatments, such as mechanical cleaning, soaking in water over various periods of time, and acid cleaning. Residue retention was quantified by organic extraction followed by gas chromatography-mass spectrometry (GC-MS) analysis. The results suggest that increasing the soaking time of a sherd in water decreases the amount of residue retained, and the addition of mechanical cleaning further reduces residue retention. The data gathered from this study can assist in predicting the condition of organic residues on ceramics based on previous conservation treatments and shed light on the integrity of organic residues on previously conserved objects.

**THE EFFECT OF CONSERVATION TREATMENTS ON ORGANIC RESIDUES IN
ARCHAEOLOGICAL CERAMICS**

A Thesis

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The Faculty of the Department of Anthropology

East Carolina University

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By

Sophia L. Carman

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ARCHAEOLOGICAL CERAMICS**

by

Sophia L. Carman

APPROVED BY:

DIRECTOR OF
THESIS: _____

Laura Mazow, Ph.D.

COMMITTEE MEMBER: _____

Susanne Grieve

COMMITTEE MEMBER: _____

Siddhartha Mitra, Ph.D.

COMMITTEE MEMBER: _____

Benjamin Saidel, Ph.D.

CHAIR OF THE DEPARTMENT
OF ANTHROPOLOGY: _____

I. Randolph Daniel, Jr., Ph.D.

DEAN OF THE
GRADUATE SCHOOL: _____

Paul Gemperline, Ph.D.

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1. Introduction

Archaeological conservation treatments are designed to preserve the structural integrity and appearance of a ceramic object for generations to come, including any information the object may contain (Appelbaum 2010; Caple 2000; Cronyn 1990; Muñoz Viñas 2005). Once a ceramic vessel is unearthed, both the artifact and the contained information continue to deteriorate until conservation treatments are implemented (Singley 1981) Although conservation treatments provide many benefits to the preservation of the object, they also have the potential to undermine the integrity of other types of information present on or in the vessel, such as organic residues.

Organic residue analysis by gas chromatography-mass spectrometry (GC-MS) is a method of chemically categorizing the composition of organic residues. Information provided by organic residue analysis has the potential of determining the contents and function of ceramic vessels (Charters et al. 1993; Jaeschke 1996), and can lead to inferences concerning the reconstruction of diets and subsistence practices of ancient societies (Charters et al. 1995; Copley 2005; Evershed 2008b; Evershed et al. 1994; Oudemans and Erhardt 1996).

Organic residues are usually found only in very small quantities or trace amounts in the archaeological record as they have undergone centuries of physical and environmental degradation (Evershed 2008b; Oudemans and Erhardt 1996). The small amount of organic residues preserved in ceramics poses a significant problem for conservators, as any chemical or physical modification that is the result of a conservation treatment has the potential to destroy, contaminate or alter the nature of the organic residues (Paterakis 1996; Strahan and Unruh 2002). If the organic residues are destroyed in the process of preserving the vessel's physical form, some of the information that the vessel could have provided is lost. The extent to which conservation treatments affect organic residues must be understood in order to effectively

conserve the object in its entirety. Therefore, there is a need to evaluate field conservation treatments and their impact on the sampling and analysis of organic residues.

The main goal of the present study is to analyze how commonly-used conservation treatments in the field and lab today affect the preservation of organic residues. A series of experiments were conducted on an assemblage of archaeological ceramics from Aqaba, Jordan, that were used as a proxy for clay materials typical of their region of origin, the Near East. A small amount of olive oil was applied to the surface of the ceramics to emulate an organic residue that is commonly identified in organic residue studies of Near Eastern ceramics. Conservation treatments, such as mechanical cleaning, water soaking for various durations of time, and hydrochloric acid cleaning, were then applied to the sherds. Subsequently, the remaining residue was first extracted and then analyzed by GC-MS analysis to quantify the amount of organic residue that remained on the surface of the sherds following each treatment. Residue recovery was used as a proxy to measure the impact of the treatments on the preservation of organic residues.

The conservation treatment that resulted in the greatest amount of residue retained was the 20-second soak in water, whereas the hydrochloric acid cleaning displayed the least amount of retained residue. The majority of conservation treatments demonstrated a reduced residue retention with the addition of subsequent mechanical cleaning. The results also suggest that increasing a sherd's soaking time in water decreases the overall amount of residue retained, with the greatest amount and rate of residue loss occurring during the first 20-seconds of soaking. After 1-hour of soaking in water, only a minimal amount and rate of residue loss was observed. Conclusions from this study may assist in predicting how commonly used conservation treatments may affect organic residue preservation.

2. Background

2.1 Archaeological conservation of ceramics

The goal of conservation is to address concerns about an artifact's state of preservation and employ the proper treatment to promote the stability and longevity. Determining which technique to use to treat a ceramic object is dependent on multiple factors, such as the object's material composition, factors of deterioration acting upon the object, and the overall goals for the object's preservation (Appelbaum 2007; Cronyn 1990). Every ceramic object exhibits differing combinations of these factors so that the treatment of an object needs to be tailored to its specific needs.

Different resources have served as guiding principles for proper conservation technique and practice. These include field conservation manuals (e.g. Sease 1994, 1999; Singley 1981), resources on conservation methodology and theory (e.g. Appelbaum 2010; Caple 2000; Cronyn 1990; Muñoz Viñas 2005), conservation science (e.g. Artioli 2010; Mills and White 1999; Oddy 1994; Stuart 2007), and the analysis, conservation, and reconstruction of ceramics (e.g. André 1976; Buys and Oakley 1993; Rice 1987). Conservators begin with these resources, but then rely on their own personal experiences and ethical perspective to further customize an object's treatment plan.

Conservation treatments for archaeological ceramics can vary in both duration and intensity. Some of the more basic treatments include mechanical cleaning by dry brushing or wet cleaning by washing or soaking ceramic sherds in water for varying amounts of time (Paterakis 1996; Sease 1999). Other more aggressive treatments to further clean the sherds and remove insoluble salts include chemical cleaning with dilute acids (Cronyn 1990; Singley 1981), such as aqueous solutions of nitric or hydrochloric acid (Sease 1994; Strahan and Unruh 2002). To

prevent flaking or cracking of the ceramic surface, the application of a dilute adhesive over areas of deterioration, a technique known as consolidation, is commonly used (Constâncio et al. 2010; Koob 1986). A more concentrated adhesive is used in the reconstruction of broken ceramic objects (André 1976; Buys and Oakley 1993). Preservation techniques also include object storage. Storage methods for ceramics can take many forms, but most commonly employ plastic (polyethylene) bags of varying sizes (Kariya and Peachey 1999).

These conservation treatments are in basic accord with a guiding principle of conservation known as ‘minimum intervention.’ This concept suggests that best practices should follow the least amount of conservation and handling needed to retain the stability of the object (Appelbaum 2010; Caple 2000; Cronyn 1990; Muñoz Viñas 2005). The minimum intervention approach suggests that conservators should strive to reveal as much information about the object while causing as little alteration as possible. It is, however, up to the conservator’s personal and ethical perspective to determine how this principle is best met by assessing proposed treatment and determine their necessity. In theory, this type of educated judgment should protect the object from loss of evidence due to over cleaning and unnecessary treatments.

2.2 Organic residue analysis

Although conservators seek to conserve the physical form of the vessel and the associated visible information, other forms of information that may not be visible to the naked eye, such as organic residues, may be negatively affected as a result. The identification of organic residues plays a key role in the interpretation of the archaeological record by providing information pertaining to a vessel’s contents and function (Beck et al. 2008a; Charters et al. 1993; Evershed et al. 2000; Jaeschke 1996; Regert 2007). This information can further be used to reconstruct subsistence practices and dietary habits of an ancient society (Charters et al. 1995; Copley 2005;

Evershed 2008b; Evershed et al. 1994; Hopkins and Armitage 2012; Malainey 2007; Oudemans and Boon 2007; Oudemans and Erhardt 1996). Organic residue analysis can assist in identifying these trace residues.

Commonly used in archaeological research today, organic residue analysis is used to identify the composition of organic compounds that may be present on the surface and/or absorbed into the matrix of archaeological ceramics (Artioli 2010; Charters et al. 1993, 1995; Copley et al. 2005; Evershed 1993, 2008a, 2008b; Evershed et al. 1990, 1992, 1994; Izzo et al. 2013; Mills and White 1999; Oudemans and Erhardt 1996; Paterakis 1996; Regert 2007; Stuart 2007). Surface residues can be obtained from a ceramic by surface sampling techniques, such as scraping the surface to remove burnt food remnants or swabbing the surface with a solvent to extract residues. Destructive sampling such as grinding a sherd into a fine powder is used to extract residues that have been absorbed into the ceramic matrix (Barnard et al. 2007).

Many analytical methods are used to examine organic residues in the archaeological record, such as thin layer chromatography (TLC), high-performance liquid chromatography (HPLC), high-temperature gas chromatography (GC), nuclear magnetic resonance spectroscopy (NMR), and others (Artioli 2010; Beck 2008; Mills and White 1999; Regert 2007; Stuart 2007). Gas chromatography-mass spectrometry (GC-MS), however, is substantially advantageous in the analysis of organic residues, as compounds in residues can be positively identified by the MS, yielding more accurate and detailed results than some of these other techniques (Beck and Stout 2008; Charters et al. 1993; Copley et al. 2005; Evershed 2008b; Evershed et al. 1994, 2000; Hopkins and Armitage 2012; Izzo et al. 2013; Oudemans and Erhardt 1996). Gas chromatography separates complex mixtures of organic compounds into molecules that the mass spectrometer ionizes and detects (Barnard et al. 2007). The final product of gas chromatography

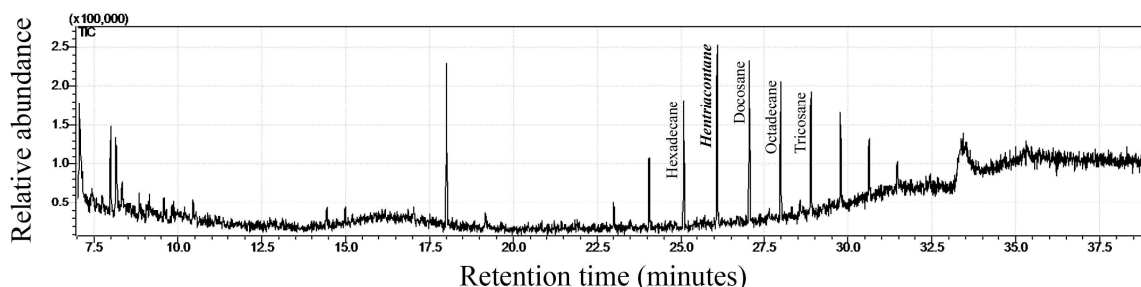


Figure 1. Example of a chromatogram (sherd #24, an extraction blank) displaying the identity of peaks.

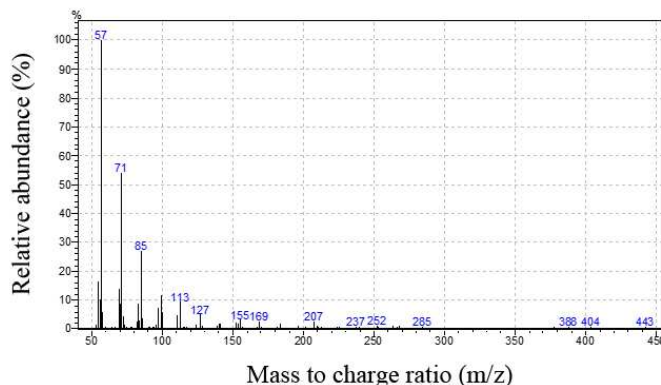


Figure 2. Mass spectrum of hentriacontane, a compound in the chromatogram of sherd #24 (see Figure 1).

is a chromatogram (Figure 1), which indicates the relative abundance of each detected molecule represented by a singular peak, and the time at which each molecule was detected, known as “retention time.” Each peak or target molecule has an associated mass fragmentation pattern (i.e. a histogram of the mass-to-charge ratio of that molecule - Figure 2) that is produced by the mass spectrometer. Target molecules are then accurately identified by comparing its mass spectra to similar spectra in a library database. By compiling information from the mass spectral signature and retention time of each detected molecule in the sample, the identity of preserved organic residues can be confirmed.

Much research has been conducted on residues that are commonly found in the archaeological record, such as lipids, carbohydrates, proteins, and other natural resins (Evershed 1993, 2008b; Oudemans and Boon 2007; Romanus et al. 2009). Lipids in particular exhibit unique chemical properties; their hydrophobic nature and strong chemical bonds enable them to

better withstand long-term degradation processes than other organic residues, and therefore they survive better in the archaeological record than other types of organics (Barnard et al. 2007; Charters et al. 1993; Evershed 2008a; Hopkins and Armitage 2012; Paterakis 1996). Ultimately, the association of an organic molecule with an artifact such as a sherd, is dependent on several factors. One of the most important of those factors is the extent to which that compound associates with the surface of the archeological artifact. Its removal over time can occur as a result of microbial degradation processes, or abiotic (physical and chemical) desorption processes, which are discussed below.

2.3 Sorption theory

Sorption theory can assist in understanding the relationship between organic residues and archaeological ceramics. Sorption is the process, physical or chemical, in which a substance becomes associated with a solid phase (Schwarzenbach et al. 1993). Organic residues become associated with ceramic sherds through two sorption processes: adsorption onto the two-dimensional surface of the sherd, and absorption into the three-dimensional matrix of the sherd (Figure 3).

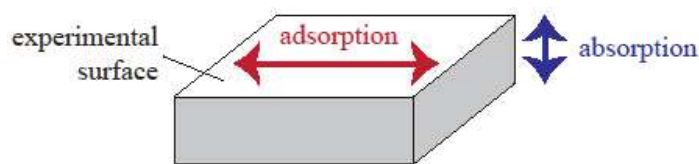


Figure 3. Illustration of the adsorption and absorption processes, whereby organic residues become associated with ceramic sherds.

