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A CONSIDERATION OF

ANCIENT RESIDUES AND THEIR ANALYSIS

By

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ABSTRACT

Identification of specific use(s) of ancient pottery vessels through empirical verification is currently very limited for archaeological investigations. Although we can postulate a range of purposes or functions for certain vessels, empirical confirmation of actual use has been determined only for a minuscule portion of the available vessels. This thesis will provide a broad review of organic analyses as applied to foodstuff residues left on ancient artifacts as well as discuss several considerations for such analysis that are unique to their application to archaeological specimens.

Chemical methods of identification in archaeology are not new, but substantial work on organic materials has been done only since the early 1980’s. The composition of organic residues produced by past human activity are microscopically or chemically identifiable, and methods of analysis have been borrowed from or developed in collaboration with the fields of chemistry, geology, and biology. Most methods of chemical analysis require destruction of the finite sample itself, and standard sampling methods can also negatively affect both artifacts and remaining residues by introducing contaminants or otherwise compromising sample viability.

Chemical residues sampling of archaeological specimens by non-destructive means, however, is a much more recent development. There are many forms of light spectroscopy including Raman spectroscopy, Fourier transform-infrared [FT-IR], ultraviolet-visible [UV-Vis]) which are all non-destructive methods safe for archaeological specimens.
INTRODUCTION

Identification of specific use(s) of ancient pottery vessels through empirical verification is currently very limited for archaeological investigations. Although we can postulate a range of purposes or functions for certain vessels, empirical confirmation of actual use has been determined only for a minuscule portion of the available vessels. There are two methods to determine a vessel’s use empirically: visibly identifiable macrofossil or other material residues, and analysis of chemical signatures of residues left by the former contents. Visual identification is rarely successful due to issues of material preservation, and is often compounded by the common methods of handling and cleaning of artifacts during excavation and later curation of the objects. Despite these obstacles, chemical residue analysis is still rarely pursued. Contributing to the limited utilization of residue analyses are cost, time, fragility of artifacts, and the limited success rate of finding viable residues – only an estimated 17-20% of sampled artifacts have produced identifiable material.

Most methods of chemical analysis require destruction of the finite sample itself, and standard sampling methods can also negatively affect both artifacts and remaining residues by introducing contaminants or otherwise compromising sample viability. Sampling methods that require scrapping, coring, or crushing part of the artifact preclude analysis of many rare, precious, or fragile artifacts that cannot be damaged. Additionally, the cost of residue analyses conducted by a specialist can be substantial and is often impractical for archaeological projects with limited funding. Finally, while there are numerous methods of productive analyses for organic materials, few (if any) have been specifically designed to address the wide range of unknown substances or the deterioration of material over time that are both common with archaeological samples.
This thesis will provide a broad review of organic analyses as applied to foodstuff residues left on ancient artifacts. To do so, I will first evaluate recent methodological advancements and novel applications when analyzing archaeological materials. In general, archaeology as a discipline studies the material remains of past humans and human behavior, including the recently deceased. I will include studies that address materials greater than 500 years old. Material objects used more recently by humans would likely retain residues readily identifiable by well-established chemical methods. Moreover, materials that predate living human populations, or the collective memory of object use, involve too many unknown and unknowable possible variables that could affect the interpretations of content. In addition, I will review the ability for chemistry to identify unknown organic residues of extreme age (relative to living populations). This area of study remains distinctly under-developed because of the tremendous challenges inherent in such analysis. Chemical identification of an unknown substance, compounded by the difficulties of evaluating an unknown rate and degree of degradation of that unknown substance, present substantial scientific challenges.

Chemical methods of identification in archaeology are not new, but substantial work on organic materials has been done only since the early 1980’s. The absence of empirical evidence is a common limitation to archaeological interpretations. Without empirical evidence, archaeologists must infer reasonable content by ethnographic or ethnohistorical analogy, hieroglyphic texts, images, and other indirect information that limits interpretation (Rice 1987:207-41). This leads to a constant issue of imprecision – use (and thereby artifact purpose and function) is attributed primarily through analogical inference. Thus, unverified hypotheses are often incorporated into broader interpretations of archaeological research, which then become “common knowledge” or “fact” as the original circumstantial limitations of those interpretations
are forgotten or obscured through time. This process undermines our understanding of actual ancient behaviors, which can lead to critical misunderstandings and misinterpretations of significant ancient human practices.

A more immediate issue, particularly when investigating past cultures in the Americas, is that residue analyses are more likely to be applied to rare or unique artifacts. These idiosyncratic objects are generally recovered from burials or ritual deposits associated with elite social classes. The successful identifications of alkaloid biomarkers indicating the presence of substances such as cacao, tobacco, or datura are useful points of knowledge, but these identifications are also limited in that they were: 1) identified on a rare or unique vessels that are not directly comparable in form or function to any other commonly used vessel types, and 2) these artifacts were recovered from archaeological contexts that cannot be directly compared to more commonplace contexts of use. These findings frequently used for analogies with which archaeologists then infer contents for related artifact forms, despite critical differences in their original contexts of excavation, for the unique character of the originating artifact. These types of analogical interpretations cannot be supported directly without substantially corroborating empirical evidence.

Currently there are at least millions of artifacts, if not billions, held in museums, universities, and other curation facilities that are rarely utilized for further research after their excavation or collection. They are widely available to scholars, but still tend to elicit limited attention. These institutions typically maintain artifacts from multiple sites, geographic regions, and time periods. In some cases, these institutions hold the only collections of objects from certain archaeological sites, especially sites with limited periods of occupation or from smaller or less studied sites or areas. Therefore, the range of artifacts available from these collections is
often far greater than what is produced by site-specific fieldwork. These larger institutional collections also allow dynamic and wide-ranging studies of materials by regions and time periods. These collections are under-explored and under-utilized materials for addressing archaeological research questions.

