

# A Practical Approach to the Chemical Analysis of Historical Materials

Ray von Wandruszka · Mark Warner 

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**Abstract** Chemical analysis is an underused tool in historical archaeological investigations, despite the fact that much valuable information can be obtained from a chemical study of historical artifacts. Such analyses usually focus on the identification of materials, with the aim of elucidating their origins and historical uses. In a chemical sense, this proceeds through a number of stages, starting with simple observations and often ending with sophisticated measurements. It is work that can employ many different wet-chemical and instrumental methodologies, their use depending on both the analyst's insights and the availability of equipment in the laboratory. It is important to recognize which instruments cannot be done without in the analytical process and which may be too costly to warrant the investment. The diverse nature of the samples often leads to methodological challenges, underscoring the uncertainties inherent in the chemical analysis of historical artifacts.

**Extracto** El análisis químico es una herramienta subutilizada en las investigaciones arqueológicas históricas, a pesar del hecho de que mucha información

valiosa puede obtenerse de un estudio químico de artefactos históricos. Tales análisis suelen enfocarse en la identificación de materiales con el objetivo de dilucidar sus orígenes y usos históricos. En un sentido químico, se pasa por una serie de etapas, empezando con simples observaciones y a menudo terminando con mediciones más complejas. Es trabajo que puede emplear muchas metodologías instrumentales y de químicos húmedos y su uso depende tanto de la perspicacia del analista como de la disponibilidad de los equipos en el laboratorio. En el proceso analítico, es importante reconocer los instrumentos imprescindibles, así como los que pueden ser demasiado costosos como para justificar una inversión. La diversa naturaleza de las muestras a menudo resulta en retos metodológicos, subrayando las incertidumbres inherentes en el análisis químico de los artefactos históricos.

**Résumé** L'analyse chimique est un outil sous-utilisé dans les enquêtes archéologiques historiques, et ce, même si les études chimiques peuvent fournir plusieurs renseignements utiles sur les artefacts historiques. Lesdites analyses portent généralement sur l'identification des matériaux afin d'en élucider les origines et les usages historiques. Du point de vue chimique, ce processus comporte plusieurs étapes, dont l'observation initiale simple et la prise de mesures définitives sophistiquées. Ces travaux peuvent faire appel à plusieurs méthodologies chimiques par voie humide et instrumentales variées, dont l'usage dépendra de l'analyste et de la disponibilité de l'équipement de laboratoire. Durant le processus analytique, il est

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R. von Wandruszka  
Department of Chemistry, University of Idaho, 875 Perimeter  
Drive MS 2343, Moscow, ID 83844-2343, U.S.A.  
e-mail: rvw@uidaho.edu

M. Warner (✉)  
Department of Sociology and Anthropology, University of Idaho,  
875 Perimeter Drive MS 1110, Moscow, ID 83844-1110, U.S.A.  
e-mail: mwarner@uidaho.edu

important de reconnaître les instruments essentiels et ceux qui sont trop coûteux pour justifier l'investissement. La diversité des échantillons donne souvent lieu à des défis méthodologiques, soulignant les incertitudes implicites de l'analyse chimique des artefacts historiques.

**Keywords** archaeochemistry · methods · bottle glass · metal analysis

## Introduction

It is common for archaeologists to enlist the help of analytical chemists, biochemists, and material scientists to elucidate the chemical and physical properties of prehistoric objects. Among historical archaeologists, however, such collaborations are not widespread. The reason for this is not entirely clear, but there is little doubt that the discipline of historical archaeology does not take full advantage of the important information regarding the nature and origin of recovered materials that can be provided by chemical analysis. We hope to show in this article that there are good reasons for changing this. The information presented here comes from an 10-year collaboration between chemists and anthropologists at the University of Idaho. During that time, chemical analyses were carried out on about 200 samples of materials and artifacts recovered from excavations on more than a dozen archaeological sites throughout the United States and Canada.

It is desirable for historical archaeologists to become acquainted with the possibilities, requirements, and limitations associated with the chemical analysis of unknown historical materials. Our collaborations have shown that archaeologists often do not know where to begin when confronted with residues in bottles and jars. Certainly, in the rare instance of a sealed bottle with intact contents being recovered, a visit to an analytical laboratory may be undertaken. Mostly, however, items, such as glass fragments coated with small quantities of material or medicine vials containing a few grains, are just cataloged and stored. Indeed, approximately 70% of the materials that we have tested over the past ten years were from collections that had already been sitting on repository shelves for over a decade. The central issue is that these bottles are significant sources of information that many archaeologists tend to overlook.