Applying a conservation treatment to a ceramic sherd containing organic residues results in disrupting this sorption and facilitates desorption or abiotic removal from the surface of the sherd into its surrounding environment (Figure 4). Once the organic molecule is desorbed from the surface of the sherd, it can be readily mobilized away. The extent of desorption may be a

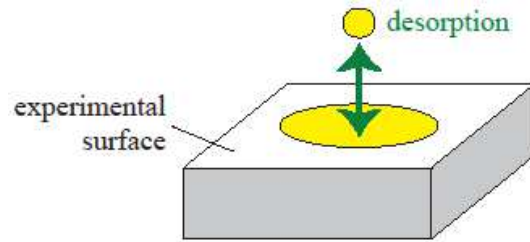


Figure 4. Illustration of the desorption process, whereby conservation treatments remove organic residues from ceramic sherds.

function of the conservation treatment being implemented. Thus, the goal of conservation should be to clean the surface of ceramics while minimizing desorption of organic residues.

2.4 Conservation treatments and organic residues

The trace amount of organic residue that is preserved in archaeological ceramics should be preserved by conservators who desire to use that information to supplement contextual archaeological information. However, any chemical or physical modification to the ceramic that is the result of a conservation treatment has the ability to destroy, contaminate or alter the nature of organic residues (Paterakis 1996).

Conservation techniques can also introduce contaminants into the sample that have the potential to alter the results of organic residue analysis or render organic residues unidentifiable. Although not assessed in this study, contamination can occur at various points and is often the result of improper handling or storage of an object (Martlew 2008). Factors such as oils from manual handling of objects, transportation in organic-rich substrates that leach organic polymers such as plastics, and inadequate storage environments (Beck et al. 2008a; Kariya and Peachey 1999; Sease 1999; Singley 1981) are examples of sources of contamination that interfere with extraction and accurate identification of target organic compounds from the artifact. For example, plasticizers (from plastic storage containers) are known contaminants that coelute with

target compounds and interfere with GC-MS peak interpretation of those compounds (Beck et al. 2008a, 2008b; Lattuati-Derieux et al. 2013; Mazow et al. 2014).

2.5 Significance of research

A major problem in using organic residue analysis in archaeology is that the opportunity to sample recently excavated objects may not always present itself. Objects may be distant geographically, or excavation regulations and restrictions may inhibit access. Additionally, objects may not come directly from a recently excavated archaeological site but from a museum where they have already undergone conservation treatments. Reexamination of artifacts is not uncommon, nor is it uncommon for organic residue samples to come from such previously conserved objects (Jaeschke 1996). It is therefore important that the effect of common conservation treatments on the preservation of organic residues be studied as understanding treatment impact would enable us to determine the likelihood of organic preservation on a conserved vessel before residue analysis is conducted. A better understanding of the impact of conservation treatments on the preservation of organics can also assist in determining best treatment practices that encourage the preservation of organic residues on archaeological ceramics.

Few scholars have addressed the issue of the post-excavation treatment of archaeological artifacts with specific reference to the preservation of organic residues. Paterakis (1996), Oudemans and Erhardt (1996), Martlew (2008), and Strahan and Unruh (2002) limit their discussion to avenues by which contamination and degradation can be introduced during the excavation process and problems that may arise in future analyses as a result of common conservation treatments. In these studies, they recommend that objects should not be treated and should be handled minimally if an object will undergo organic residue analysis.

2.6 Research hypotheses

The aim of this study is to investigate the impact of conservation treatments on organic residues on the surface of ceramics (for a full description of the conservation treatments used in this research, refer to section 3.4 *Applied conservation treatments*). As described above, while conservation treatments are designed to promote the preservation and longevity of objects and the information they contain, the effects of these treatments on organic residues have never been studied. Some conservation treatments are assumed be better for residue preservation than others. However, quantitative data do not exist validating those assumptions. Theoretically, some of the most common treatments used may have a negative effect on the preservation of organic residues. Thus, four hypotheses were proposed:

Hypothesis 1: All conservation treatments conducted on ceramics will on some level be destructive to organic residues.

Hypothesis 2: The 20-second soak in water treatment will have the least negative effect on the preservation of organic residues than any other water soaking time period.

Hypothesis 3: The acid cleaning treatment will have a more negative effect on the preservation of organic residues than any other conservation treatment.

Hypothesis 4: The addition of mechanical cleaning to any conservation treatment will have a negative effect on the preservation of organic residues.

3. Methodological Approach

3.1 Introduction

Experiments were conducted in a laboratory environment that replicate common field conservation treatments of ceramic objects that contain an organic residue. A known amount of a reference material was applied to the surface of archaeological ceramic sherds. These sherds then underwent specific conservation treatments. Once a treatment was performed, surface sampling was conducted on each sherd to obtain the any residue remaining on the surface of the sherd. Residue retention was assessed by organic extraction and subsequent analysis by gas chromatography-mass spectrometry (GC-MS). The resultant data were then evaluated to determine the extent to which the organic residues were affected by the conservation treatments.

Certain precautions were used to reduce the amount of contamination introduced into the experiment. First, all glassware used in this experiment, which includes beakers, pipettes, vials, and glass wool, was cleaned of organic residue by “ashing” (450 °C for 4-hours) prior to being used. Stainless steel forceps used to handle samples were wrapped in Teflon tape and then rinsed with acetone. All of the chemicals used, such as acetone, hexane, dichloromethane (DCM), and hydrochloric acid, were GC-MS grade. Finally, all water used in this experiment was distilled deionized (DDI) water.

3.2 Experimental materials

3.2.1 Archaeological ceramic sherds

Archaeological ceramic sherds used in this experiment were lent by Dr. S. Thomas Parker (North Carolina State University) and Dr. Megan Perry (East Carolina University) (Figure 5). These sherds were excavated from the 2003 field season at Aqaba, Jordan (4th-7th c. AD). For the present study, these sherds were used as a proxy for fired clay materials that are typical

of the Near East. The actual use-life of these sherds was not studied; the sherds functioned only as the experimental medium on which conservation treatments were conducted.

Approximately 100 sherds were chosen for analysis. This number accounted for multiple sherds to be used in the preliminary experiment, in each conservation treatment, as extraction blanks and controls, and included a few extra sherds if needed.



Figure 5. Archaeological sherds from Aqaba, Jordan.

Sherds were chosen from the Aqaba assemblage based on the following criteria:

- (1) *All sherds were fired.* Fired ceramics are relatively durable and very common in the archaeological record of the Near East. Conservation treatments are less commonly applied to unfired clay materials as any conservation work can jeopardize the structural integrity of an unfired clay object.
- (2) *All sherds were unglazed.* Glazed ceramics do not absorb organic residues in the same manner as unglazed ceramics. The glaze acts as a barrier to the underlying ceramic matrix, enabling a vessel to hold solids or liquids without permeation into the vessel's clay matrix. Unglazed ceramics do not necessarily prevent organic residues from being absorbed into the ceramic matrix, at least to some extent depending on the density of the ceramic matrix. The ceramic matrix, then, can sometimes preserve absorbed residues. It is the possibility of such preservation in post-conservation contexts that is being studied in this experiment. Thus only unglazed sherds were used.

- (3) *All sherds were from the vessel body.* A body sherd has the greatest surface exposure in comparison to a rim, base, or handle sherd, thus maximizing the experimental surface area.
- (4) *All sherds had a similar ceramic composition.* A consistent composition helped to standardize the experiment and enabled better comparative analysis in regards to absorption.
- (5) *All sherds had a surface area greater than or equal to $\sim 12 \text{ cm}^2$.* This minimum allowed for a sufficient amount of surface area for analysis.
- (6) *All sherds had not undergone any previous conservation treatments.* This includes any and all cleaning techniques or attempts at consolidation or reconstruction as these could introduce contaminants and irregularities into the experiment.

Pre-treatment documentation was conducted on each sherd. This included photographs and drawings of each sherd. The dimensions, weight, and ceramic ware was also noted.

3.2.2 Reference material

Commercial extra virgin olive oil (Napa Valley Naturals, Corte Madera, California) was the reference material used to emulate an organic residue for the purposes of this experiment. Since the sherd assemblage used in this study is from a Near Eastern context, olive oil was chosen because it has been found in great frequency in residue studies throughout the Near East (Foley et al. 2009; Hansson and Foley 2008; Romanus et al. 2009). Additionally, olive oil is a lipid and thus exhibits hydrophobic properties and has strong chemical bonds that enable it to preserve well in the archaeological record (Charters et al. 1993; Evershed 1993, 2008a, 2008b; Paterakis 1996).

3.2.3 Internal standard

The internal standard, 5 α -cholestane (Sigma-Aldrich, St. Louis, Missouri, Lot: 096K4068), was used in this research to monitor the experiment's extraction efficiency and assist in the quantification of the results produced by GC-MS analysis (see section 3.7 *Quantification*).

3.2.4 Application of reference material and internal standard

To emulate an organic residue, a glass Pasteur pipette was used to apply two droplets of olive oil (avg. 0.03 g, *SD* = 0.004 g) to the center of the interior surface of each sherd, referred to as the *experimental surface* (Figure 6). Each sherd was then briefly tilted in multiple directions to distribute the olive oil across the surface. Since only a small amount of



Figure 6. Sherd experimental surface with olive oil applied.

olive oil was used, the area of application remained small and centralized and did not coat the entire sherd surface. Once the olive oil was applied, a second glass pipette was used to place a single drop of 5 α -cholestane solution (the internal standard) in the center of the experimental surface on top of the olive oil. The sherds were then left to sit at room temperature inside the laboratory for 24-hours (see section 3.3 *Preliminary experiment*).

3.3 Preliminary experiment

A preliminary experiment was conducted in order to: (1) establish if residues can be extracted after the first sampling wipe; and (2) to assess differences in extraction efficiency as

the duration of time between the application of the reference material and conservation treatments increased.

Three sherds were randomly selected from the ceramic assemblage. Olive oil and 5 α -cholestanone were applied to each sherd following the procedure detailed in section 3.2.4 *Application of reference material and internal standard*. Surface sampling was conducted on each sherd using two glass wool swabs that each contained a cocktail of acetone (Mallinckrodt Chemicals, Phillipsburg, New Jersey, Lot: E11E61) and hexane (Fisher Scientific, Fair Lawn, New Jersey, Lot: 104751) (1:1, v/v). The cocktail was applied to the first swab (first wipe) which was then wiped for 10-seconds in a back-and-forth motion across the experimental surface of the sherd with a pair of forceps and then placed in a vial. The second swab (second wipe) was saturated with the same cocktail and then applied to the sherd after which it was placed in a second vial. This was done for each of the three sherds, totaling six samples—three from the first wipe of each of the three sherds and three from the second wipe of each of the three sherds. By separating the swabs from the first and second wipes of each sherd, the extraction efficiency of each wipe was able to be analyzed (first goal of the preliminary experiment).

To assess the second goal of the preliminary experiment, each of the three sherds' set of swabs, which includes the swabs from both the first and second wipes, were left to sit for 24-hours, 8-days, and 14-days, respectively, before undergoing organic extraction and GC-MS analysis. For example, both swabs from the first and second wipes of the first sherd were left to sit for 24-hour, whereas the swabs from the second sherd were left to sit for 8-days, and the swabs from the third sherd were left to sit for 14-days. These time periods simply reflect different and increasing time periods between the application of the olive oil and 5 α -cholestanone.

The results of this preliminary experiment demonstrated that the second wipe also extracted residue but to a lesser extent than the first wipe (Table 1). Thus, in order to ensure that a large amount of residue was extracted, it seemed advantageous to wipe the experimental surface of each sherd multiple times.

Table 1. Preliminary experiment data.

	Sherd #	Peak area of squalene		
		Wipe 1	Wipe 2	Total
<i>1-day</i>	2	1061052	1178223	2239275
	16	385680	126912	512592
	82	*	*	-
	<i>Total</i>	<i>1446732</i>	<i>1305135</i>	<i>2751867</i>
<i>8-days</i>	1	196859	*	196859
	45	912483	783212	1695695
	64	*	76019	76019
	<i>Total</i>	<i>1109342</i>	<i>859231</i>	<i>1968573</i>
<i>14-days</i>	33	316644	67607	384251
	44	171874	238614	410488
	50	88450	90220	178670
	<i>Total</i>	<i>576968</i>	<i>396441</i>	<i>973409</i>

*Indicates no data available.

The results of this preliminary experiment also demonstrated that as time increased, the amount of residue extracted decreased. Specifically, the sherds that were left to sit for 24-hours had a greater amount of residue extracted than those with a greater time interval. These results can most likely be attributed to the olive oil sorbing further into the ceramic matrix as time increased. While an even longer time interval more closely resembles residues in an archaeological context, the objective of this research beyond the preliminary experiment is to analyze the effect of conservation treatments on organic residues on the surface of ceramics, not to test the effect of time on the extraction efficiency of organic residues. By choosing the time interval that yielded the greatest amount of residue, extraction efficiency could be maximized and data trends in this research could be made more apparent. In addition, the short wait time suggests that the extracted residues are not those that have been absorbed into the ceramic

matrix, but rather those that remain on the surface, which are the ones that this research aims to study. Therefore, in order to maximize extraction efficiency, the sherds used in this research were left to sit for 24-hours between the application of the reference material and conducting the conservation treatments in order to limit the amount of olive oil absorbed.

3.4 Applied conservation treatments

In this study, mechanical cleaning, wet cleaning, and chemical cleaning were chosen to be analyzed as they emulate common conservation treatments used on archaeological ceramics. The conservation treatments studied here derive from common practices described in the literature on the conservation of ceramics (e.g. Cronyn 1990; Paterakis 1996; Sease 1994). The experiments were designed to analyze each potential step in the conservation process of ceramics in order to view the effect of each treatment on the organic residue.

Each treatment listed below was conducted on a set of three sherds that were randomly selected from the assemblage, after olive oil and 5 α -cholestane was applied to the sherds as detailed above.

The conservation treatments (Table 2) studied here include:

Table 2. Design matrix of conservation techniques.

Treatment	None	Mechanical cleaning
None	<i>Control</i>	<i>A.</i>
20-sec soak in water	<i>B.</i>	<i>C.</i>
1-hr soak in water	<i>D.</i>	<i>E.</i>
24-hr soak in water	<i>F.</i>	<i>G.</i>
Acid (HCl) cleaning	<i>H.</i>	<i>I.</i>

A. Mechanical cleaning. Sherds were mechanically cleaned (also referred to as “brushing”) by using a toothbrush (Sease 1994) to brush the experimental surface in a circular motion for 10-seconds. This time period replicates the average amount of time used to brush loose sediment from a ceramic surface as observed from personal field experience

throughout the years. The same brush was used throughout the experiment. In between the treatment of each sherd, the brush was rinsed with DDI water and dried with Kimwipes to prevent the transfer of any residue from one sherd to the next.