The composition of organic residues produced by past human activity are microscopically or chemically identifiable, and methods of analysis have been borrowed from or developed in collaboration with the fields of chemistry, geology, and biology. Despite the numerous methods of analysis, archaeological use of these methods must be carefully adapted to contend extended periods of chemical and environmental degradation that affect sample size, availability, and usability. No single method has yet been developed that accurately and reliably identifies all archaeological organic residues in all cases and conditions. Instead, archaeologists must consider both the strengths and weaknesses of available methods, the selection of which may jeopardize both residue identification and the future viability of samples for further analysis. The available sample size, potential damage to artifact, total analysis costs, intellectual merit of potential information, and practical feasibility of obtaining the sample and analysis also factor into the selection of analytical methods.

HISTORY OF ANALYSIS

Material analysis of artifacts – their construction, materials, or the substances they held – have been central questions of archaeologists since at least the 19th century. Initially, researchers focused their attention to the analysis of the inorganic materials, specifically the composition of pottery and ceramics, metals, glass, pigments, paints, and glazes. Inorganic analyses are the earliest known material chemical studies conducted on archaeological materials. The first recorded chemical study artifacts was conducted in the late 18th century by M. H. Klaproth. He
identified the composition of Roman and Greek metals (mainly coins) and glass gravimetrically. “Gravimetry is the determination of an element through the measurement of the weight of an insoluble product. It was a principal tool of quantitative analytical chemistry until the development of instrumental techniques in the early 20th century” (Kaluzna-Czapinska et al. 2018:67). This was followed in 1815 by H. Davy, who conducted chemical analysis of ancient pigments collected in the ruins of ancient Rome and Pompeii and presented to the Royal Society of Sciences. Around the same time in the early 19th century, M. Faraday studied the material compositions of copper alloy coin, glass, and enameled bronze. Faraday also conducted some of the early examinations of organic residues, such as fuel residue and foodstuffs.

Most early studies were considered wet chemistry – analytical chemistry that typically involves observation to analyze materials in the liquid phase. Conducted from lab benches with basic laboratory glassware such as beakers and graduated cylinders, gasoline, Bunsen burners, and crucibles, samples were separated by evaporation to isolate substances in their dry forms. Scales or balances were used to measure the weight of a substance before and after a change occurred. One of the first wet chemical investigations of ancient ceramics was conducted by H.T.W. Richards in 1895 on Athenian pottery held by the Boston Museum of Fine Arts. The first chemical analysis of osteological materials dates to approximately the same period. In 1892, Marie-Adolphe Carnot suggested that fluorine uptake in a buried bone might be used to determine its age (Pollard et al. 2017; Kaluzna-Czapinska et al. 2016).

For most of the 18th and 19th centuries, archaeology was treated as an academic pursuit for wealthy, upper class, young men keen on traveling the world. Scholarship focused on the antiquity of the artifacts and ruins. Systematic scholarship on past human cultures and their ancient ways of life was not truly pursued until the end of the 19th century. The collaboration
between chemists and archaeologists was part of this scholarly evolution from the study of antiquarian curiosities to archaeology as a social science. Similar investigations steadily became more common into the 20th century, when chemical studies became more often included in excavation reports.

Scientific developments in the early 20th century, in combination with scientific instruments that permitted increasingly selective and sensitive measurements, allowed for unparalleled scholarship. New techniques were introduced, such as optical emission spectroscopy (OES), that were quickly adopted into archaeological analyses (Pollard et al. 2017). During World War I and World War II, the collaborative efforts of allied countries resulted in significant advances in science and technology. Subsequently, new analyses such as x-ray, mass spectrometry, and electron microscopy became more common and widely available to the scientific communities. After their adoption in the medical arts, possible applications of these technologies were quickly realized in archaeological research. X-ray fluorescence (XRF) became a particularly favored tool of archaeologists at that time and is still widely used. XRF analysis is nondestructive, requires little or no sample preparation, and can simultaneously provide multi-element measurements (Pollard and Heron, 2008; Pollard et al., 2007).

Among the most active areas of archaeological chemistry more recently is the use of stable isotopes for residue identification. The pioneering work of Morton and Schwarz in 1988 (Dudd et al., 1999; Evershed et al., 1994, 1999) investigated the bulk 13C and 15N values of organic residues hypothesized to originate from cereal maize. Hastorf and DeNiro (1985) and Sherriff et al. (1985) used bulk stable isotope measurements to characterize prehistoric carbonized plant and animal remains (Dudd et al., 1999; Evershed et al., 1994). The first application of compound-specific stable carbon isotope measurements to archeological samples
was reported by Evershed et al. (1994). Gas chromatography with isotope ratio mass spectrometry (GC-C-IRMS) enabled the measurement of carbon and nitrogen isotope ratios on single compounds within complex mixtures. This method promises further differentiation of the source of ancient lipid residues, such as discrimination of ruminant from non-ruminant animal fats in cooking vessels (Copley et al., 2005a; Evershed et al., 1997; Ogrinc et al., 2012).