From an archaeological perspective the value of the information gleaned from this work can be quite varied. Certainly there are functional questions to be answered by analyzing what was in the bottle or jar, but what we have found is that content analyses may also provide data for broader questions about behavior. Those questions are dependent on the type of site being excavated, but we would note two examples of content analyses contributing to broader questions. First, one consistent theme that has emerged from our work is that the results regularly illustrate the complexity of interpreting the use of everyday material culture as it applies to consumption practices. We frequently identify materials used for purposes other than their original intent, such as a liquor bottle that was repurposed to store glue (von Wandruszka et al. 2015:28–29). A second example would be how chemical analyses have contributed to understanding aspects of immigrant life in the United States. Many of our samples have come from Chinese-occupied sites in the West. Examination of the contents of several medicine bottles has demonstrated the continuation of traditional Chinese medicinal practices as manifested through the identification of “stone drugs” in several bottles (Voss et al. 2015) and, as discussed later in this article, the use of coins for medicinal purposes.

While there are considerable analytical benefits for historical archaeologists to undertake chemical analyses of bottles, jars, etc., it is important to also recognize that the chemical identification of materials recovered from historical archaeological excavations can also present serious challenges. These have various causes, but they are usually related to chemical changes that occur in samples during prolonged exposure. The aim of this article is to provide archaeologists some foundational information on how to overcome some of those challenges and a brief “how-to” guide for their chemistry colleagues when they are confronted with a box of old bottles.

## Preliminary Considerations

### Clues from Containers

It goes without saying that chemical analysis is easier when the container provides clues regarding its content. This may be the remnant of a label (rare) or embossing on a glass surface. Shapes and sizes of bottles can also be revealing, although most chemical analysts would

need to seek the advice of an archaeologist on the details of such deductions! In many instances, unfortunately, bottles, jars, and cans are generic and provide little or no indication of the material in them. In addition, it is not uncommon for containers to be repurposed by users, thereby further blurring the question of contents.

### Sample Limitations

Chemical analysis of historical materials is often confounded by the small quantity of sample available. For example, the remnants of a solution dried onto the inside surface of a bottle may amount to only a few milligrams, precluding the use of good analytical techniques that require larger sample sizes. Another frequently encountered problem is the effect of time and exposure on the materials. Slow chemical reactions that can happen between the compounds of interest (the “analytes”) and oxygen and water in the atmosphere can leave these analytes in a near-unrecognizable form as the decades pass. In some cases, for instance, where the reaction in question is a polymerization, the sample can also become difficult to handle—e.g., by being practically insoluble in any solvent. These considerations lead to the inescapable conclusion that chemical analysis of historical artifacts rarely, if ever, provides answers with 100% certainty. The words “probable” and “likely” appear frequently in reports.

### Instrumentation

Analytical chemistry is an expensive discipline. Instrumentation providing the most accurate answers or requiring the smallest quantity of analyte can cost tens, even hundreds of thousands of dollars. Not surprisingly, therefore, laboratories rarely feature a full complement of desirable instruments. The discussion below identifies some instruments that “cannot be done without,” while making no, or only peripheral, mention of apparatus that may be available in some laboratories but not in others.

## Appearance of Material

### Phase

The first examination of an unknown historical material by an analyst naturally reveals whether it is a solid or a

liquid. While generally this is fairly straightforward, in cases where the two phases are mixed one of them may be difficult to discern. It should especially be noted that a suspension of a solid in a liquid may be of a colloidal nature, in which the particles are perpetually suspended and give the liquid a cloudy appearance. Separating the solid from the liquid is usually required for subsequent analysis and should be carried out by centrifugation. In most cases, a small bench-top centrifuge is suitable for this.

### Color

The next step in the initial examination is to observe the color of the sample. This is especially important for inorganic solids, where the color can be a good indicator of the type of metallic species present (see below). More often than not, materials found in historical containers are mixtures—either through original formulation or through contamination. In a solid mixture, the components may differ in color and/or morphology. For samples consisting of small particles, it is advisable to examine them with a microscope. Usually large magnification is not called for, and digital microscopes that range up to 250 $\times$  are suitable. The images produced, which are typically viewed on a computer screen, give a good sense of the heterogeneity of the sample and can, as a bonus, be subsequently used as illustrations (Fig. 1). Digital microscopes appropriate for this kind of work are relatively inexpensive, with prices in the \$500–\$600 range.



**Fig. 1** Example of a 250 $\times$  image of an historical material obtained with a digital microscope. The material shown is a highly heterogeneous grain of a yellow-orange substance used as a paint. (Photo by authors, 2016.)

## Odor

An important feature of an unknown sample is its odor. Odors are caused by the evaporation of the liquid or solid components of a sample and detection of their gaseous molecules by the human nose—which can be a sensitive and discerning “instrument.” In historical materials, for obvious reasons, most volatile compounds (liquids) tend to be long gone. Some solids, although obviously less volatile, can also be odiferous and, thereby, provide valuable clues to the analyst. The identification of odors is clearly a function of the analyst’s experience with the same, but to chemists the smells of compounds, such as waxes, esters, and phenols, are bound to be familiar. The production of odiferous compounds in chemical reactions falls in a different category and will be touched on later.