- B. Wet cleaning by submersion in water for 20-seconds.* Sherds were placed in individual glass beakers that were filled with 300 mL of DDI water. This quantity of water ensured that every sherd was fully submerged. After a 20-second soak, the sherds were removed with forceps. The treatment and soaking time replicates a field situation where it is desirable to only briefly wet a sherd to remove surface sediment. An example of when this treatment might be used would be with Iron Age II ceramic assemblages where there is a possibility that some of the sherds may be ostraca (writings in ink on pottery sherds) (Laura Mazow, personal communication, February 1, 2015). It has been assumed that this short-term wet cleaning would remove extraneous soil particles that obstruct the view of the ceramic surface but would not damage the ink inscription.
- C. Wet cleaning by submersion in water for 20-seconds, followed by mechanical cleaning.* Sherds underwent the same 20-second submersion procedure described in treatment B, immediately followed by mechanical cleaning as described in treatment A. This combination of treatments replicates a situation where the surface sediments were not fully removed by a quick rinse in water and required further mechanical cleaning.
- D. Wet cleaning by submersion in water for 1-hour.* Sherds were placed in individual glass beakers, which were filled with 300 mL of DDI water. After a 1-hour soak, they were removed with forceps. This treatment and soaking time replicates a situation where soaking sherds with well adhered surface sediments in water for a longer time could result in their easier removal.

E. *Wet cleaning by submersion in water for 1-hour, followed by mechanical cleaning.*

Sherds underwent the same 1-hour submersion procedure described in treatment D, immediately followed by mechanical cleaning as described in treatment A. This combination of treatments replicates a situation where many sherds are placed into a bucket of water and removed individually to be mechanically cleaned (personal experience, Pompeii Archaeological Research Project: Porta Stabia, Italy).

F. *Wet cleaning by submersion in water for 24-hours.* Sherds were placed in individual glass beakers, which were filled with 300 mL of DDI water. After a 24-hour soak, they were removed with forceps. This treatment and soaking time replicates a situation where a long-term soak in water is desirable, for example, to loosen extraneous surface sediment that may not have been removed by shorter soaking time periods.

G. *Wet cleaning by submersion in water for 24-hours, followed by mechanical cleaning.*

Sherds underwent the same 24-hour submersion procedure described in treatment F, immediately followed by mechanical cleaning as described in treatment A. This combination of treatments replicates a situation where sherds were soaked for 24-hours and subsequently removed to be mechanically cleaned (personal experience, Hesi Regional Project: Khirbet Summeily, Israel).

H. *Chemical cleaning with 5% (aq) hydrochloric acid.* This treatment (also referred to as ‘acid cleaning’), which uses acid to remove extraneous surface sediment, follows the procedure described by Sease (1994). Sherds were first soaked in deionized water for 1-hour, following the procedure detailed in treatment D, to enable the ceramic matrix to absorb water (Sease 1994). As Sease (1994) states, “This soaking prevents the acid from being pulled deep into the fabric of the pottery” (80). Following the water soak, the

sherds were soaked in a 5% (aq) hydrochloric acid solution for 5-minutes. A concentrated hydrochloric acid (Alfa Aesar, Ward Hill, Massachusetts, Lot: H19Z031) was diluted to make a 5% acid solution. The 5-minute time period was chosen as long enough to loosen the extraneous surface sediment but short enough to not cause damage to the sherd itself. After the 5-minute soak in the acid solution, the sherds were removed with forceps and placed in a beaker of DDI water for 20-seconds to rinse any remaining acid solution from the sherd.

I. Chemical cleaning with 5% (aq) hydrochloric acid, followed by mechanical cleaning.

Sherds underwent the same acid procedure described in treatment H, immediately followed by mechanical cleaning as described in treatment A. This treatment and soaking time replicates a potential situation where tough surface sediment or insoluble salts require additional mechanical cleaning to be removed following an acid cleaning treatment.

It should be noted that although other conservation treatments such as consolidation and reconstruction are commonly used, they were not analyzed in this research. This was due to the negative effects that the adhesives used in such treatments would have on the gas chromatograph-mass spectrometer that could cause significant instrument damage.

3.5 Blanks and controls

Three sherds were randomly chosen to serve as extraction blanks. The extraction blanks did not have any olive oil or 5 α -cholestane applied to the experimental surface, nor were any conservation treatments conducted on them. The compounds in the chromatograms of the extraction blanks are representative of the organic material originally present on the archaeological sherd (see Figure 1). Because the focus of this research was the recovery of olive

oil and 5 α -cholestane, the presence of these compounds were not relevant to this research. These extraneous compounds did not affect the study of the reference material and internal standard.

Six sherds were randomly chosen to serve as a treatment control. The treatment control did have both olive oil and 5 α -cholestane applied to the experimental surface of each of the six sherds in accordance as described earlier. However, no conservation treatments were applied to them.

3.6 Sampling, extraction and analysis by GC-MS

3.6.1 Sampling of sherds

Surface sampling, as opposed to destructive sampling techniques, was used in this research. Although destructive sampling is more commonly used in organic residue analysis, the method's negative impact on the studied artifact was at odds with basic principles in conservation concerned with preserving the artifact in its entirety. Therefore, surface sampling was the preferred technique as it more closely fits with the concepts and goals of conservation, where the destruction of any aspect of an object is greatly discouraged.

Surface sampling was conducted on each sherd using sampling procedures adapted from the preliminary experiment (see section 3.3 *Preliminary experiment*). In order to ensure a more robust extraction efficiency, the number of swabs was increased from two to four and each swab contained either acetone or hexane to maximize the amount of residue extracted. Thus a total of four glass wool swabs were used to sample each sherd: two with acetone and two with hexane. First a swab with acetone was wiped across the experimental surface of the sherd with a pair of forceps in a back-and-forth motion for 10-seconds, then a swab with hexane was used in the same manner. This procedure was followed a second time on the same experimental surface. All four swabs were collected together in a vial.

3.6.2 Organic extraction

The samples of glass wool swabs from each sherd were combined and extracted using 15 mL of a solvent cocktail solution of hexane and acetone (1:1, v/v) while sitting at room temperature for 24-hours. Swabs were then removed from the vial and discarded. The remaining organic extract was concentrated to a small volume (~1 mL) by rotary-evaporation. The residual solvent was then reconstituted with ~1 mL of DCM (J. T. Baker, Center Valley, Pennsylvania, Lot: K29S10) and transferred to a storage vial for analysis.

3.6.3 Gas chromatography-mass spectrometry (GC-MS)

All samples were analyzed for trace organic molecular signature on a Shimadzu QPP5050A gas chromatograph-mass spectrometer (GC-MS) equipped with a Restek Rxi-5Sil MS 30m column (0.25 mm film thickness and 0.25 mm inner diameter). For every analysis, approximately 2 μ L of sample was injected into the GC-MS with the MS set in scan mode. Injector temperature was set at 250 $^{\circ}$ C, with an initial column temperature of 50 $^{\circ}$ C held for one minute. The oven was ramped at 10 $^{\circ}$ C min^{-1} until 150 $^{\circ}$ C, then 8 $^{\circ}$ C min^{-1} until 310 $^{\circ}$ C and held for 20-minutes. The mass spectrometer's interface was set to 310 $^{\circ}$ C. The total flow of helium, the carrier gas, was 22 mL min^{-1} .

3.7 Quantification

The chromatograms illustrate the relative abundance of olive oil, the reference material, and 5 α -cholestane, the internal standard (Figure 7; Appendix 1). 5 α -cholestane appears in the

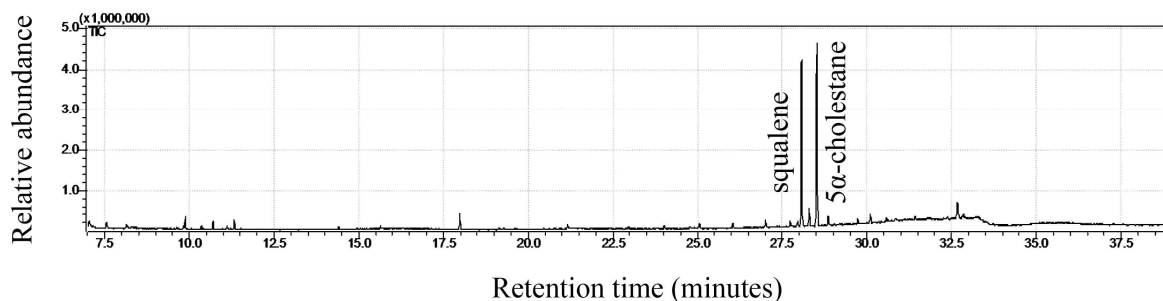


Figure 7. Chromatogram of sherd #75 (an extraction control) displaying the squalene and 5 α -cholestane peaks.

chromatogram as a singular peak. The many different compounds which make up olive oil appear as individual peaks; the most abundant component is squalene and was therefore used in this research as the identifying marker for olive oil. The relative abundance of each compound needed to be converted into a mass so as to quantify the amount of 5α -cholestane and squalene remaining on the surface of the sherd post-conservation treatment.

First, the peak area of 5α -cholestane was quantified as a mass through a series of dilutions and linear regression analysis. To accomplish this, a series of dilutions of 5α -cholestane of varying concentrations were prepared and analyzed by GC-MS. Since the concentration of each 5α -cholestane dilution was known, each dilution was therefore associated with a specific peak area as displayed in each chromatogram (Figure 8). From this information, the peak area and concentration of each 5α -cholestane dilution was plotted in a graph, a linear regression line was drawn, and the associated linear regression equation was calculated. Since the peak area of

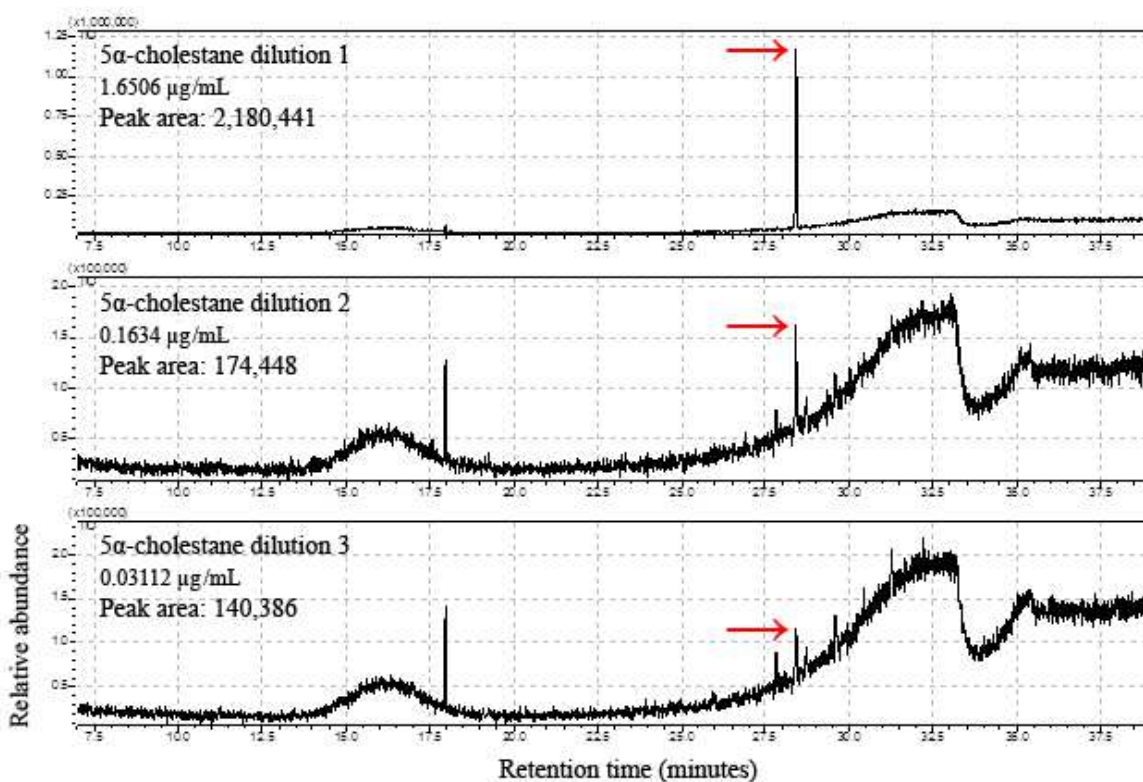


Figure 8. Chromatograms of 5α -cholestane dilutions displaying their concentration and peak areas. The 5α -cholestane peak is indicated by the arrow.

5 α -cholestane is known (from the chromatogram), that equation can be used to calculate the mass of squalene (the unknown target compound) associated with its peak area (Figure 9).

From the known concentration of 5 α -cholestane, a series of calculations were used to quantify the peak area of squalene into a concentration (see Appendix 2 for full details and an example calculation). The calculations took into consideration many experimental variables, including the amount of olive oil initially applied to the surface of each sherd, the amount of total extract obtained from organic extraction, the density of the solvents used in the extraction, and the volume of sample injected into the GC-MS. The resulting concentration of squalene ($\mu\text{g sq./g}$ oil) was interpreted as the remaining surface residues recovered from the experimental sherd after a conservation treatment was conducted.