Chemical analysis of organic residue from archaeological contexts is a relatively new field. The earliest analyses took place in the first half of the 20th century, but systematic research took off in the late 1970s and early 1980s (Stacey, 2009). In 1933, Johannes Gruss (Buckley et al., 2013; Craig, 2002) first used residue analysis to identify that an amorphous, visible black residue was created by the burning of milk fats on archeological ceramics. The first reported analysis of absorbed residues from unglazed ancient pottery was the identification of olive oil in amphorae of unspecified date and in a Gallo-Roman lamp by the Condamin team in 1976. More recently, researchers have focused their attention on natural products (waxes, resins), remains of human activity (food residues), and human remains (bone, protein, and DNA). The most effective approach is a molecular marker analysis, in which the presence of a specific unique compound or known quantitative distribution of compounds of an unknown sample is matched with a contemporary natural substance. Lipids are typically chosen for use as molecular markers because they are hydrophobic and not susceptible to hydrolysis by water compared to most amino acids and DNA. Alkaloids have more recently become the biomarkers of interest in the Americas, where the greatest natural abundance of intoxicants are found.

Presently, archaeological residue analyses can be divided into four natural areas of research. The first involves lipid biomarkers and inorganic microfossils that are indicative of daily foodstuffs found in food vessels or service wares. These are typically grains, vegetables,
and meats commonly consumed by people. The second focus is on foodstuffs that are not necessarily used as daily consumables but on more limited occasions such as drugs, alcohols, and spices used for social rituals or in religious events and rites. The third area of study is analysis of pollens, phytoliths, and starches from the processing, presence, and manipulation of foodstuffs. In addition to analysis of residues from food and food containment, another significant study of archaeological residue relates to things such as adhesives, hide working, tars and tree pitch, oils, and other non-food related activities. This fourth area of study is broadly informative to the others, but largely addresses production of materials rather than consumption practices.

Organic residues, by definition, “lack the clearly discernable morphological features that characterize other biological materials that survive in the archaeological record, such as wood, bone, leather, seeds, and pollen” (C. Heron and R.P Evershed 1993:249). They result from something that can decay or is the result of decay. Inorganic remains are materials that are typically fossilized. In the past 40 years, analyses such as these have become sufficiently common that a separate field has been designated to address the use of methods from the physical sciences to address archaeological research questions, termed “Archaeometry”.

**REVIEW OF ARCHAEOLOGICAL CONSIDERATIONS**

Unlike traditional chemistry, archaeological applications are rarely straight forward. Archaeological data is often a series of unknowns, and various analyses are used to constrain the range of possible interpretations. The methods are based on measurements, controlled excavations, and artifactual evidence. Artifacts, broadly defined, are any material manufactured object or modified for use by humans. A related concept is a feature, which is an area of activity, concentrations of artifacts, or built or modified landscape elements that cannot be reasonably moved (e.g., fire pit, house, pyramid, tomb, etc.) but are the products of human actions or
activities. From these, the basis of human behavior is interpreted by patterns in these material remains. Logically we cannot see human behavior in the past, only the outcomes. While physical sciences generally require confirmation and replicability, archaeology cannot address behavior directly. Instead, archaeologists work inductively. The analysis of the material remains is our primary medium for “experiments” in archaeological analysis, which serve to limit alternative explanations by inference.

Artifacts have several attributes that are not immediately apparent. Firstly, every artifact is distinct for its “life-use” or active period of employment. Its purpose, function, and subsequent deposition and degradation provide unique histories of the objects use. Although artifacts are commonly grouped in terms of types based on their form or function, discussed collectively as part of that grouping, and studied as such – the matter of uniqueness must always be taken into consideration. It follows that all samples taken from a particular vessel are a reflection of its life-use as well as its post-use depositional transformations. Even though identification of foodstuffs or pigments may speak to the broader grouping of similar artifacts (or features), the artifact’s residues must also be kept distinct as a reflection of that artifact’s use alone. Human interaction with items is highly varied, and it may be are that an object served one purpose exclusively. Therefore, artifact uses have to be considered, both individually and collectively, as a series of events through time.

Since each of these artifact histories are unique, one of the greatest concerns for archaeological materials is the destruction of a finite sample. The vessel/container/artifact is considered a singular event – meaning that the vessel and its samples are unique, finite, and irreplaceable resources for analysis (as discussed above). Any sample that is taken from that artifact is expending a part of that limited resource. Since each unique object and the information
it can provide is such a limited resource, it is very important that the effects of sampling and analysis on future research are minimized as much as possible.

Pottery technologies differ greatly among ancient cultures, and the differences in firing practices significantly affect a clay vessel’s physical properties. There is evidence of prehistoric use of kilns in the Old World (circa 7000 B.C., see Rice 1987:7), but scant evidence of kilns used in the Americas (at least before 500 A.D.). The use of a kiln dramatically increases the temperature at which the clay body is fired. Ceramics (and glazes) are produced in temperatures exceeding 1100ºC, at which temperature they become vitrified. Vitrification is the result of silica and other particles, contained in the clay or glaze, fusing together to produce glass. Pottery or low-fired clay bodies are fired under 900ºC, and typically do not achieved vitrification. Unfired pottery is generally baked by the sun. Under extremely dry conditions, such as in the Near East, archaeologists can recover unfired clay artifacts (Rice 1987:5-12). Most of the ancient ‘ceramics’ we find in the Americas are not true ceramic, but pottery.

Mayan pottery is highly porous (although this mitigated according with surface treatments) and absorbs some portion of any liquid on contact. When possible, it would be better to take samples from the inner core of pottery, in which portions of residues may be trapped and protected within the ceramic fiber itself. According to Evershed, the greatest chance for successful analyses of pottery are these absorbed residues, stating “… Analyses performed to date suggest that absorbed organic residues survive in >80% of domestic cooking pottery assemblages worldwide” (2008:904, see also Charters et al. 1993; Stern et al. 2000).