## Magnetism

It is a simple and practical expedient to check the magnetism of an unknown historical material. If it is attracted by a magnet, it is either elemental iron or ferrosferric oxide (magnetite). The latter is used in traditional Chinese medicine (TCM) (Yu et al. 1995) and is sometimes recovered in excavations of historical Chinese dwellings.

## Organic or Inorganic?

The next big question facing an analyst in the evaluation of an historical material concerns its chemical nature: Is it organic or inorganic or a mixture of both? An organic compound is one that contains carbon (C), usually as the main, “backbone,” element, while inorganic compounds do not. The very common carbonate ion,  $\text{CO}_3^{2-}$ , is an exception. It does contain carbon, but is considered an inorganic species. Many organic species are of plant or animal origin, but, in recent history (especially during the last century), large numbers of manmade organic compounds have appeared.

The best way to determine whether an unknown sample contains organic components is to take an infrared (IR) spectrum (Pasto and Johnson 1969). IR spectroscopy is quick, uncomplicated, and nondestructive; in addition, it requires only small amounts of material. IR spectra consist of absorption peaks that are indicative of specific molecular features—i.e., chemical bonds

between atoms. The great majority of organic compounds contain carbon (C) bonded to hydrogen (H), and the presence of a C–H bond, indicated by absorption of light at a “frequency” at or around  $2900\text{ cm}^{-1}$ , therefore suggests that the material in question is organic. The absence of this absorption peak usually means that the material is inorganic. There are many more peaks in an IR spectrum, giving more detailed information about the compounds. These will be discussed later.

While the occurrence of a  $2900\text{ cm}^{-1}$  peak indicates the presence of organic species in a material, it does not exclude the concomitant presence of inorganic components. This can be clarified further by subjecting the sample to high temperatures. A weighed quantity of material is put in a crucible (usually ceramic, but possibly platinum or titanium) and placed in a muffle furnace at  $800^\circ\text{C}$  (red heat) for a period of 6–8 hours. Under these conditions any organic materials will burn off, leaving only inorganic components. The organic/inorganic ratio of the sample can now be calculated from the weight difference of the material before and after the heat treatment. There is one caveat in this methodology: there are a number of inorganic materials that also volatilize under high heat. The most notable of these are mercury compounds, especially cinnabar (see the discussion below, under “Some Specific Cases and Caveats”).

Two more considerations warrant mention: (1) While most carbonates, especially limestone ( $\text{CaCO}_3$ ), start to decompose into oxides and thereby lose weight (calcination) at temperatures well above  $800^\circ\text{C}$ , in some carbonates the process starts at that temperature and leads to weight loss; and (2) hydrated materials will lose water (and weight) when heated. This latter circumstance is revealed in the IR spectrum: water shows a strong peak around  $3400\text{ cm}^{-1}$ , and this will disappear after heating.

## Inorganic Materials

Once a material has been identified as inorganic or an inorganic component has been isolated through heat treatment, analysis of the compound(s) in question can proceed. In the likely case that the material is a solid, the first step is to examine its IR spectrum. Inorganic compounds have less informative IR spectra than organic materials, but certain features can be highly revealing.

### Infrared Spectra: Silicates

A frequently encountered IR feature in historical materials is a strong peak at a wave number slightly above  $1000\text{ cm}^{-1}$ . This is indicative of the silicate group ( $\text{SiO}_4$ ), which constitutes a major portion of rock and sand. Its presence in many instances means that the sample has been contaminated with invading dirt. This, however, is not a necessary conclusion. Many silicates may constitute the original contents of an historical bottle or jar. TCM “stone drugs,” for instance, are often silicates, as are many cosmetics. Talcum (talc powder), a magnesium silicate, is an example of a material that is widely used in health and beauty products. Household products, such as cleaners or scouring powders, are also often silicate based.

Silicates are a broad class of compounds that are generally found in association with metal ions. The kinds of metals present and their disposition in the silicate structure determine the exact nature of the silicate. For the analyst this means that, subsequent to silicate identification, a metal analysis has to be carried out. This will be discussed below. There is one form of silicate that contains no metals: silica ( $\text{SiO}_2$ ), or, in crystalline form, quartz. This compound is a major component of sand, and in powder form it is sometimes used as an excipient in medicinal preparations.

### Infrared Spectra: Carbonates

This class of inorganic compounds contains the  $\text{CO}_3^{2-}$  ion, which provides the compounds with a recognizable IR signature. The peak in question is located at approximately  $1430\text{ cm}^{-1}$ , but is sometimes obscured by absorption peaks of organic compounds in the sample. The carbonates come in a wide variety of metal salts, among which calcium carbonate ( $\text{CaCO}_3$ , limestone, chalk, calcite) and magnesium carbonate ( $\text{MgCO}_3$ ) are especially prominent. They are widely used in man-made products, including building materials (e.g., cement), pharmaceuticals (e.g., antacids), and ceramics (glazing). They are also a common soil and rock constituent. Their interactions with acidic solvents are especially telling (see below).