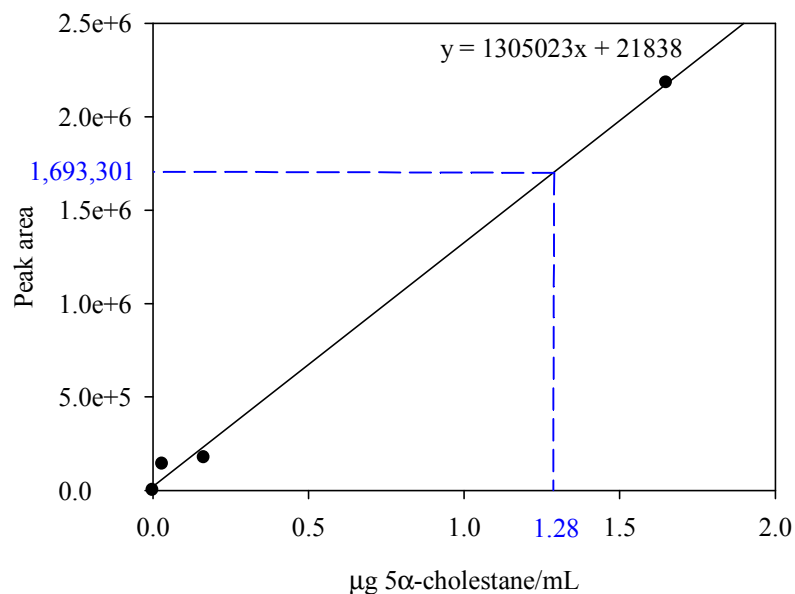


Figure 9. Linear regression plot displaying the concentration and peak area of 5 α -cholestane. The values in blue demonstrate the use of linear regression to predict the concentration of 5 α -cholestane from the peak area (sherd #4).

4. Results

4.1 Extraction controls

GC-MS analysis of the six controls revealed three outliers in the data which were not considered in the study (Table 3). The three remaining controls represent the closest values to both the mean and median of the data.

Table 3. Concentration of squalene ($\mu\text{g sq./g oil}$) in controls.

Sherd 13	Sherd 32	Sherd 41	Sherd 49	Sherd 75	Sherd 92
345.19*	386.68 [^]	31.37*	252.21 [^]	206.27 [^]	6.66*

* Indicates an outlier.

[^] Indicates an experimental control used in data analysis

4.2 Variation in extraction efficiency

In general, the concentration of residue recovered from each sherd varied with conservation treatment (Figure 10; Appendix 3). This demonstrates that each conservation treatment had a different effect on the preservation of organic residues.

The three sherds within each treatment group generally displayed similar concentrations of squalene recovered, but variation was also observed (Table 4). The conservation treatments that demonstrated similar extraction efficiencies, as indicated by a relatively low standard deviation (i.e. $\text{SD} < 15 \mu\text{g sq./g oil}$), included the 24-hour soak in water ($\text{SD} = 14.89 \mu\text{g sq./g oil}$), the acid cleaning ($\text{SD} = 11.69 \mu\text{g sq./g oil}$), and the acid cleaning with subsequent brushing ($\text{SD} = 4.99 \mu\text{g sq./g oil}$). Two conservation treatments, however, displayed a relatively high standard deviation (i.e. $\text{SD} > 100 \mu\text{g sq./g oil}$): the brushing treatment ($\text{SD} = 125.23 \mu\text{g sq./g oil}$) and the 1-hour soak in water ($\text{SD} = 101.80 \mu\text{g sq./g oil}$).

Figure 11 displays the average concentration of squalene recovered from the sherds for each conservation treatment. The brushing treatment displayed the greatest extraction efficiency on average ($192.69 \mu\text{g sq./g oil}$). In contrast, the hydrochloric acid cleaning treatment demonstrated the lowest extraction efficiency on average ($30.33 \mu\text{g sq./g oil}$).

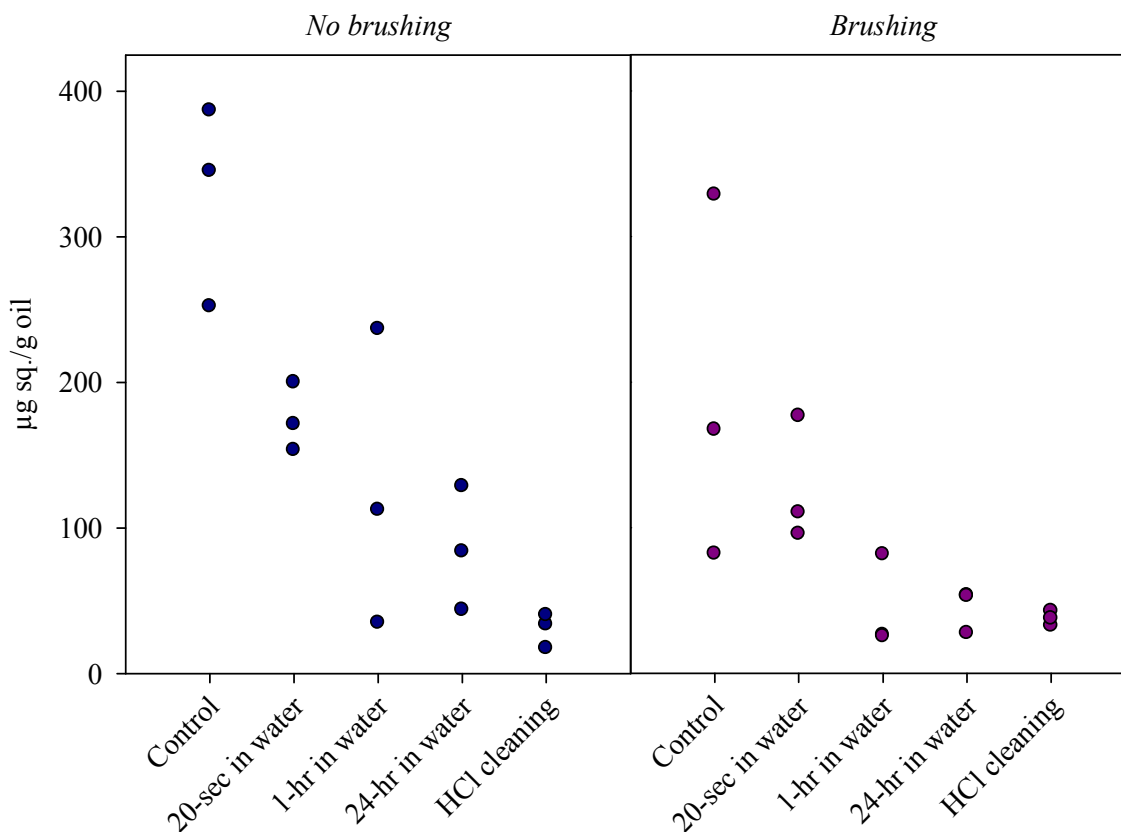


Figure 10. Concentration of squalene ($\mu\text{g sq./g oil}$) per sherd, comparing non-brushed and brushed sherds groups. The conservation treatments are arranged by the average concentration of squalene, greatest to least.

4.3 Effect of soaking time in water

A trend between squalene recovered and the sherds' soaking time in water during wet cleaning is apparent: as the soaking time in water increased from 20-seconds, to 1-hour, to 24-hours, the extraction efficiency decreased (Figure 12).

Table 4. Concentration of squalene ($\mu\text{g sq./g oil}$) per sherd.

Treatment	Sherd A	Sherd B	Sherd C	Mean	Std. Dev.
Control	345.19	386.68	252.21	328.03	68.86
Control*	167.27	328.69	82.12	192.69	125.23
20-sec water	171.10	153.40	199.98	174.83	23.52
20-sec water*	110.45	176.71	95.72	127.63	43.14
1-hr water	34.82	236.62	112.26	127.90	101.80
1-hr water*	26.29	81.66	25.46	44.47	32.21
24-hr water	128.58	43.70	83.74	85.34	42.46
24-hr water*	27.45	53.49	52.99	44.64	14.89
HCl	33.61	40.04	17.35	30.33	11.69
HCl*	32.65	42.63	37.63	37.63	4.99

* Indicates the addition of mechanical cleaning.

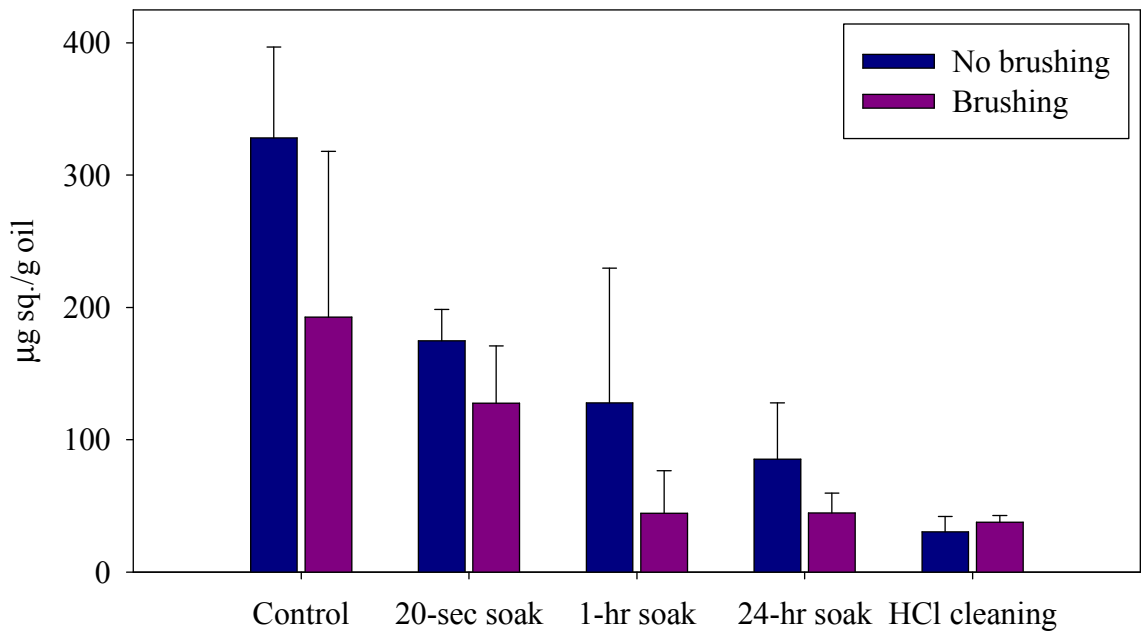


Figure 11. Average concentration of squalene ($\mu\text{g sq./g oil}$) per conservation treatment. The treatments are arranged by the average concentration of squalene, greatest to least.

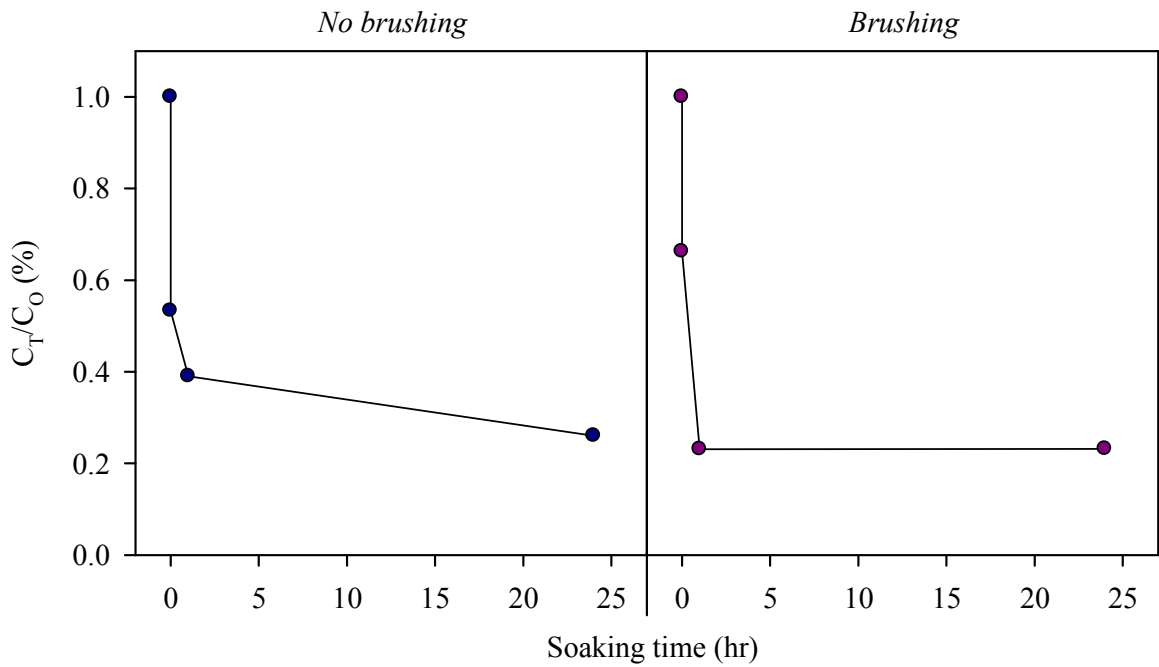


Figure 12. Average percentage of the control's concentration (C_0) that is changing as a function of the sherd's soaking time in water (C_T), comparing non-brushed and brushed sherd groups.

Table 5 displays the residue recovered from one treatment to the next. In the non-brushed group of sherds, the soaking period that demonstrated the greatest average extraction efficiency was the 20-second soak (174.83 $\mu\text{g sq./g oil}$). The extraction efficiency decrease over the next hour (127.90 $\mu\text{g sq./g oil}$), and the lowest extraction efficiency was observed in the 24-hour soaking interval (85.34 $\mu\text{g sq./g oil}$). The brushed sherd group demonstrated a similar trend, with the greatest extraction efficiency among the soaking time intervals was observed in the 20-second soak (127.63 $\mu\text{g sq./g oil}$), which decreased over the next hour (44.47 $\mu\text{g sq./g oil}$), and was relatively unaffected by additional soaking time to 24-hours (44.64 $\mu\text{g sq./g oil}$).

Table 5. Average concentration of squalene per water soaking time interval.

Treatment	Time (hr.)	Average squalene ($\mu\text{g sq./g oil}$)		Slope ($\mu\text{g sq./g oil hr}^{-1}$)	C _t /C _o (%)
		Mean	Loss		
Control	0	328.03	0	-	100%
20-sec soak	0.0056	174.83	-153.20	-27357.14	53.30%
1-hr soak	1	127.90	-46.93	-47.19	38.99%
24-hr soak	24	85.34	-42.56	-1.85	26.02%
Control*	0	192.69	0	-	100%
20-sec soak*	0.0056	127.63	-65.07	-11617.86	66.24%
1-hr soak*	1	44.47	-83.15	-83.63	23.08%
24-hr soak*	24	44.64	0.17	0.0074	23.17%

* Indicates the addition of mechanical cleaning.