Absorbed organic residues result from a portion of the contents being drawn into the porous body of the pottery, and are not necessarily visible on the object’s surface. They are, however, an especially important means of identifying contents. Once contents are drawn into
the clay body, they have a greater chance of being protected from degradation from environmental contamination, bacteria, and handling. The variation in firing temperatures and surface treatments (e.g. burnishing or slipping) results in vessel surfaces that react with and retain residues accordingly. Porous surfaces allow liquid substances (especially water, minerals, fats, and oils) to migrate into the clay body itself (Condamin, et al. 1976; Gerhardt, et al. 1990; Stern, et al. 2000). Additionally, inorganic residues, such as microfossils like pollen and phytoliths, are often retained within these pores. Unfortunately, early archaeological investigations did not recognize the important information contained in residues. Common practices of the time (and often continued even now) were to scrub artifacts clean and clear away dirt, debris, and char. Visual analysis was limited to simply recognizing that residues indicated evidence of intentional human use.

The porosity of an interior surface is inversely related to firing temperature (Rice 1987:106-107). Pottery pores allow thermal expansion and contraction, which such vessels are typically exposed to during cooking (Rice 1987:107; Schiffer 1988; Young and Stone 1990). The technical ability of low-fired pottery to withstand these conditions is attested by baked-on and charred residue found on the interior of the vessel and burn marks found on the exterior surface, particularly on the bottom and lower body of the vessel, resulting from repeated use. In many cases, food residues were allowed to accumulate to reduce the porosity of the vessel.

The degree of permeability of non-glazed vessels is directly related to porosity (Schiffer 1988:27). As Schiffer (1988), Rice (1987), Young and Stone (1990), and others have discussed, the surface treatment of vessels also directly affects what function the vessel could effectively serve. For example, ribbed and unglazed water jars allow contents to evaporate slowly through the body of the vessel, thereby cooling its contents. As discussed previously, low-fired porous
vessels allow for thermal expansion and contraction during cooking processes. Lidded porous vessels keep out moisture. Amphorae with conical bottoms allow sediment to collect, wide mouthed basins allow fermentation to occur rapidly, and constricted neck or small mouthed vessels reduce spills and hinder evaporation.

ORGANIC RESIDUES ANALYSES IN ARCHAEOLOGY

Presently, the most common technique applied in archaeological studies is one that involves characterization by chromatography and mass spectrometry (see for example Evershed, et al. 1990; Heron, et al. 1991; Evershed, et al. 1992; Evershed, et al. 1994; Charters, et al. 1995; Evershed, Charters, et al. 1995; Evershed, Bethell, et al. 1997; Hurst 2006; W. Jeffrey Hurst, et al.; W. J. Hurst, et al. 2002; Trivedi 2002; McNeil, et al. 2006; J. W. Hurst, et al. 2002; Powis, et al. 2007; Hurst, et al. 1998; Zagorevski and Loughmiller-Newman 2012; Condamin, et al. 1976; Patrick, et al. 1985; Hill and Evans 1987; Rottländer 1990; Copley, et al. 2001). These methods are commonly used because the sample size required for analysis is only a few grams, the sensitivity of the instrumentation has proven to detect compounds in samples that are several thousand years old, the nature of foodstuffs can be efficiently described, and the technology is accessible.

Gas chromatography-mass spectrometry (GC-MS) and gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS) are among the invasive ceramics research methods causing irreversible damage to the samples. Gas chromatography-mass spectrometry allows the determination of substances in very low concentrations, and therefore it is one of the most widely used techniques in analytical chemistry. Mass spectrometry is a valuable detection technique because it provides information on the molecular structure of the compounds and is highly sensitive and selective. Coupled chromatography and mass spectrometry can separate a
mixture into its individual components and subsequently analyze each compound in the mixture. This technique is mainly used to determine volatile organic compounds and organic gasses.

Gas Chromatography coupled with one or more method of Mass Spectrometry (GC-MS) facilitates identification and “semi-quantitative determination of organic acids and many other substances, like alcohols, alkanes, cholesterol, nicotine, and caffeine” (Kaluzna-Czaplinska et al 2016:69). As mentioned above, there are an increasing number of archaeological based studies focused on the determination of specific compounds known in foodstuffs (e.g., Mitkidou et al., 2008; Olsson and Isaksson, 2008; Reber and Kerr, 2012; Regert et al., 2003; Zagorevski and Loughmiller-Newman, 2012; Evershed et al. 2006; Hurst et al. 1989). Some studies of organic residues are focused on lipids and fatty acids because they are nonpolar water-insoluble compounds; therefore, they are not washed out of the walls of the ceramics (Eerkens, 2005).

Organic acids and lipids are the most often determined substances (Kauzna-Czaplinska and Modecka, 2008; Kauzna-Czaplinska et al., 2013). These molecules have a distinct longevity and remain stable. In addition, they are water-insoluble compounds, so are not eluted from ceramic fibers. Through Eerkens’ work (and collaborators) they established, “a range of appropriate acid ratios on the basis of the putative source of identified and determined compounds” (Eerkens, 2005 referenced in Kaluzna-Czaplinska et al 2016).