### Infrared Spectra: Nitrates

These inorganic compounds contain the  $\text{NO}_3^-$  group, which has an IR peak around  $1350\text{ cm}^{-1}$ . Nitrates are not

as commonly found in historical containers as some of the other compounds listed here, which is partially due to their water solubility. The main uses of nitrates are in fertilizers and explosives.

### Dissolution

The solubility of unknown materials in different solvents can provide important clues regarding their identity. The solvents in question may be aqueous (water based), such as many acids and bases, or they may be organic, such as ethanol, ether, and chloroform. Based on the recognition that “like dissolves like,” conclusions may be drawn from the (total or partial) solubility of a material in a solvent. What is more, for important follow-up analyses, solutions are generally required.

The “obvious” solvent to be tried with solid samples is plain water, but the vast majority of recovered materials are not water soluble. In most historical samples prolonged exposure to the environment has leached out most or all water-soluble components. Better dissolution of inorganics is usually achieved with concentrated hydrochloric acid (HCl), especially when attempted with the aid of an ultrasonic cleaner. (The use of “sonication,” often accompanied by heating, is generally recommended for better and quicker results.) If a sample fails to dissolve, or completely dissolve, in HCl, it is worthwhile to add hydrofluoric acid (HF) to the solution (HCl:HF=3:1). This has to be done in a plastic, e.g., Teflon, container, since HF attacks glass. If the addition of HF results in the dissolution of the sample, then it is strongly indicated that it contains silicates, since HF is one of the few solvents that dissolves those materials.

While the presence of an IR absorption peak at  $1000\text{ cm}^{-1}$  combined with solubility in HF is strong evidence for silicates, it does not automatically follow that the sample is just sandy soil. Often that is so, but sometimes a “legitimate” sample is, in fact, a silicate. This may, for instance, be the case with makeup, especially foundations that frequently contain talcum powder, or medicines that contain silicate excipients (see above). Most notably, the so-called stone drugs widely used in TCM (Yu et al. 1995) are ground-up natural minerals that are either entirely composed of silicates or contain them in greater or lesser quantities.

The carbonates mentioned above are often insoluble in water, but are always soluble in acid. Their dissolution in acidic media is accompanied by the evolution of carbon dioxide ( $\text{CO}_2$ , an odorless gas), and a



nonmetallic sample that effervesces when placed in acid, but does not smell, is almost certainly a carbonate. Sulfides also often evolve gas when in acidic solution, but this gas is hydrogen sulfide ( $\text{H}_2\text{S}$ ), which has an unmistakable foul smell (rotten eggs) to which the human nose is extremely sensitive.

Inorganic materials found in historical containers, including minerals other than silicates, oxides, and sulfates, can sometimes be difficult to dissolve, even in acid media. Heating often promotes dissolution, but a more “aggressive” solvent, such as aqua regia (3 HCl:1  $\text{HNO}_3$ ), may be called for. Refluxing a sample in this solvent is especially effective, even for dissolving noble metals, such as silver, gold, and platinum. Solutions tend to assume a yellow color, which is due to the formation of nitrosyl chloride ( $\text{NOCl}$ ) and has no relation to the dissolved material. It is not recommended to use aqua regia solutions as such in subsequent analyses; they first should be copiously diluted with water.

#### Further Analysis: Anions

If the characterization of an inorganic historical material requires further identification of the anionic portion thereof (e.g., sulfate, nitrate, phosphate, sulfite, chloride, fluoride, etc.), ion chromatography is an effective tool, both in a qualitative and quantitative sense. In ion chromatography the ionic (electrically charged) components of a dissolved sample are separated by being forced, under high pressure, through a column filled with an ion-exchange resin. The ions emerge sequentially from the column and are detected and identified. This is carried out with an ion chromatograph, and, if no such instrument is available, the analyst will have to resort to old-fashioned spot tests or gravimetric/volumetric determinations. Descriptions of the latter, for instance, for chlorides and sulfates, can be found in any basic chemistry laboratory manual. Extensive compilations of spot tests, all of which are qualitative in nature, are presented in the seminal book by Feigl and Anger (1972). In this context, the test for phosphates warrants special mention. It is carried out by the molybdenum-blue method, in which a blue complex is formed in a series of reactions and can be measured colorimetrically (Murphy and Riley 1962).