The difference in residue recovery from one soaking time interval to the next was not the same between the brushed and non-brushed sherd groups. A decrease in residue recovered was observed in the non-brushed sherd group. Within this group, the greatest reduction in residue recovery occurred in the first 20-seconds of submersion in water (-153.20 $\mu\text{g sq./g oil}$). A less dramatic reduction occurred between 20-seconds and 1-hour (-46.93 $\mu\text{g sq./g oil}$). Finally, a loss of -42.56 $\mu\text{g sq./g oil}$ occurred from 1-hour to 24-hours. The group of sherds that were brushed display a slightly different trend to what was observed in the non-brushed sherd group. The first 20-seconds that a sherd was submerged in water demonstrated the second greatest reduction in residue recovery within this group (-63.07 $\mu\text{g sq./g oil}$), while the greatest reduction in residue

recovery occurred between 20-seconds and 1-hour (-83.15 $\mu\text{g sq./g oil}$). In contrast, a slight increase in residue recovery occurred between 1-hour and 24-hours (0.17 $\mu\text{g sq./g oil}$).

The greatest rate of residue loss occurred in the first 20-seconds of the soaking process and is apparent in both the non-brushed (-27357.14 $\mu\text{g sq./g oil hr}^{-1}$) and brushed (-11617.86 $\mu\text{g sq./g oil hr}^{-1}$) sherds groups. This rate of loss is notably larger than longer soaking periods. Between 20-seconds and 1-hour of soaking time, the rate dramatically decreased to -47.19 $\mu\text{g sq./g oil hr}^{-1}$ with the non-brushed sherds, and -83.63 $\mu\text{g sq./g oil hr}^{-1}$ with the brushed sherds. This rate continued to decrease to -1.85 $\mu\text{g sq./g oil hr}^{-1}$ with the non-brushed sherds between 1-hour and 24-hours, and almost completely ceased with the brushed sherds (0.0074 $\mu\text{g sq./g oil hr}^{-1}$).

4.4 Effect of mechanical cleaning (brushing)

Table 6 displays the difference in average squalene concentration between sherds that underwent brushing compared to those that did not, grouped by conservation treatment. Generally, brushing a sherd resulted in a negative effect on residue recovery, with the exception of hydrochloric acid cleaning (see Figure 11). The greatest difference in residue recovery between brushed and non-brushed sherds was the control group ($M_{diff} = 135.33 \mu\text{g sq./g oil}$), whereas the smallest difference was demonstrated by the hydrochloric acid cleaning ($M_{diff} = -7.30 \mu\text{g sq./g oil}$).

Table 6. Average concentration of squalene ($\mu\text{g sq./g oil}$).

Treatment	No brushing	Brushing	Difference (M_{diff})
Control	328.03	192.69	135.33
20-sec water	174.83	127.63	47.20
1-hr water	127.90	44.47	83.43
24-hr water	85.34	44.64	40.70
HCl	30.33	37.63	-7.30

5. Discussion

The results of this study were derived from a laboratory setting and are not necessarily reflective of the way organic residues behave in an archaeological context. Further research building off this study should test its applicability in an archaeological context. The results of this study do, however, have implications for the study of archaeological residues preserved on excavated ceramics. The results presented in this study can be extrapolated to residues in an archaeological context where residues are found in far more trace amounts, posing an even greater threat to the integrity of organic residues. In this sense, the results are relevant to archaeologists and conservators alike.

5.1 Desorption and the robustness of conservation treatments

As previously stated, the application of a conservation treatment is a desorption process that affects organic residues (see Figure 4). The extent to which a conservation treatment removes, or desorbs, residues from a sherd can be defined as the robustness of a treatment. The results of this research suggest that increasing the robustness of a treatment will facilitate greater desorption of organic residues. For this reason, the conservation treatments analyzed in this research can be ranked on an increasing scale of manipulation.

For example, the brushing treatment displayed the greatest residue recovery on average and therefore can be considered the least robust treatment analyzed in this research. The hydrochloric acid cleaning treatment, on the other hand, demonstrated the lowest residue recovery on average and can be considered the most robust treatment analyzed in this research. In terms of the water soaking treatments, the data suggests that increasing a sherd's soaking time in water, increases residue desorption and decreases residue recovery. Therefore, increasing the sherd's soaking time in water increases the treatment's robustness.

5.2 Effect of water on residue retention

5.2.1 Water soaking time intervals

The data suggests that as a sherd's soaking time in water increases, the amount of residue recovered decreases. Residue loss did not, however, occur at the same rate in these water soaking treatments. This trend is apparent in both brushed and non-brushed sherd groups.

The 20-second soak in water treatment not only displayed the profound reduction in residue recovery relative to other soaking time intervals, but also demonstrated the greatest rate of residue loss. Over the course of 20-seconds, more residue was washed away and at a quicker rate than any other time interval. The implications of this result is that even a quick rinse can have a dramatic effect on the integrity of organic residues.

Sherds that are soaked for 1-hour will also sustain the initial loss of residue seen in the 20-second interval and continue to lose residue for the duration of the 1-hour period. Beyond 1-hour, the amount and rate of residue loss can be considered minimal. These observations indicate that soaking a sherd for any period of time beyond 1-hour will have a minimal effect on extraction efficiency. In other words, the majority of residue loss will occur within the first hour of soaking, and any additional soaking time will only have a minor effect, if any, on the recovery of residues.

5.2.2 Water soaking and hydrochloric acid cleaning

The conservation treatment that retained the least amount of residue on average was the hydrochloric acid cleaning without the addition of brushing. Since the acid cleaning treatment is designed to remove insoluble salts from the surface of ceramics (Sease 1994), it is not difficult to recognize that the acid would not assist in the preservation of organic residues. This result

demonstrates that even a dilute acid can have a negative effect on the preservation of organic residues and residue recovery.

The acid cleaning treatment used in this study was a compilation of conservation treatment as it required a sherd to be soaked in water prior to acid cleaning and rinsed with water afterwards. Since this research demonstrated that both the 20-second and 1-hour soak in water treatments resulted in residue loss, the use of multiple treatments was also a prominent factor in the loss of residue that occurred in the acid cleaning treatment.

5.3 Mechanical cleaning

The majority of the conservation treatments demonstrated a reduction in the amount of residue recovered from sherds that were brushed over those that had not been brushed, with the exception of the hydrochloric acid treatment. This can be attributed to the brushing action removing some surface residue and possibly redistributing other residue across the sherd's surface.

The hydrochloric acid cleaning treatment group, on the other hand, displayed the smallest difference in residue recovery with brushed sherds than non-brushed sherd. The minimal effect of mechanical cleaning on residue retention in the acid cleaning treatment can be attributed to the acid cleaning process itself. The dilute acid likely removed the majority, if not all of the residue from the sherd's surface, with only the absorbed residue just below the surface remaining. These absorbed residue would not have been affected by brushing, since brushing is a method of surface cleaning. If no residue is present on the surface of a sherd after acid cleaning, it is not surprising that the effects of the addition of brushing was not necessarily observed in the data presented here.

5.4 Testing research hypotheses

5.4.1 Hypothesis 1

Hypothesis 1 stated that “all conservation treatments conducted on ceramics will on some level be destructive to organic residues.” The results from this research demonstrated that every conservation treatment had a reduction in residue recovery that varied by amount and rate. From a literal perspective, it is possible to order the conservation treatments analyses in this research from most to least destructive. This ranking, however, may not be relevant to ancient residues that are in varying states of preservation and abundance in the archaeological record. The important point to take away from this study is that any treatment applied to archaeological ceramics has the potential to remove organic residues from the object.

5.4.2 Hypothesis 2

Hypothesis 2 stated that “the 20-second soak in water treatment will have the least negative effect on the preservation of organic residues than any other water soaking time period.” This hypothesis was demonstrated to be true in that the 20-second soak in water treatment recovered the most residue when compared to other water soaking time intervals, but false in that this treatment displayed the greatest rate of residue loss than other time intervals. Thus, the 20-second soak in water treatment was the most destructive time interval to organic residues.

5.4.3 Hypothesis 3

Hypothesis 3 states that “acid cleaning treatment will have a more negative effect on the preservation of organic residues than any other conservation treatment.” This hypothesis has demonstrated to be true for multiple reasons. First, this treatment was a compilation of multiple conservation treatments, all of which were shown to have a negative effect on the preservation of

organic residues. Second, it was demonstrated that the majority of residues will be lost in the first hour of soaking in water, which is the treatment that sherds underwent prior to being soaked in the acid solution. Third, the acid solution removed most of the residues from the surface of the sherd, and therefore had a very negative effect on residues. These factors combined led to the hydrochloric acid cleaning treatment recovering the least amount of residue and demonstrating the greatest residue loss.

5.4.4 Hypothesis 4

Hypothesis 4 states that “addition of mechanical cleaning to any conservation treatment will have a negative effect on the preservation of organic residues.” This hypothesis is, for the most part, true. The ambiguity is introduced by the hydrochloric acid cleaning treatment that displayed similar amounts of residue extracted from brushed and non-brushed sherds. The small difference (discussed in section 5.2 *Mechanical cleaning*) has been attributed to the acid removing residues from the sherd’s surface, so additional brushing would not have an effect. Apart from this treatment, all other treatments analyzed in this study are in accordance with *Hypothesis 4* as true.

5.5 Assessment of experimental procedure and results

The precision of the results as indicated by the relatively low standard deviation within most of the treatment groups suggest that consistency in the sampling techniques and efficiency in the extraction process. Thus it is unlikely that the data reflect experimental error and likely that the results are accurate.

In addition, the hydrophobic properties of lipids, such as olive oil, may have played a key role in the relatively high degree of residue preservation, as lipids would not have been easily

washed off with water. The results of these experiments might be different if the organic residue was a compound that is soluble in water.

5.5.1 Sources of error

The two treatments that indicated a relatively high standard deviation (i.e. brushing control and 1-hour soak in water) may have been a reflection of experimental error even though the same error is not necessarily demonstrated in other treatments. Such error could have been introduced at any point during the treatment, sampling, or extraction process. Pre-existing dirt or other obstruction on the surface of the sherds also could have caused variation in the results within a treatment group.

The density of the ceramic matrix almost certainly played a role in extraction efficiency. Although some attempt was made to control for density in choosing the sherd assemblage, it is possible that there was some variation in density and that the denser the ceramic matrix of the sherd, the less residue that could be absorbed into the matrix. This decrease in absorption may have forced more residue to remain on the surface of the sherd that was then manipulated by the various conservation treatments. Alternatively, sherds with a matrix that was less dense may have absorbed more residues and therefore surface sampling was less effective. Ceramic density, therefore, must be taken into consideration when conducting surface sampling.

5.6 Future research

Further analysis on the effect of water soaking time intervals will refine the data presented here and provide the amount and rate of residue loss of more specific time intervals. Studies on how conservation techniques affect absorbed residues, instead of those on the surface, would provide an additional perspective to the results of this study. Further, conservation treatments could be conducted on sherds that have undergone artificial degradation processes.

This type of study could lead to results that may be considered to better emulate and therefore be more applicable to archaeological residues. Additional research also needs to be conducted on the effect of conservation treatments on other material types that are sampled for organic residues, such as stone and metal objects. These few examples of additional research would complement the results and implications presented here and add to the growing body of knowledge of the factors that affect the preservation of organic residues.

6. Conclusion

This research studied the effect of conservation treatments on the preservation of organic residues in archaeological ceramics. Treatments studied included mechanical cleaning, soaking in water, and acid cleaning—all commonly used in the conservation of ceramics today. The study demonstrated that the more intense and invasive a treatment, the less residue was extracted. A 20-second soak in water was shown to have the greatest average extraction efficiency when compared to other treatments; acid cleaning had the lowest. Other findings included a decrease in the amount of residue extracted as the time a sherd soaked in water increased, and that mechanical cleaning decreased the amount of residue extracted when compared to sherds that were not mechanically cleaned. In general, water was shown to have a negative effect on the preservation of organic residues, as exemplified in the water soaking treatments.

If a ceramic is being considered for organic residue analysis, the results of this study support the recommended idea of ‘minimum intervention’: the minimum amount of handling and conservation needed to retain the stability of the object. However, the study results also demonstrate that any action applied to a ceramic has the potential to negatively affect the preservation of organic residues. Since residues are usually found in trace amounts, even actions as simple as brushing a sherd’s surface for 10-seconds or soaking a sherd in water for 20-seconds have a dramatic impact on the loss of residue. More intense treatments, such as acid cleaning, have the potential to remove organic residue from the sherd altogether.

When considering sampling an object from the field or a museum for organic residues, one should take into consideration any previous conservation treatments the objects has undergone, and the effect of that treatment on the integrity of the organic residues. The results and trends presented in this research can be extrapolated to residues in the archaeological record.