“In most archeological ceramic samples many saturated fatty acids such as dodecanoic (C12:0, lauric acid), tetradecanoic (C14:0, myristic acid), pentadecanoic (C15:0), hexadecanoic (C16:0, palmitic acid), heptadecanoic (C17:0, margaric acid), and octadecanoic acid (C18:0, stearic acid) and also unsaturated acids such as cis-9-heksadecenoic (C16:1, palmitoleic acid), cis-9-oktadecenoic (C18:1, oleic acid), and cis-
9, cis-12-octadecadienoic (C18:2, linoleic acid) have been identified.” (Kaluzna-Czaplinska et al 2016:68)

Among the most notable and prolific examples of this work are the numerous finds of Evershed and colleagues: Dudd, et al. (1998); Dudd and Evershed (1999); Evershed, et al. (1990); Evershed (1990); Evershed, et al. (1991); Evershed (1992); Evershed, et al. (1992); Evershed (1993a, b); Evershed, et al. (1994); Evershed, Stott, et al. (1995); Evershed, Charters, et al. (1995); Evershed (1996); Evershed and Tuross (1996); Evershed, Bethell, et al. (1997); Evershed, van Bergen, et al. (1997); Evershed, Vaughan, et al. (1997); Evershed, Mottram, et al. (1997); and Evershed, et al. (1999).

NON-DESTRUCTIVE RESIDUE ANALYSES

As described above, there are multiple methods that have been productive for the identification of archaeological foodstuffs (as evidenced by the works noted above). There are, however, many foods, drugs, and drinks that have not been detected yet. In part, this is due to a lack of methods for unknown or yet unidentified foodstuffs, or foodstuff that have degraded. Additionally, there are numerous issues of acquiring samples from curated collections (e.g., objects that are precious, rare, or fragile and/or cleaned, repaired, and protectively sealed).

There are many forms of light spectroscopy including Raman spectroscopy, Fourier transform-infrared [FT-IR], ultraviolet-visible [UV-Vis]) which are all non-destructive methods safe for specimens. Raman spectroscopy is of particular interest. Raman was introduced nearly a century ago and is now commonly used in a variety of fields as a molecular fingerprint for material identification and characterization. Raman spectroscopy is well known as one of the
most selective spectroscopic technique (Williams and Collette 2001). Archaeologically, Raman spectroscopy is best known for inorganic studies.

Raman spectroscopy has been a major source of material identification and analyses for over a century. For Raman, a sample of material is illuminated with monochromatic (i.e., single wavelength or single frequency) laser light. The photons from the laser are absorbed, transmitted, reflected, or scattered by the sample. Light scattered from the sample is due to either elastic collisions (Rayleigh scatter) or inelastic collisions (Raman scatter) of the light with the sample's molecules. The magnitude of the Raman effect correlates with polarizability of the electrons in a molecule. Raman is a form of inelastic light scattering, where a photon excites the sample and this excitation puts the molecule into a virtual energy state for a short time before the photon is emitted. Inelastic scattering means that the energy of the emitted photon is of either lower or higher energy than the incident photon (the photon that interacts with the sample). After the scattering event, the sample is in a different rotational or vibrational state. Raman scattered light returns from the sample at different frequencies corresponding to the vibrational frequencies of the bonds of the molecules in the sample. The resulting signal captured at the detector provides a representative molecular ‘fingerprint’ of the chemical composition for the sample.

Since Raman spectroscopy involves only the interaction of light and the target sample, it is noninvasive and nondestructive. Raman also does not require samples to be removed from the vessel and can be directly applied to the artifact itself. This eliminates the time and cost of sample preparation, shipping and permitting, and proper storage and handling. Sampling precious, rare, or visually interesting vessels using the current destructive methods is often difficult, if even permissible. A great number of specimens would be added to the list of potential candidates for analysis if a non-destructive method could be applied. We would also be able to
dramatically increase the number of artifacts, in general, that would be analyzed and analyzable. Further, Raman spectroscopy is commonly available, and widely employed, in museums for material analyses such as pigments in rock art (Smith and Barbet 1999), ceramic pastes and glazes (Bruno et al. 1997; Clark and Curri 1998), glass (Bouchard and Smith 2002), stone and metals tools (Smith and Gendron 1997; Gendron et al. 2002; McCann et al. 1999), as well as textiles and fabric pigments (Catalano et al. 2006; Edwards et al. 1997; Wiedemann et al. 2002). Therefore, if methods were available for organic contents, most work could be done with a museum laboratory’s own facilities and equipment, thus facilitating the research. Since Raman is non-destructive, such analyses may alleviate many (if not all) curatorial or conservation concerns.

In order to apply Raman effectively, a comparative database must be available for substances of interest. Currently, such a database does not exist for archaeological residues in a form directly useable for this type of analyses. In other words, to find the fingerprints of distinct foodstuffs within the sample, each foodstuff needs to be discretely identified by its Raman signature. Establishing and populating a database of potential ancient foodstuffs would be necessary. Much of this data will could come from published Raman work conducted by biologists and chemists, however additional sample from archaeological contexts would be needed for comparison. Since Raman requires a known (or at least comparable) sample spectra for identification, analyzing macrofossils that can be visually identified can (ideally) establish spectra from a known source.

A second issue in applying Raman is the potential for either complicated signals difficult to decompose into substances or signals that are overwhelmed by interfering fluorescence. Fluorescence is the property of some atoms and molecules to absorb light at a specific
wavelength and subsequently emit light of longer wavelength after a brief interval. This effect can obscure the Raman signal. Furthermore, with archaeological samples where unknown residues, the artifact, and containments will all provide spectra, the complicated signal will require filtering methods and noise reduction to reveal the signatures of interest as well as solve both descriptive and predictive problems in experimental natural sciences. There are several statistical methods designed to eliminate identifiable noise can be applied, which can filter the effects of fluorescence. The use of chemometrics is the application of mathematical and statistical methods to filter and improve the chemical information. In order to find the significant patterns, to model these patterns, and to compare them future data a clearly identifiable signal must be defined. In other words, the method of bridging data and measurements in statistically verifiable manners.