#### Further Analysis: Metals

The determination of the metal ion in historical materials is usually of considerable value in identifying the

substances in question. Metals may be present in elemental form or as oxides, minerals, or salts. As such, they are often part of a mixture with other inorganic or organic compounds. A number of sophisticated techniques exist by which metals may be both identified and quantified. These include neutron activation analysis, x-ray fluorescence, and inductively coupled plasma (ICP) spectroscopy. Portable x-ray fluorescence (pXRF) spectrometers have come into general use in recent years, and they work well in the determination of metallic elements in a variety of matrices. However, the samples recovered from historical containers often amount to no more than microgram-sized scrapings of inhomogeneous materials, and, although modern pXRF instruments with 3 mm spot sizes are available, such measurements can be challenging. What is more, many laboratories do not have the budget for the acquisition of more expensive instruments and will have to make do with the more basic (and cheaper!) atomic-absorption spectroscopy (AAS) and flame photometry.

A serviceable flame photometer can be purchased for \$500–\$600 at the time of this writing (2016), but it must be kept in mind that the technique is only practical for alkali metals (Na, Li, K) and, to a lesser extent, calcium (Ca). The instruments, which require dissolved samples, consume relatively large sample volumes (several milliliters) per determination. This can be a problem when the amount of material available is limited—as is often the case. Sensitivity for alkali metals is good.

AAS is without doubt the go-to method for elemental analysis of metals. The technique can handle a great variety of metals, and sensitivity is generally very good. The main drawback is that each element requires a separate atomic light source (hollow cathode lamp, HCL)—or at least a separate setting on a multi-element HCL—limiting the number of potential measurements and making complete analyses slow, laborious, and solution intensive. Depending on the type of instrument, sample atomization is achieved with a flame (usually air/acetylene) or with a small, electrically heated, graphite furnace (better, but more expensive). Common flame AAS is not very sensitive for aluminum and does not work for mercury. For the latter, a special cold-vapor generator must be installed.

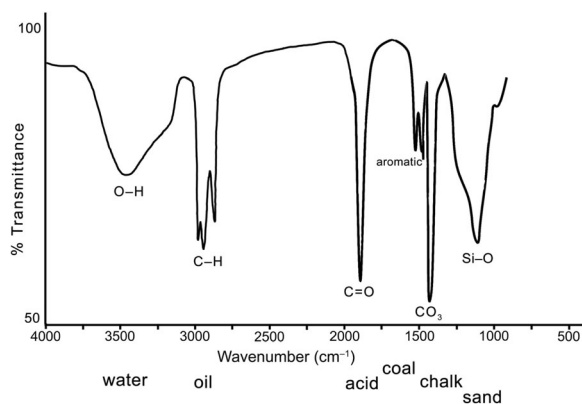
A common problem with the AAS analysis of inorganic historical materials is that the analyst often has little or no idea about the metals that may be present. This results in a trial-and-error process that is limited by the HCLs on hand and the quantity of sample available.

A far more effective and efficient technique is ICP analysis, which, as noted above, requires a greater capital investment. Prices of ICP spectrometers have fallen in recent years, and a suitable ICP-atomic emission (ICP-AE) instrument can be purchased for around \$50,000. ICP-AE can be used for the determination of as many as 67 different elements, including even phosphorus (P). It is desirable that the instrument be of the *simultaneous* type, i.e., one that captures the emission spectrum in a single measurement, rather than sequentially. It should also be checked whether this measurement encompasses the *entire* emission-wavelength range, rather than only part of it. These considerations are important, because historical samples can be very small, yielding sometimes less than a milliliter of solution with which to work. ICP analysis provides a wealth of information, avoiding the possibility of overlooking important components.

### Organic Materials

If the initial investigation with IR spectroscopy indicates (see above) that organic material is present in the sample, it is very likely that the IR spectrum reveals a great deal more about the compound(s). IR spectral analysis can be rather intricate, and, in view of the fact that historical samples are rarely, if ever, pure or unaffected by time and exposure, it is probably not worth the analyst's time to scrutinize small shifts and minor peaks. However, the major features of the IR spectrum can provide much useful information. Some of these major peaks are summarized in the (artificially assembled) spectrum shown in Fig. 2. It must be kept in mind that IR spectra of different molecular groups frequently overlap, and the peaks may conceal each other.

Once it has been established that the material has organic content and that the molecules have certain features (e.g., a hydrocarbon chain, a double bond, or a benzene ring), the solubility of the sample should be investigated. As with inorganic compounds, water is still a solvent to be looked at, but organic solvents have to be tested also. These include alcohols (methanol and ethanol), possibly acetone, and a hydrocarbon such as hexane. Chlorinated solvents, such as carbon tetrachloride, should be avoided because of waste-disposal issues. The distinction between alcohol and hexane is that the former is polar, while the latter is nonpolar. This polarity designation refers to a degree of charge



**Fig. 2** Artificial IR spectrum showing major absorption peaks that may be found in historical materials. (Spectrum by authors, 2016.)

separation in the molecule: a polar molecule has a “negative end” and a “positive end,” while a nonpolar molecule does not. The rule is that like dissolves like, i.e., a polar molecule such as sugar dissolves in alcohol (and water, of course, which is also very polar), while the nonpolar candlewax molecules dissolve in hexane. The solubility characteristics of an unknown historical compound will always be reflected in the molecular groups shown in the IR spectrum.