Archaeological residues may appear in even smaller quantities than what was used in this study, which could amplify the effect of conservation treatments and pose an even greater threat to the integrity of organic residues. Predicting the condition of organic residues prior to sampling can minimize time and finances spent on analyses and prevent any damage to an object as a result of the sampling process. Such information on the predicted condition of residues may assist in choosing appropriate objects to be sampled and produce more robust results

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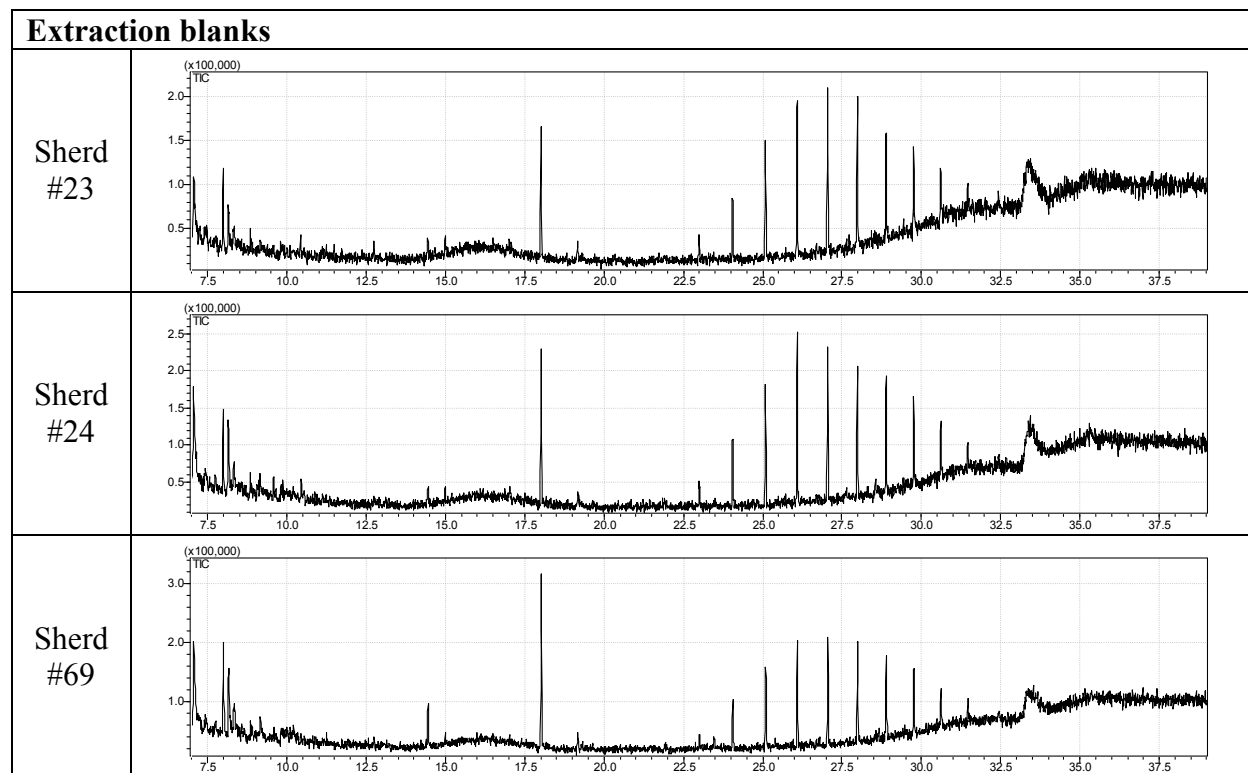
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APPENDIX 1. Chromatograms



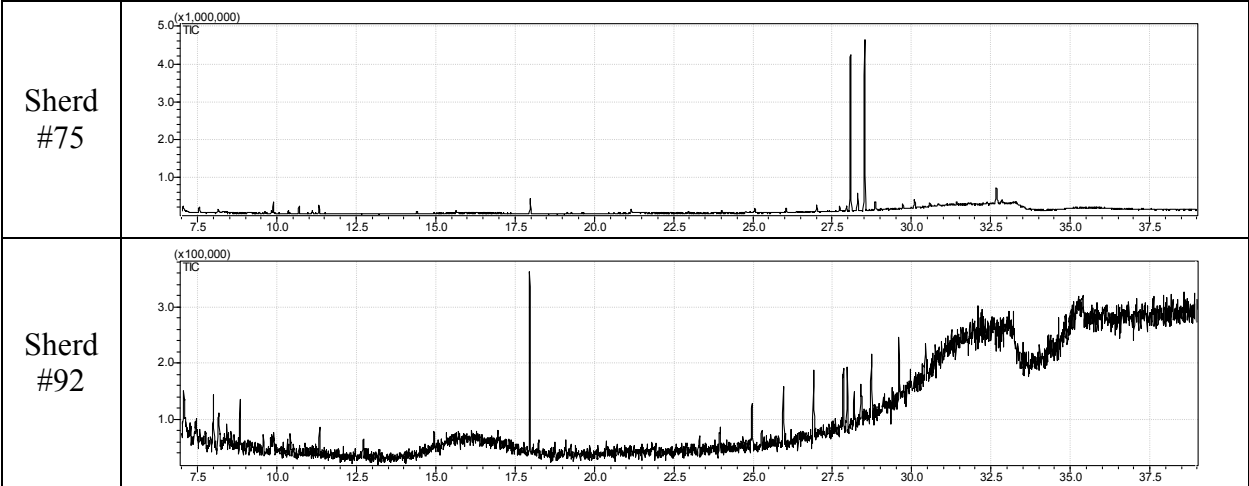
Sherd #23	
<i>Retention time (minutes)</i>	<i>Peak ID</i>
18.008	Benzenedicarboxylic acid
24.050	Octadecane
25.075	Tetradecane
26.083	Nonadecane
27.050	Nonadecane
27.983	Eicosane
28.892	Eicosane

Sherd #69	
<i>Retention time (minutes)</i>	<i>Peak ID</i>
18.017	Benzenedicarboxylic acid
24.067	Octadecane
25.083	Heptacosane
26.092	Tridecane
27.058	Eicosane
27.992	Eicosane
28.892	Nonadecane

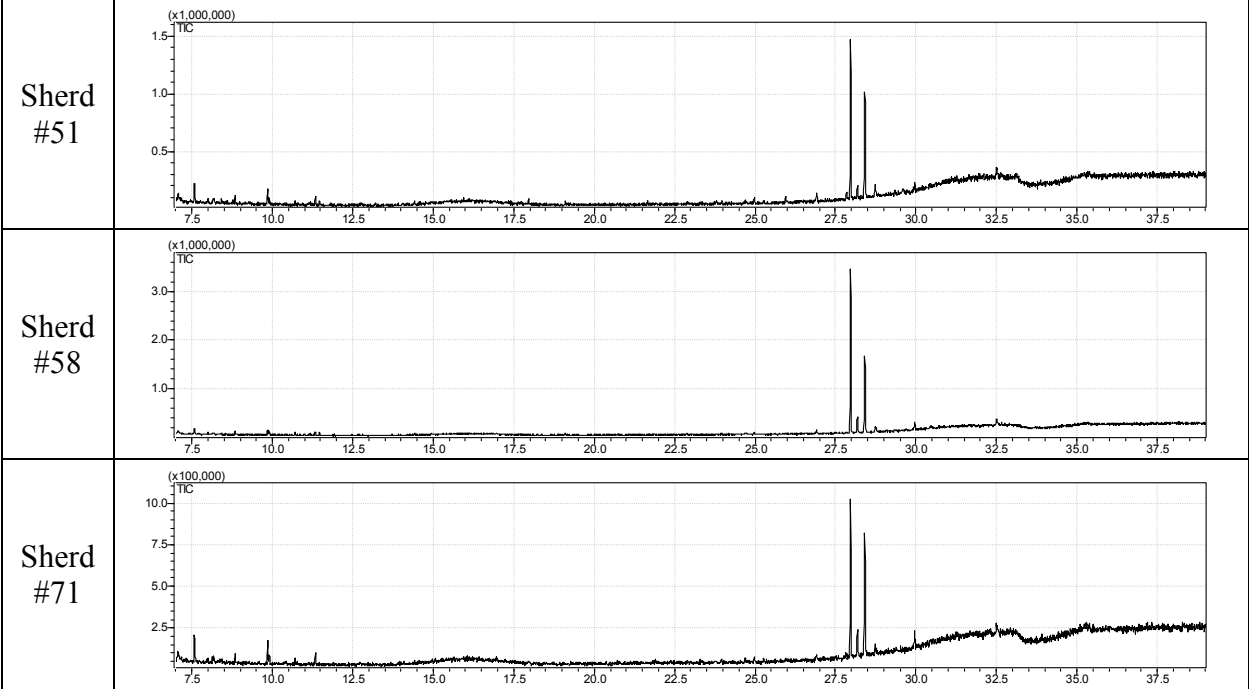
Sherd #24	
<i>Retention time (minutes)</i>	<i>Peak ID</i>
18.008	Benzenedicarboxylic acid
24.058	Eicosane
25.075	Hexadecane
26.083	Hentriacontane
27.050	Docosane
27.983	Octadecane
28.892	Tricosane

<i>Experiment name</i>	
<i>Sherd number</i>	<i>Chromatogram (example). Retention times for squalene and 5α-cholestane in the figures below are consistently 27.950 and 28.400, respectively.</i>

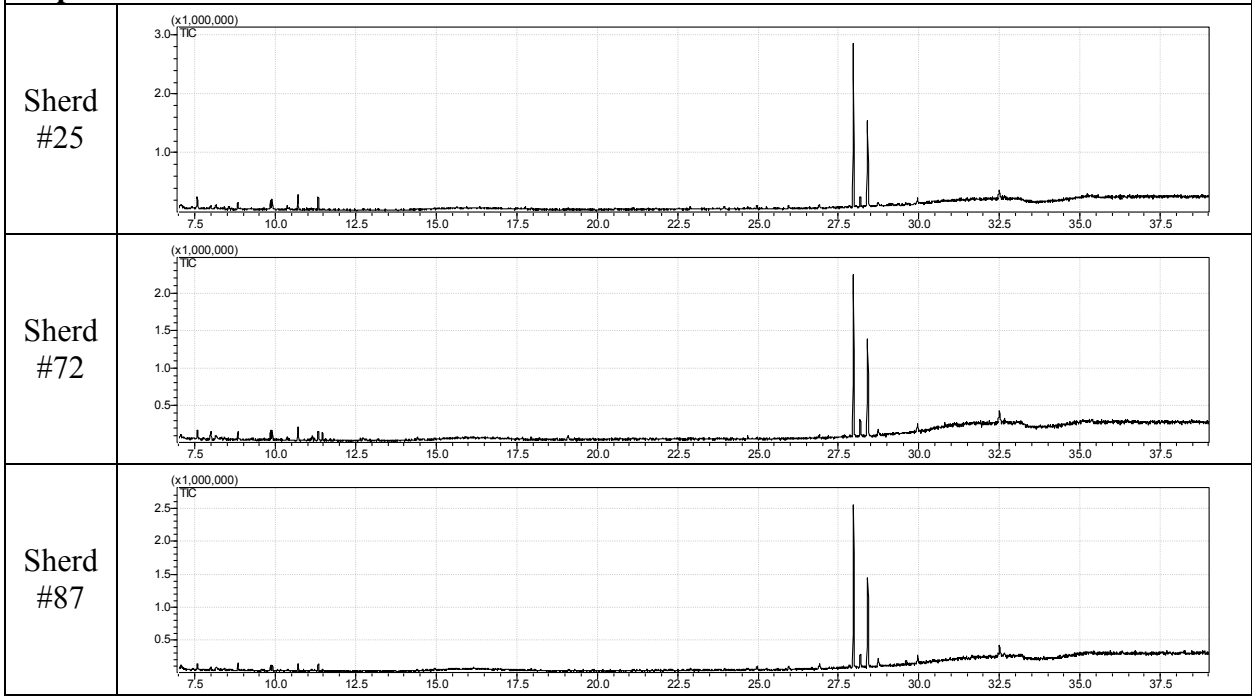
Controls	
Sherd #13	
Sherd #32	
Sherd #41	
Sherd #49	



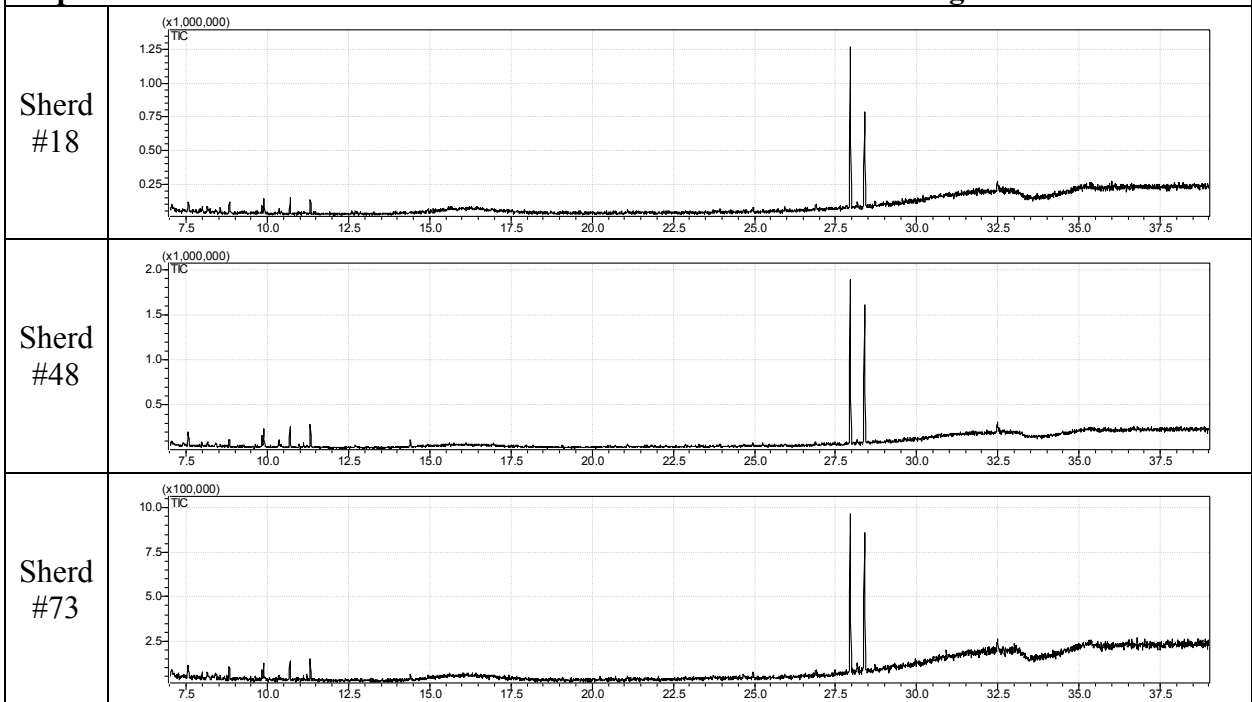
Experiment A. Mechanical cleaning



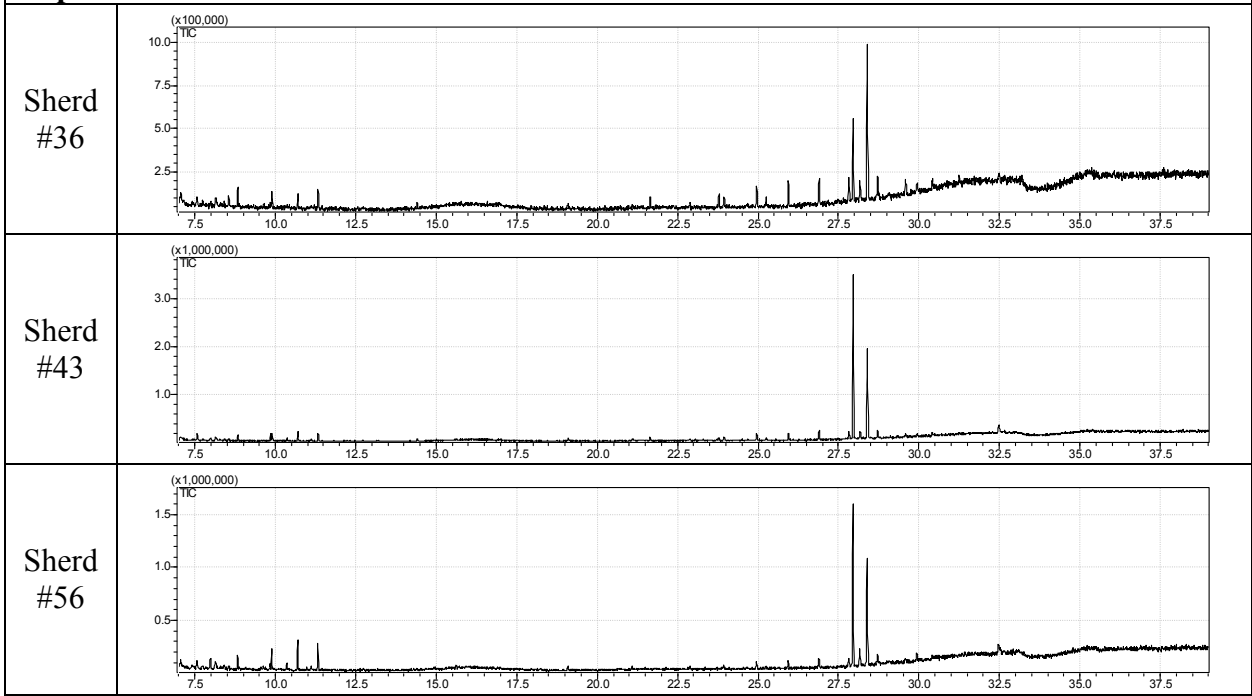
Experiment B. Soak in water for 20-seconds