Although the term chemometrics is a relatively recent term (Wold 1971) fundamentals and foundations to the methods has a far deeper origin. Multivariate analysis is a critical facet in the application of chemometrics. Complicated data resulting from certain forms of spectroscopy can easily number into the thousands of measurements per sample. Managing the data effectively is the objective, and to develop predictive models to find the signals of interest by their unique measurement properties. As well established for Raman, the output is a multi-wavelength spectral response to analyte concentration. To interpret the output, we require base calibration or training data set, and reference values as well as the measured attributes corresponding to these properties of interest.

Among the multivariate calibration techniques, including partial-least squares regression, principal component regression is used to construct mathematical models that relate the spectrum to the concentration of the analyte of interest. These generated models can be used to
efficiently/effectively predict the concentrations of new samples (and for excellent comparison). Most importantly in the presence of heavy interference of other analytes multivariate calibration allows for accurate quantitative analysis. With thorough consideration and selectivity of the analytical method, in addition to the mathematical calibration, the mode of analytical measurement is directly proportional.

**CONTAMINATION**

Although residues can survive for many thousands of years, archaeological site formation processes affect archaeological residues drastically and often limit the quantity and viability of residues available for study (Schiffer 1987). Archaeologists rarely have the chance to collect more than the necessary sample size for analysis. Most organic constituents are prone to environmental degradation by fluctuating temperature, precipitation and other water action, sedimentation and natural soils movement, animal and insect action, in addition to degradation and reactions caused by chemicals in the immediate environment (including soil pH and rain pH). Artifacts recovered from an unsealed context are typically contaminated by their uncontrolled surroundings, further reducing the available samples for analysis (Schiffer 1987).

Archaeology works with several concepts of contamination that are frequently conflated. These can be defined according with the stage of life-use or post depositional aspect being discussed. Each is significant in the total consideration of the artifact and potential analyses. These definitions however are not the same as those Merriam-Webster defines (accessed at www.merriam-webster.com on December 2018) *Contaminate* as, “to soil, stain, corrupt, or infect by contact or association”, *Contamination* as, “a process of contaminating: a state of being contaminated” and *Cross-Contamination* as, “inadvertent transfer of bacteria or other
contaminants from one surface, substance, etc., to another especially because of unsanitary handling procedures”.

All artifacts are primarily considered for their life-use, or the period of active use, of the artifact in a living environment. Here we are primarily concerned with how an object was used, what function did it perform, by the people who created it. This use may or may not result in residues. The concept of accumulation of residues is not ‘contamination’ in the same sense as defined above by Merriam-Webster, even though the object in question encountered an additional substance. ‘Contamination’ at this stage, might also be defined as cross-contamination, where more than one substance is being intentionally introduced to the artifact, for example a vessel serving as a cooking pot then used as a flower pot.

Although multiple-use objects are rather common in daily use, it is the termination – the final act of the vessel – that often is unexpected. This is especially noted for burial goods, where a vessel of normal use is filled with something and buried with the deceased owner. In ancient Mexico daily use vessels are often found filled with red pigment during the burial rites. We note cross-contamination as multiple substances found on one artifact that appear to be distinct deposits (acquired at different points in time during the life-use, see Loughmiller-Newman 2012, 2016). Intention reuse by the former owners is not contamination archaeologically speaking.

A second consideration of contamination, and following with the more traditional sense, begins after disposal or deposition. This includes the period that an artifact is buried. The accumulation of residues at this point is of considerable interest as it has the potential to affect the life-use residues. The wealth of potential contaminates during the deposition is beyond the scope of this thesis, the reader is recommended to Shiffer (1987) for a more complete
presentation of these agents. Regardless of the number of agents contributing or reducing the former residues, in analytic design this long list of concerns must be addressed. Soil composition of the depositional context can contribute to the rate and severity of the degradation of organic compounds. The breaking down of organic molecules naturally occurs over time, however improper identification of the original source can happen without proper attention (see for instance Science News 2018). Recently (November 2018) vanillin compounds were identified in Israel for a context dated to 3,600 years old. The researchers had identified the find as the fermented orchid known only to the Americas. Vanilla is a New World crop (Americas) not from the old world (Europe, Asia, Australia, and Africa). The academic reaction highlighted the lack of attention to detail, and the more reasonable interpretation that the former contents of wood and the olive oils were breaking down into the vanillins.

Finally, once an artifact is removed from its depositional context (i.e., its location of discovery) the greatest potential for contaminates are introduced. This would include: exposure to the dirty/dusty conditions of excavations, human aspect of handling and caring for the artifact, and weather conditions (rain, wind, snow). Contamination is also introduced during transport and storage. The packaging can itself introduce contaminates (such as plastics or paper bags). Finally, traditional lab practices consisted of numerous people handling, cleaning (washing), and manipulating the artifacts. This is often followed by secondary laboratory practices of restoring, stabilizing, and repairing the artifacts for display. The list of potential containments is far too numerous to discuss in any comprehensive manner within the limited space of this paper but can be consulted through any number of textbooks such as the Encyclopedia of Food and Culture (Volumes I & II Katz 2003).
In terms of laboratory practices for residue analysis, the most relevant here is the issue of Quality Control, especially in the matter of sample preparation. Without doubt, any contact with human skin, hair, clothing, or laboratory equipment may introduce contamination to the samples. Findings of sunscreen, make-up, hair products, and bug spray have all contributed to the contaminants found in the analyses (see Loughmiller-Newman 2012). Our best means to avoid that will include attention to protocols that remove ourselves (as best as possible) from the addition of contaminants. We should then be taking precaution of protective gloves worn to minimize the possibility of labware contamination. Only solvents of high purity should be used, and we need to ensure that all glassware is washed with appropriate lab grade detergents, rinsed with distilled water, and when possible rinsed with acetone before each use. Finally, all samples should be stored in a protected environment.