Next, more specific tests are carried out. For instance, if the IR spectrum has a peak at  $1600\text{ cm}^{-1}$ , then this is probably due to an aromatic group (a benzene ring), but it may also come from an organic nitrate. One way to resolve this is to check whether the compound fluoresces. If the laboratory has a fluorimeter, then this is simply a matter of measuring the fluorescence of the solution. If no fluorimeter is available, it often suffices to observe the sample under a handheld ultraviolet lamp. If the UV radiation causes the sample to “glow,” i.e., emit visible light, then it definitely contains an aromatic molecule.

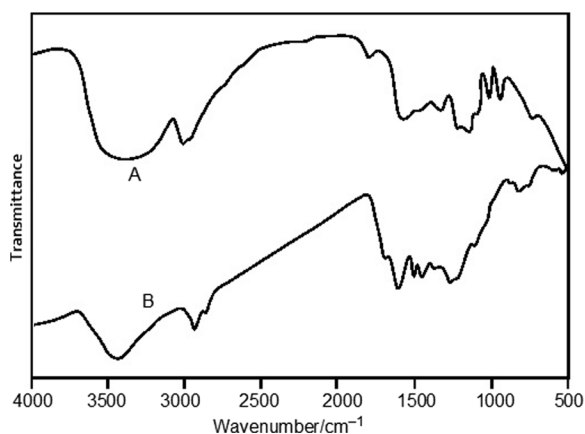
If the organic material dissolves in water, then the acidity (pH) of the resulting solution is an important parameter to investigate. This is especially true if the IR spectrum of the unknown has peaks at  $1700\text{ cm}^{-1}$  and  $3400\text{ cm}^{-1}$ , as these could be due to an organic (carboxylic) acid or to moisture in a sample that also contains an ester. Testing the aqueous solution of the sample with pH paper is usually good enough: if the compound is an acid the pH paper will turn red, indicating an acidic solution.

If observation and chemical intuition lead the analyst to suspect that the sample may be a certain material, but

further confirmation is required, an IR “fingerprint” of the sample may be obtained and compared to a known material. This is especially useful if an unknown is not a distinct compound, but a mixture of different related molecules. An example of this is wood tar, which is a complex mixture of hydrocarbons and phenols that are difficult to isolate. An unknown material, suspected to be wood tar, was investigated in our laboratory, and the IR spectrum of the material was obtained (Spinner et al. 2011). It was compared, in its entirety, to a spectrum of known wood tar in a manner in which fingerprints could be compared (Fig. 3). Their similarity led to the conclusion that the material was indeed wood tar.

In instances where mixtures of organic compounds cannot be identified satisfactorily, chemical separation has to be carried out. The method of choice for this is chromatography, which comes in many varieties—from paper chromatography to high-performance liquid chromatography/mass spectrometry (HPLC/MS)—and many levels of instrument investment. The most versatile technique for historical samples is gas chromatography/mass spectrometry (GC/MS), which requires a capital outlay of around \$45,000.

In the “GC” portion of the operation, the sample, dissolved in an organic solvent such as methanol (not water!), is separated into its components. In the “MS” portion, the instrument generates a mass spectrum for each of these components. The individual, unknown, mass spectra are compared to mass spectra of known compounds in a vast data base (usually from NIST, the National Institute of Standards and Technology). The entire operation is automated and managed by the instrument software. Unlike any of the other techniques



**Fig. 3** IR spectra of (A) an unknown material, and (B) a known wood-tar sample. (Spectra by authors, 2009; offset for clarity.)

described in this article, GC/MS provides a definite structural identification of the compound under investigation. While this is a great advantage to the analyst, it is subject to a serious caveat. Matching mass spectra invariably gives rise to a degree of uncertainty, and it is a matter of choice which probability level is deemed acceptable. Generally speaking, the probability of positive identification, as provided by the instrument’s statistical software, should be at least 80%, and preferably >90%. Any lower percentages cannot be considered to signify *reliable* identification.

This consideration constitutes a limitation on the applicability of GC/MS to historical samples. Moreover, as noted in the introduction, materials can undergo significant chemical changes (oxidation, hydrolysis, polymerization, etc.) through long exposure to the environment. It can therefore happen that a GC/MS analysis supplies answers that have no apparent bearing on the original state of the material in question.

#### Organic Spot Tests

As is the case for inorganic materials, a vast array of spot tests is available for organic compounds. These, too, have been compiled in a comprehensive volume published by Feigl and Anger (1966). The tests are often very sensitive, generally quite specific, but not quantitative.