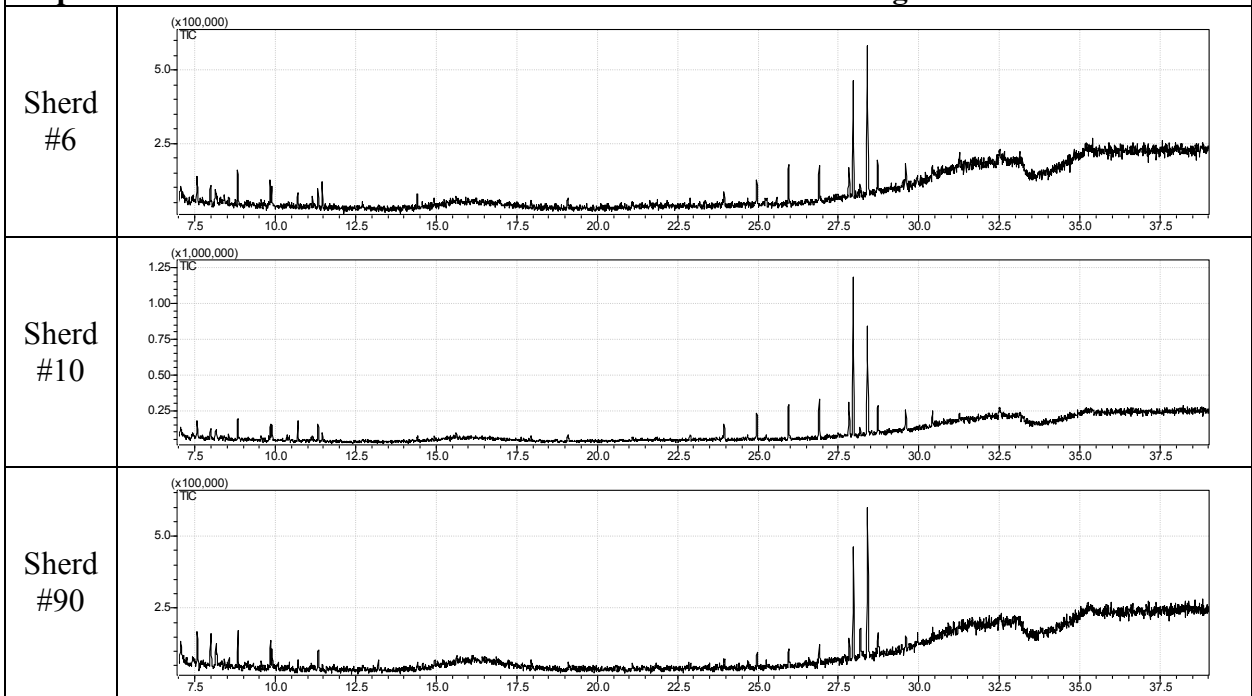
Experiment C. Soak in water for 20-seconds and mechanical cleaning



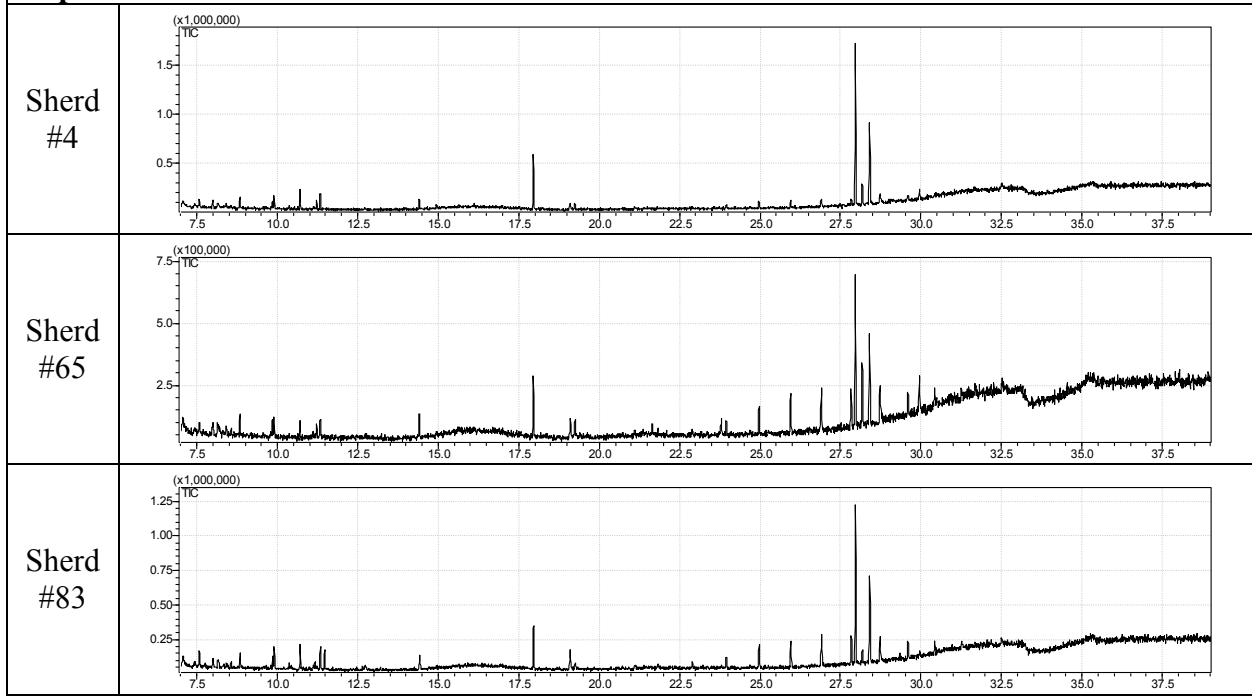
Experiment D. Soak in water for 1-hour



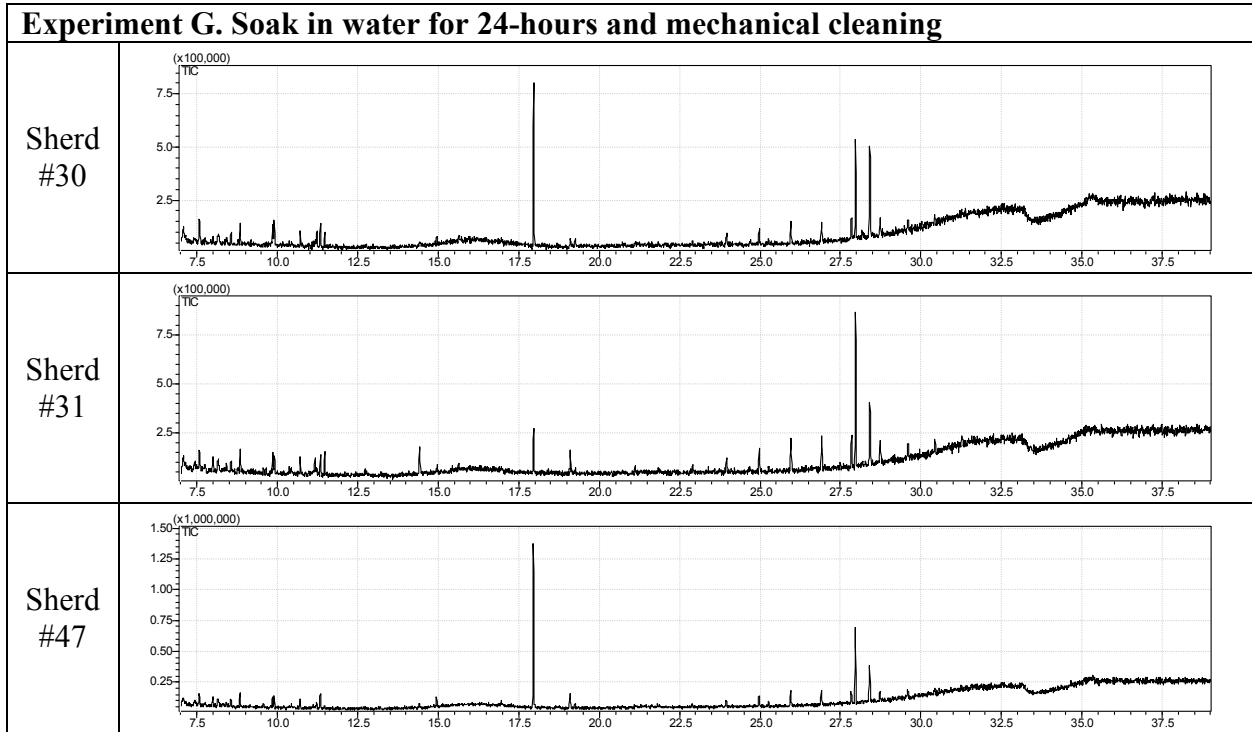
Experiment E. Soak in water for 1-hour and mechanical cleaning



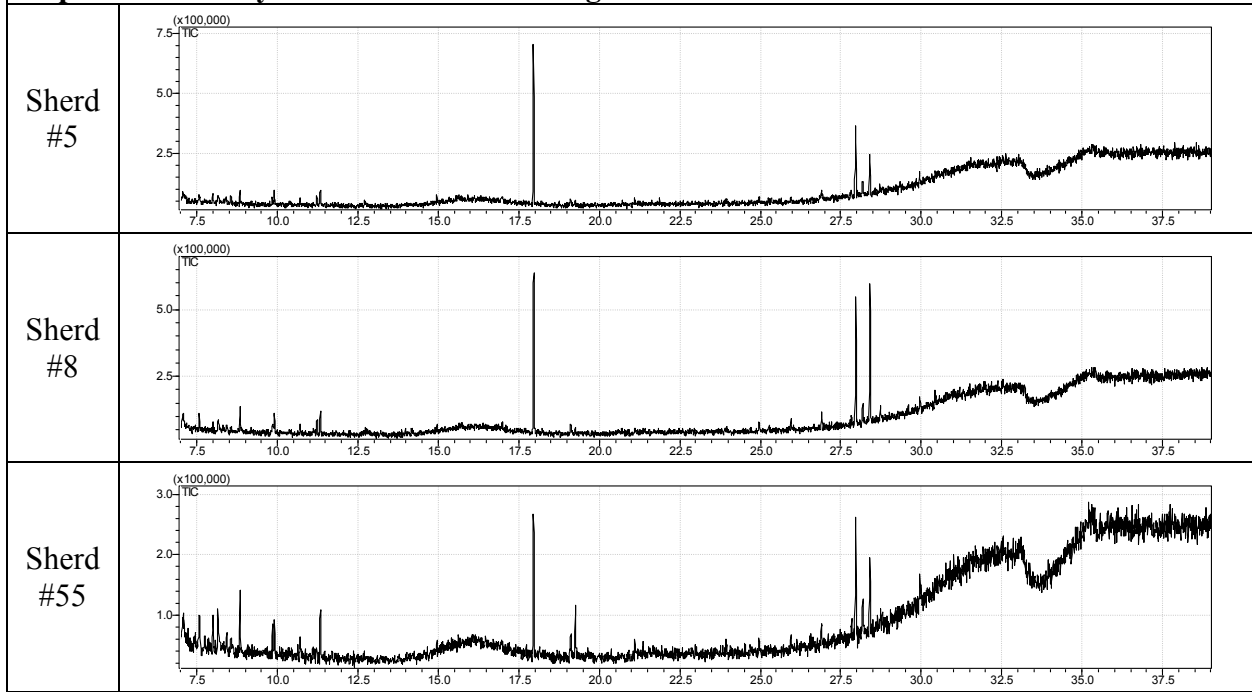
Experiment F. Soak in water for 24-hours