Protocol wise, cautious care in the analysis such as the calibration of instruments with blank samples is essential. When such measures are taken, we have a better ability to identify the source of contamination (Buonasera, 2007; Fraser et al., 2012; Gregg and Slater, 2010; Isaksson and Hallgren, 2012; Mayyas et al., 2013; Pecci et al., 2010; Reber and Hart, 2008; Reber and Kerr, 2012; Zagorevski and Loughmiller-Newman, 2012). Blanks should be used at all stages and follow the same procedure as that are applied to the samples.

Validation is an extremely significant component of the quality assurance and outcome of the analyses. For the validation process, special attention should be paid to documenting the analytical method or procedure to ensure that it meets its specifications, that the method is suitable, and that parameters are appointed and marked. The validation process consists of several stages as listed here, (Adapted from Namiesnik and Konieczka, 2007):
• Selectivity: specificity; refers to the extent to which the method can determine a particular analyte in a matrix without interference from other components in the matrix

• Accuracy: the closeness of agreement between the value that is accepted either as a conventional true value or an accepted reference value and the value found

• Precision: the closeness of agreement between a series of measurements obtained from multiple sampling of the same homogeneous sample, described by:
  o Repeatability: precision under the same operating conditions and analyst over a short interval of time
  o Intermediate precision: variations within laboratories such as on different days, with different analysts, different equipment, etc.
  o Reproducibility: precision between laboratories

• Linearity: the ability (within a given range) to obtain test results that are directly proportional to the amount of analyte in the examined sample

• Range: the interval between the upper and lower amounts of analyte in the examined sample for which it has been demonstrated that the analytical procedure has a suitable level of precision, accuracy, and linearity

• Detection limit (DL); the lowest amount of analyte in the examined sample that can be detected

• Quantitation limit (QL); the lowest amount of analyte in the examined sample that can be quantitatively determined with suitable precision and accuracy

This list is not intended to serve as a deterrent to future studies, nor is it academic in the sense of an insurmountable task list. Rather, these considerations are intended to provide areas of concern that should be considered when interpreting the findings. They constitute steps necessary for
verification in scientific inquiries, generally. Sine archaeological analysis involves numerous unknown variables, these considerations should be viewed as criteria by which to weigh alternative hypotheses.

**SOURCES OF PRODUCTIVE RESIDUES**

The growing trend in archaeometric studies to include analyses of anthropogenically affected soils can, with increasing resolution, identify areas of craft production, food preparation, and organic waste concentrations (see Parnell 2002). Although this may not directly indicate the presence of foodstuffs consumed or preparations thereof, the assessments may help to localize zones to target for more intensive research. As an example, the burial matrix of a Bronze Age royal tomb in Qatna, Syria produced the biomarkers indigoid and indirubinoid. Both components indicate that garments (long deteriorated), once worn by the corpse, were colored with Royal Purple dye of significant note and prestige (James et al. 2009).

“This was subsequently confirmed through microscopic examinations of the sediments from the tomb, which revealed millimetre-sized fragments of fossilized textile (gypsum replicas; confirmed by X-ray crystallography) displaying the purple dye. The morphologies of the textile fragments recorded the weave of the textile and pattern of the applied dye. The presence of the purple dye is indicative of wool being used to fabricate the textile” (Evershed 2008:909).

It should also be noted that the fabric (protein-based) had deteriorated, but the pigment biomarkers were still intact.

Tombs are regarded as one of the best possible contexts of preservation and in at least one instance cigars have been discovered protected in a burial at Tikal, Guatemala (Robischek
1978:111). Flasks are frequently encountered in Late Classic burials, which remain suggestive of the presence of tobacco (see Burial 61 El Peru, Eppich 2013). Typically, these contexts are sealed away and protected from many of the natural and manmade disturbances that normally occur (see Schiffer 1987). Therefore, when a tomb is discovered pains are taken to record and describe every bit of information possible. Burials typically receive a special concentration of archaeological effort. In reverence of the deceased, tombs are filled with goods and tribute to the person laid to rest. For the Classic Mayas, tombs generally contain for elite persons, a number of pottery vessels including plates, bowls, cups or cylinders, storage vessels, and stamps, as well as figurines. Royal figures are also bedecked in jade and shells, and on occasion burial masks and headdresses. What we are less certain about is the plants, foods, flora, seeds, and pigments as uncontained offerings that may also be present.

Less well protected and/or sealed are refuse piles or middens. These debris piles are commonly associated with housing groups and spaces for social gatherings. The amorphous contents can be generally narrowed in on by the association of the midden to a domestic or ritual space. Manos and metates are one of the most frequent domestic goods recovered. Their use is longstanding and practical. Generally, their use is ascribed to the preparation of maize, amaranth, and other foodstuffs that could be ground. Following from the small flasks containing ground tobacco mixed with lime, matates might also have been used for the processing of tobacco (see K1272 Famsi.org). It remains unknown if other means were used, but matates can and do retain minute amounts of residues including fats and microfossils remaining from use.