#### A Word about Liquids

Most historical materials are solids, since liquids tend to evaporate over time. This does not mean that liquids, either as liquid compounds or as solutions, are not recovered regularly. This is especially true in cases where the container is intact and hermetically sealed. When it is not tightly closed, for instance because of a decayed or broken stopper, the presence of a liquid in a bottle should raise the suspicion of water seepage. Water is indicated by a large, broad peak at around  $3400\text{ cm}^{-1}$  in the IR spectrum.

If a well-closed container does hold a “legitimate” aqueous solution, the substance of interest is invariably the dissolved material (the solute), not the water solvent itself. The latter is therefore generally removed by evaporation. If a freeze dryer is available, this provides the preferable method of obtaining the dry solute. Otherwise, the water is evaporated through gentle heating,



and the analysis of the remaining material is carried out as with a solid. Frequently, a liquid sample is not aqueous, but a fluid or semifluid organic material. Heavy oils (fossil or essential) and viscous plant exudates, such as tree resins, are sometimes encountered. These are a priori identified by the presence of a strong C–H peak at  $2900\text{ cm}^{-1}$  in the IR spectrum. Further analysis proceeds as with solid samples. GC/MS is often fruitful for these materials—for instance, the identification of linoleic acid as a major component in an unknown organic liquid is a good indication that the material is sunflower oil. In this last example, and indeed many others, the analyst should not be unduly disturbed by the presence of solid in the liquid. Materials can partially polymerize, forming solid particles that float in or settle out of the otherwise liquid medium.

### Some Specific Cases and Caveats

#### Traditional Chinese Medicine

Excavations of past Chinese communities and households are quite common and widespread in the American West (Voss et al. 2015). Samples related to traditional Chinese medicine (TCM) are often found among the items recovered from these sites. Single-dose medicine vials (Fig. 4),



**Fig. 4** A Chinese single-dose medicine vial containing cinnabar. (Photo by authors, 2013.)

sometimes erroneously referred to as “opium vials,” are widely used TCM containers. They rarely arrive stoppered, so materials remaining in them are invariably solids and, more often than not, of mineral origin. One should be aware of the wide use of these stone drugs in TCM practice and approach the analysis of the samples with this in mind. A case in point is cinnabar (mercuric sulfide, HgS), a red mineral that is a common mercury ore and has found various uses in Chinese culture. In TCM it was (and still is) used as a stone drug to combat intestinal infections. It was also used as a red colorant in Chinese stamp inks (Wertz 2016).

#### Carbon

It is not unusual to find elemental carbon, in the form of a black powder, in small medicine bottles. This material was, and still is, widely used in many cultures as an internal detoxification agent. The carbon, in its activated form, is an excellent adsorbent that when ingested can remove toxins from the stomach and intestines. (Activated carbon is produced by treating charcoal with superheated steam.) The IR spectrum of the material is quite featureless, although noncarbonized impurities can give rise to small peaks in the  $2900\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$  regions. In a flame it tends to glow, rather than burn with a flame. A good way of establishing its identity is to place it in a dilute aqueous solution of a dye, such as methylene blue. Activated carbon will partially or completely decolorize the solution.

#### Iron

Iron is a common element in natural materials, especially soil and rock. Iron oxide (ferric oxide,  $\text{Fe}_2\text{O}_3$ ; hematite) is a red/yellow substance that has many diverse uses, including as a pigment, a hematinic, and a polishing agent. If an unknown material of any color after a 6–8 hour treatment in a muffle furnace ( $800^\circ\text{C}$ ) turns red, then the presence of iron is indicated. If a generally acidic aqueous solution of an inorganic sample is yellow, then this may be due to iron, present as the  $\text{Fe}^{3+}$  ion. If the addition of a stannous chloride ( $\text{SnCl}_2$ ) solution decolorizes the yellow solution, then this is a good indication that iron is actually present. ( $\text{SnCl}_2$  reduces  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ , which is colorless.) Determination of iron by AAS is always a desirable option.

## Facial Creams and Lip Balms

Cosmetics and skin-care products are often recovered in historical archaeological excavations. The more volatile components of these have generally evaporated, leaving only dry solids. Among these, as noted above, silicates, such as talc, are often found. It is also advisable to look for zinc (Zn) in the residues. Zinc, in the form of zinc oxide (ZnO), is frequently included in facial preparations and lip balms, since it has good UV light-blocking properties. As an interesting aside, in the 19th and early 20th centuries the use of calomel (mercurous chloride,  $\text{Hg}_2\text{Cl}_2$ ) as a facial cream was not uncommon, for instance, “Dr. Gouraud’s Oriental Cream” (Sweetser 1876). This material is by nature unctuous and does not dry out. Like other mercury compounds, it can be identified by a mercury spot test, the lack of an IR spectrum, and total evaporation under high heat. Its use as a cosmetic was, of course, ill advised from a health perspective (Street 1916:2).