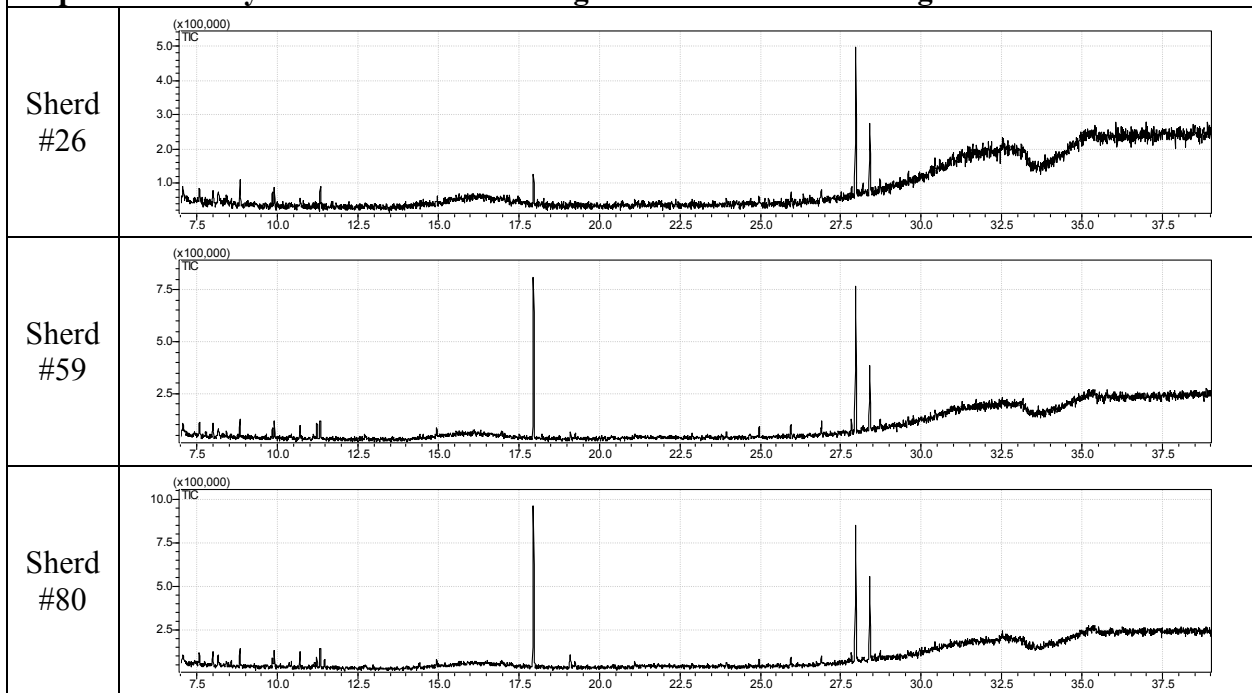
Experiment G. Soak in water for 24-hours and mechanical cleaning



Experiment H. Hydrochloric acid cleaning



Experiment I. Hydrochloric acid cleaning and mechanical cleaning



APPENDIX 2. Calculations

A. Quantification of 5 α -cholestane and squalene

A1. Obtain the peak area of 5 α -cholestane from the chromatogram.

A2. Use the linear regression equation (Eq. 1) to calculate the concentration from the 5 α -cholestane peak area.

$$\text{Eq. 1} \quad y = 1305023x + 21838$$

A3. Convert the concentration of 5 α -cholestane (5 α) to a mass.

- To convert to a mass (Eq. 2), multiply the concentration by the volume of sample injected into the GC-MS (2 μ L):

$$\text{Eq. 2} \quad \frac{\mu g \ 5\alpha}{mL} \times \frac{1 \ mL}{1000 \ \mu L} \times \frac{2 \ \mu L \ injected}{1} = \mu g \ 5\alpha$$

- This mass is the mass seen by the GC-MS.

A4. Assume the response of the GC-MS to 5 α -cholestane and the unknown (e.g. squalene (sq.)) is similar. This means:

$$\text{Eq. 3} \quad \frac{\mu g \ 5\alpha / peak \ area \ 5\alpha}{\mu g \ sq. / peak \ area \ sq.} = 1$$

- Using Eq. 3 and the peak area of the unknown (squalene), calculate the mass unknown (μ g sq.)

A5. Further calculations to account from experimental variables:

$$\underbrace{\frac{\mu g \ sq.}{1}}_{\text{Eq. 4}} \times \underbrace{\frac{1}{2 \ \mu L \ injected}}_{\text{Eq. 5}} \times \underbrace{\frac{1000 \ \mu L}{1 \ mL}}_{\text{Eq. 6}} \times \underbrace{\frac{1 \ mL}{0.9241 \ g}}_{\text{Eq. 7}} \times \frac{g \ extract}{1} \times \frac{1}{g \ oil \ on \ sherd} = \frac{\mu g \ sq.}{g \ oil}$$

- Convert the mass of squalene to a concentration by dividing the mass by the volume of sample (extract) injected (Eq. 4):

$$\text{Eq. 4} \quad \frac{\mu g \ sq.}{1} \times \frac{1}{2 \ \mu L \ injected} = \mu g \ sq. / \mu L$$

- Since the extract consists of acetone, hexane, and DCM, the density of the extract solution is the average of the densities of each solvent. Divide concentration of squalene from Eq. 4 by the density of the extract (Eq. 5):

Densities: acetone = 0.7910 g/mL
 hexane = 0.6548 g/mL
 DCM = 1.3266 g/mL
 Average = 0.9241 g/mL

$$\text{Eq. 5} \quad \frac{\mu\text{g sq.}}{\mu\text{L}} \times \frac{1000 \mu\text{L}}{1 \text{ mL}} \times \frac{1 \text{ mL}}{0.9241 \text{ g}} = \mu\text{g sq./g extract}$$

- Multiply the concentration of squalene from Eq. 5 by the amount of total extract (Eq. 6).

$$\text{Eq. 6} \quad \frac{\mu\text{g sq.}}{\text{g extract}} \times \frac{\text{g total extract}}{1} = \mu\text{g sq.}$$

- Divide the mass of squalene from Eq. 6 by the amount of olive oil that was initially applied to the experimental surface of the sherd (Eq. 7).

$$\text{Eq. 7} \quad \frac{\mu\text{g sq.}}{1} \times \frac{1}{\text{g oil}} = \mu\text{g sq./g oil}$$

The result of the calculations is μg of squalene per g of olive oil ($\mu\text{g sq./g oil}$). In other words, this is the amount of squalene recovered relative to the amount of oil initially applied to the sherd, which is indicative of extraction efficiency.

B. Example calculation – sherd #4

B1. Given:

Peak area of 5 α -cholestane: 1693301

Peak area of squalene: 3041898

Total extract: 1.6887 g

Amount of olive oil applied: 0.0327 g

B2. Linear regression:

$$\text{Eq. 1} \quad y = 1305023x + 21838$$

$$1693301 = 1305023x + 21838$$

$$x = \mathbf{1.2808 \mu g 5\alpha/mL}$$

B3. Mass of 5 α -cholestane:

$$\text{Eq. 2} \quad \frac{\mu g 5\alpha}{mL} \times \frac{1 mL}{1000 \mu L} \times \frac{2 \mu L \text{ injected}}{1} = \mu g 5\alpha$$

$$\frac{1.2808 \mu g 5\alpha}{mL} \times \frac{1 mL}{1000 \mu L} \times \frac{2 \mu L \text{ injected}}{1} = \mathbf{0.002562 \mu g 5\alpha}$$

B4. Mass of squalene:

$$\text{Eq. 3} \quad \frac{\mu g 5\alpha / \text{peak area } 5\alpha}{\mu g sq. / \text{peak area } sq.} = 1$$

$$\frac{0.002562 \mu g 5\alpha / 1693301}{x / 3041898} = 1$$

$$x = \mathbf{0.004602 \mu g sq.}$$

B5. Concentration of squalene:

$$\text{Eq. 4} \quad \frac{\mu g sq.}{1} \times \frac{1}{2 \mu L \text{ injected}} = \mu g sq./\mu L$$

$$\frac{0.004602 \mu g sq.}{1} \times \frac{1}{2 \mu L \text{ injected}} = \mathbf{0.002301 \mu g sq./\mu L}$$

B6. Mass of squalene per gram of extract:

$$\text{Eq. 5} \quad \frac{\mu\text{g sq.}}{\mu\text{L}} \times \frac{1000 \mu\text{L}}{1 \text{ mL}} \times \frac{1 \text{ mL}}{0.9241 \text{ g}} = \mu\text{g sq./g extract}$$

$$\frac{0.002301 \mu\text{g sq.}}{\mu\text{L}} \times \frac{1000 \mu\text{L}}{1 \text{ mL}} \times \frac{1 \text{ mL}}{0.9241 \text{ g}} = \mathbf{2.4897 \mu\text{g sq./g extract}}$$

B7. Squalene mass:

$$\text{Eq. 6} \quad \frac{\mu\text{g sq.}}{\text{g extract}} \times \frac{\text{g total extract}}{1} = \mu\text{g sq.}$$

$$\frac{2.4897 \mu\text{g sq.}}{\text{g extract}} \times \frac{1.6887 \text{ g total extract}}{1} = \mathbf{4.2044 \mu\text{g sq.}}$$

B8. Mass of squalene per gram of olive oil applied:

$$\text{Eq. 7} \quad \frac{\mu\text{g sq.}}{1} \times \frac{1}{\text{g oil}} = \mu\text{g sq./g oil}$$

$$\frac{4.2044 \mu\text{g sq.}}{1} \times \frac{1}{0.0327 \text{ g oil}} = \mathbf{128.58 \mu\text{g sq./g oil}}$$

The concentration of squalene recovered from sherd #4 was 128.58 $\mu\text{g sq./g oil}$.

APPENDIX 3. Data table

Table A. Conservation treatment experiment data.

Sherd #	Experiment group	Olive oil applied (g)	Total extract (g)	Peak area 5 α -cholestane	Peak area squalene	Eq. 1 ($\mu\text{g } 5\alpha/\text{mL}$)	Eq. 2 ($\mu\text{g } 5\alpha$)	Eq. 3 ($\mu\text{g } 5\alpha$)	Eq. 4 ($\mu\text{g } 5\alpha/\mu\text{L}$)	Eq. 5 ($\mu\text{g } 5\alpha/\text{g}$)	Eq. 6 ($\mu\text{g } 5\alpha$)	Eq. 7 ($\mu\text{g } 5\alpha/\text{g oil}$)
49	Control	0.0285	1.5834	3892115	5505628	2.9657	0.0059	0.0084	0.0042	4.5395	7.1879	252.21
13	Control	0.0295	1.4249	12379590	8634154	9.4694	0.0189	0.0132	0.0066	7.1466	10.1832	345.19
32	Control	0.0386	1.0879	11574621	16577723	8.8526	0.0177	0.0254	0.0127	13.7199	14.9259	386.68
51	A	0.0276	2.0958	1963410	2686571	1.4878	0.0030	0.0041	0.0020	2.2029	4.6168	167.27
58	A	0.0338	2.0776	2826972	6499146	2.1495	0.0043	0.0099	0.0049	5.3473	11.1096	328.69
71	A	0.0379	2.0148	1526525	1890020	1.1530	0.0023	0.0029	0.0014	1.5447	3.1123	82.12
25	B	0.0339	1.4454	2778485	4878056	2.1123	0.0042	0.0074	0.0037	4.0130	5.8004	171.10
72	B	0.0279	1.2773	2685849	4074061	2.0414	0.0041	0.0062	0.0031	3.3507	4.2798	153.40
87	B	0.0269	1.4285	2840575	4576906	2.1599	0.0043	0.0070	0.0035	3.7659	5.3796	199.98
18	C	0.0287	1.7423	1476880	2227110	1.1150	0.0022	0.0034	0.0017	1.8194	3.1699	110.45
48	C	0.026	1.6652	2843739	3353181	2.1623	0.0043	0.0051	0.0025	2.7590	4.5943	176.71
73	C	0.0275	1.9364	1526251	1663280	1.1528	0.0023	0.0025	0.0013	1.3594	2.6324	95.72
36	D	0.0306	1.5566	1778077	835776	1.3458	0.0027	0.0013	0.0006	0.6845	1.0655	34.82
43	D	0.0293	1.3217	3784089	6362824	2.8829	0.0058	0.0097	0.0048	5.2455	6.9329	236.62
56	D	0.0308	1.4193	1990562	2970693	1.5086	0.0030	0.0045	0.0023	2.4362	3.4577	112.26
6	E	0.0312	1.389	1006754	727977	0.7547	0.0015	0.0011	0.0005	0.5905	0.8202	26.29
10	E	0.0293	1.3379	1548694	2187658	1.1700	0.0023	0.0033	0.0017	1.7884	2.3927	81.66
90	E	0.0298	1.1769	1023338	794586	0.7674	0.0015	0.0012	0.0006	0.6448	0.7589	25.46
4	F	0.0327	1.6887	1693301	3041898	1.2808	0.0026	0.0046	0.0023	2.4897	4.2044	128.58
65	F	0.0307	1.4419	794292	1153870	0.5919	0.0012	0.0017	0.0009	0.9305	1.3416	43.70
83	F	0.0311	1.4444	1264312	2212805	0.9521	0.0019	0.0033	0.0017	1.8031	2.6044	83.74
30	G	0.0374	1.598	877809	794598	0.6559	0.0013	0.0012	0.0006	0.6425	1.0267	27.45
31	G	0.0371	1.5583	604257	1593411	0.4463	0.0009	0.0024	0.0012	1.2735	1.9844	53.49
47	G	0.0307	1.645	606538	1237194	0.4480	0.0009	0.0018	0.0009	0.9889	1.6268	52.99
5	H	0.0294	2.323	307395	552182	0.2188	0.0004	0.0008	0.0004	0.4253	0.9880	33.61
8	H	0.035	1.8729	979333	922958	0.7337	0.0015	0.0014	0.0007	0.7482	1.4014	40.04
55	H	0.0333	1.8056	286342	417782	0.2027	0.0004	0.0006	0.0003	0.3200	0.5778	17.35
26	I	0.0327	1.7124	335484	804295	0.2403	0.0005	0.0012	0.0006	0.6235	1.0677	32.65
59	I	0.0378	1.675	593844	1204480	0.4383	0.0009	0.0018	0.0009	0.9620	1.6113	42.63
80	I	0.0429	1.5876	842728	1258806	0.6290	0.0013	0.0019	0.0009	1.0167	1.6142	37.63
41	Control	0.0304	1.5489	331941	794911	0.2376	0.0005	0.0011	0.0006	0.6158	0.9537	31.37
92	Control	0.0297	1.549	132504	184454	0.0848	0.0002	0.0002	0.0001	0.1277	0.1979	6.66
75	Control	0.0345	1.0448	9400748	8233668	7.1868	0.0144	0.0126	0.0063	6.8113	7.1165	206.27