Typically, Mayan illustrations (especially those featured on vessels) were not static representations of a moment, but rather represented a view of an on-going action (Loughmiller-Newman 2008). Such scenes typically depict political deliberations, noteworthy discussions,
mythological events, war, hunting, or sacrificial processional, or patrician rites. These scenes depict noteworthy segments of time but hint at a more protracted sequence of events surrounding that timeframe. This can be identified through the depiction of regularly occurring objects and accoutrements associated with event type and actor status (such as Kings, lords, or secondary nobles). These items were culturally identifiable elements and would have been immediately recognized for their intended purpose or use within that scene. Thus an object depicted within such a scene necessarily performed an understood role within that sequence of action.

Unfortunately for modern researchers, most of these cultural symbols are still poorly understood.

We should also be looking to the images that were made by the people that are the source of the material remains. In theory, the images they create should demonstrate some aspect of life as they performed it. Therefore, if we should find an image of a depicted vessel (e.g., a cup, bowl, or large storage vessel) information might also be presented for the intended function associated with its form. This is true in our own lives, such as a wine glass noted on a reception invite. In general performance a cup is what will hold, is holding, or has held a beverage. This meaning is present when a vessel is depicted in a scene, regardless of whether it is depicted as actively being employed in consumption. Its presence in a scene simply represents the performance of some activity related to beverage consumption as well as a *pars pro toto* indication the sequence of events that necessitated its presence. The depiction of a drinking vessel, therefore, represents some larger series of behaviors involving a beverage. The beverage itself had to be acquired or produced, possibly stored, provided or served, and finally consumed. Each of these activities would have had some set of associated actions related to material artifacts, and possibly some set of associated ritual or other socially recognizable behavior as well. Each such set of actions is indirectly implied by the depiction of a drinking vessel.
There are very few liquids, if any, that would have been immediately available for consumption to the Classic Mayans without some form of preparation. Water would need to be purified, fruit would have had to have been processed, and the fermented beverages would have undergone specific preparatory steps. Colonial documents and recent ethnographic work has highlighted the significance of the rituals involved in the preparation of certain beverages – ritual drinks were born out of ritualized acts (e.g. Balche rituals, see Boremanse 1981; McGee 1984, 1988; Tozzer 1907; Hoil and Roys 1967; Slotkin 1954). This underscores the fact that the act of drinking a beverage is not a self-contained event, but instead, one intrinsically linked to the preparation of the liquid. The act of preparation would conclude with consumption, but the consumption would not be the only aspect considered significant.

A cup directly symbolizes only the final act of consumption by an individual, but consumption itself further necessitates and symbolizes by implication all the prior events as well. An olla generally indicates a penultimate state of consumption where a liquid is expected to be served in a cup. The presence of ollas also suggests either that a number of participants will be consuming the beverage or that the participants will be consuming a greater quantity than that held by a single cup.

The production of alcohol requires specific steps and care, as does the production of significant foodstuffs. Recipes and required steps or content can reasonably be assumed. Significant goods would not have been reasonably left to experimentation, especially those that are rare, difficult to procure, or require a great amount of effort to produce. This would likely be especially true if they were required for use in an imminent ritual. Ritualized production would function broadly as a recipe, thus ensuring a reasonable amount of success leading to a predictable and consistent final product.
CONCLUSION

The nature of archaeological residues is complicated. It is rare that residues can be properly or completely predicted. While there are many methods of identification, none are designed specifically with archaeology and its conditions in mind. Chemically, dealing with residual unknowns can be managed through various methods whether is it by mass or by weight. When dealing with residual unknowns that are in unknown states of deterioration, the analysis becomes only slightly more complex. However, if all of the above are true and the additional constraints of cost, time, damage, and limited sample are considered the situation changes dramatically.

For the past 60 years archeological residue studies have been primarily conducted with some form of separation method followed by mass detection. These methods have proven that even with thousands of years of environmental and natural agents working against preservation the samples can be identified. And each point of knowledge helps frame the archaeological data and interpretation. However, given the general limitations and the more extraordinary needs of archaeological materials, in addition to the cost, damage, and time involved residue analysis is still relatively rare when compared to the millions of artifacts that are excavated each year.

Methodologically, the tools that would most ideal such as Raman spectrometry or Fourier-transform infrared spectroscopy (FTIR) are already widely used in museums and in research institutions for material studies, mainly inorganic compositions of pigments, material characterizations, and other inorganic substances. The methods however are lacking for the same application to the organic foodstuff remains. Among the most obvious reasons is the complicated signal involving unknown analytes.
With increasing precision, the instruments can be tuned to cope with the fluorescence potentially obscuring weaker or minor signals of interest. Additionally, chemometric methods not only reveal the lesser bands within the spectra, but also highlight analytes of interest. These two factors are key developments that are suggestive of future potentials in the application of the characterizing of archaeological residues. Also, a point in which the investment of further refinement of methods specifically designed to address aged, deteriorating, and multicomponent samples should be promoted.

While the humanities and the natural sciences have often been considered to deal in bifurcated academic spheres, this is not historically nor developmentally true. Chemistry has been the direct product of human interest, trends, and curiosity. Moreover, that as the world has experience periods of collaboration among confederate countries, the shared achievements have been transformative in all academic spheres. Furthermore, that as the instruments are developed and refined to discuss the world around us, we still respectively measure curiosities, ourselves, and our world. This is as it has always been. Now, the humanities through archaeology are looking for answers of how we have always been, why despite time and distance we share experiences, and furthermore with the aid of chemistry why the human experience encompasses so many commonalities.
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