### Glass Is not Forever

Historical materials of interest to archaeologists are often contained in glass vessels—bottles, jars, vials, etc. The glass in question, usually of the soda-lime variety, is a durable material, but it does not necessarily last forever. Depending on the prevailing environmental conditions, the bottle glass itself may undergo chemical reactions and form secondary products that are easily mistaken for remnants of the contents of the container. A mild form of glass decay manifests itself as patination, in which surface reactions produce tightly adhering neoformed mineral phases, including calcium sulfate ( $\text{CaSO}_4$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), various silicates, syngenite ( $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ ), and thenardite ( $\text{Na}_2\text{SO}_4$ ), giving the glass the familiar multicolored “oil slick” appearance. More serious decomposition may occur in glasses with high sodium (Na) content: these materials tend to be hygroscopic, i.e., they slowly take up water, lose their structural integrity, and, given enough time, disintegrate. Bottles and jars made of high-Na glass and exposed to a moist environment sometimes actually appear to be “rotting” (Fig. 5). This impression can be further enhanced if the glass in question contains a trace of manganese (Mn), which is added by the glassmaker as a decolorizing agent. When the glass decomposes, this element is released from its fixed place in the glass



**Fig. 5** Decomposing high-Na glass (a Lundborg perfume bottle). The various glass fragments are pink in color. (Photo by authors, 2012.)

matrix and forms manganese silicate, which is insoluble and has a bright pink color.

Confusion between glass-decay products and presumed bottle contents can easily occur when there are surface reactions that go beyond patination. These happen when the glass “sweats out” some of its elements, especially calcium (Ca). Exposure of this exudate to carbon dioxide ( $\text{CO}_2$ ) in the atmosphere can lead to the formation of layers of calcium carbonate ( $\text{CaCO}_3$ ) on the surface. Other glass constituents can likewise form carbonates, oxides, hydroxides, and (meta)silicates that may easily be mistaken for remnants of bottle contents (Fig. 6, this bottle was broken during recovery). The phenomenon is primarily observed on the inside surfaces of bottles in which moisture was trapped, usually through condensation. Precipitation of this kind can be distinguished by the way it covers all parts and contours of the bottle—often extending from the bottom through the top of the neck.

### Costs

As a final consideration, archaeologists need to be aware that doing this work can be expensive. As noted above, equipment costs can run to hundreds of thousands of



**Fig. 6** Bottle fragments covered with glass exudate (primarily  $\text{CaCO}_3$ ). (Photo by authors, 2014.)

dollars. Our work at Idaho actually began with \$15,000 from a large cultural resources management contract. The funds went to support labor, materials, and equipment for testing a series of materials from Sandpoint, Idaho (Warner et al. 2014). Subsequent analytical work has been partially subsidized by a series of grants. All of the more recent work done through Idaho's Department of Chemistry has been done free of charge to archaeologists, as the project has now been incorporated into the department's academic curriculum. It is work that now generates information for archaeologists and provides real-world experience for budding analytical chemists.

The point we want to emphasize is that archaeologists should consider the potential cost of the work to their projects and evaluate whether the outcomes are worth the burden on their budgets. For the near future, testing at Idaho can be done at no charge to archaeologists (so send samples!), but it is important to emphasize that some of the testing that has been discussed in this article, through a commercial lab, could cost an archaeologist several hundred dollars for a single sample—a figure that may be cost prohibitive for archaeologists' budgets. Another issue with commercial labs is that they tend to focus on the determination of specific analytes and rarely, if ever, engage in open-ended analyses. In other words, they are unlikely to carry out complex analyses in order to answer the key question for archaeologists: What is this?

## Conclusion

Chemical analysis of historical materials can be carried out in a rough-and-ready manner or with a great deal of sophistication. Since the latter is bound to be more time

consuming and expensive, a question often arises regarding the degree of refinement that is desired or, indeed, justified in a particular case. Little general guidance can be given on this issue, and it must be left to the archaeologist and the analyst to decide whether the projected result is worth the effort and expense. One thing, however, should always be kept in mind: materials, especially organic ones, tend to change over time. This means that sometimes their original states can only be deduced from a series of inferences based on likely reaction paths.

Chemical analysis often provides surprising insights. Who, for instance, would have thought that the 17th-century Chinese coin from John Day, Oregon, that we investigated had been used for the traditional medical practice of “coining” (*gua sha*), in which it is forcefully scraped along a patient's skin (Lee et al. 2010). Our discovery of human skin cells along its periphery, via hematoxylin and eosin staining and microscopic examination (Kiernan 2008), proved this to be the case. That coin is arguably our most distinctive finding, but, more importantly, it is an example that illustrates the many ways that historical archaeology and analytical chemistry can generate unique understandings about the past.

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