Urine on the Shelves

Odious Materials in Archaeological Collections

Mark S. Warner and Ray von Wandruszka

ABSTRACT

For 15 years, the University of Idaho has conducted chemical testing of excavated materials from historical sites throughout North America. The most common artifacts tested are sealed containers. Some come from current excavations, but most are from repository shelves. The immediate purpose of the archaeochemistry work is twofold: to identify the contents of the containers for researchers and to provide training for students in analytical chemistry. After testing more than 500 items, project personnel have recognized some unexpected outcomes that have implications for institutions housing the artifacts. Specifically, tested materials identified the small, yet consistent, presence of certain artifacts that can have health implications for personnel working with the items. The article concludes with general guidance on identifying and assessing those risks.

Keywords: archaeochemistry, health and safety, collections management, historical archaeology, residue analysis

Durante 15 años la Universidad de Idaho ha realizado pruebas químicas en materiales excavados de sitios históricos norteamericanos. Los artefactos que se analizan con más frecuencia son recipientes cerrados, algunos provenientes de excavaciones actuales, pero mayormente de estantes de depósito. El propósito inmediato de la labor arqueoquímica es doble: identificar los contenidos para los investigadores y capacitar los estudiantes en química analítica. Después de analizar 500 objetos, el personal del proyecto ha identificado unos resultados inesperados que tienen consecuencias para las instituciones que almacenan los artefactos. Específicamente, los materiales estudiados revelaron una pequeña pero consistente presencia de artefactos cuya presencia puede tener consecuencias de salud para el personal que trabaja con ellos. El artículo concluye con recomendaciones generales para los gerentes de colecciones para identificar y evaluar esos riegos.

Palabras clave: arqueoquímica, higiene y seguridad, gestión de colecciones, arqueología histórica, análisis de residuos

Most archaeologists and collections managers are aware of the "curation crisis" in the profession. It is a topic that scholars have been writing about for over 40 years. Many of the associated problems with archaeological collections—such as lost collections, lost contexts for materials, lack of space, and overall lack of care—have been thoroughly documented for decades (e.g., Bawaya 2007; Childs 1995; Kersel 2015; Marquardt et al. 1982). Unfortunately, we will now add to this list, albeit in a relatively small way. Specifically, we highlight some of the results of a 15-year archaeochemistry project that has identified the infrequent, yet consistent, presence of unpleasant materials stored on the shelves of many different repositories. We emphasize that these are not items discovered in bags of unprocessed/orphaned collections, but rather items that originated from well-curated assemblages throughout the United States. The problem we raise is that being unaware of the specific contents on repository shelves can be a significant issue for collections management staff. The problem can range from generic (albeit extremely noxious) clean-up problems in the event of container breakage to moderate health-and-safety concerns for staff due to ignorance of contents, to extremely rare instances of potentially life-threatening issues.[1]

Prior to reporting our findings, we wish to provide some context for our work and situate it as part of ongoing discussions on the relationship between archaeology and the collections that fieldwork generates. Our archaeochemistry collaboration began in response to materials recovered from a large field project in northern Idaho in 2008, where archaeologists recovered almost 600,000 artifacts (Weaver et al. 2014). A portion of the materials recovered had contents that required chemical analysis for identification—such as sealed bottles—leading to archaeologists reaching out to the chemistry department at the University of Idaho (Spinner et al. 2011; Warner et al. 2014). What began as a project-specific partnership between an archaeologist (Warner) and a chemist (von Wandruszka) at the University of Idaho ultimately morphed into a much larger endeavor. Over the past 15 years, archaeologists and chemists at our institution have

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collaborated on an ever-expanding archaeochemistry project in which materials from historical archaeology sites throughout North America are chemically tested and identified (von Wandruszka and Warner 2018). The project not only generates unique information for archaeologists that is regularly incorporated into reports (Campbell et al. 2018; Prouty et al. 2020; Swope and Grenda 2023; von Wandruszka et al. 2016; Voss et al. 2015) but also provides extensive training for analytical chemistry students. Since its inception, 36 students have participated in the project and analyzed more than 500 items.[2] The bulk of the items tested have been glass bottles and jars, but we have also tested slag from blacksmith shops, fabric, concrete, mortar, a tooth filling, gunpowder, and many other objects and materials.

Although our collaboration was initiated in response to a fieldwork-driven need, the project has continued based largely on testing materials that archaeologists had previously excavated and are now part of their collections. In this sense, our archaeochemistry project is now part of the growing body of scholarship on collections-based research. Given the volume of materials sitting on repository shelves—and the many reasons for emphasizing collections-based research—we strongly believe that this is an area on which archaeologists should focus their attention (e.g., Childs 2006; King 2014, 2019; King and Samford 2019; Schiappacasse 2019; Voss 2012).

However, as researchers expand work on archaeological collections, there can be unexpected findings unrelated to the original intent of the work. This has been the case with a number of items that we have investigated over the years. They include artifacts that could have health and safety implications for people working in repositories—or, on a more prosaic level, have been identified as *disgusting* materials that people may not want to put on their shelves if they knew what they were!

In addition to being part of a growing stream of collections-based research, our work also connects to present-day efforts of raising consciousness about health and safety issues in archaeology. Although the bulk of the scholarship in this area has focused on safety in the field (Klehm et al. 2021; Meyers et al. 2021; Poirier and Feder 2001; Stapp and Longenecker 2009; White 2012), there is also a small body of work on hazards associated with collections (Caldararo and Palmer 2008; Odegaard 2019; Suits 1998). Our work will add to this, but it should always be understood that the risks involved in these scenarios are relatively minor. In 15 years of work, we have identified one object (discussed below) that posed an immediate and serious health threat, and overall, about 6% of the artifacts that we have analyzed could be described as noxious, toxic, or disgusting. This includes materials containing toxins such as mercury, arsenic, lead, selenium, strychnine, and phosphine-producing compounds. It excludes substances that are only poisonous when used unwisely. In other instances, potential risks to personnel could arise through imprudent behavior, such as touching unknown materials or breathing their vapors. This is somewhat more of an issue with people working in archaeological labs given that lab technicians are generally not made aware of possible health risks while processing routine items such as bottle glass.

What follows is a compendium of the odious materials identified in our work with a brief summary of the investigative processes undertaken by the student chemists.

FIGURE 1. Gouraud's Oriental Cream bottle from Sandpoint, Idaho (Warner et al. 2014:281).

MERCURY

The toxicity of mercury (Hg) is well known. Its toxicity was established in the second half of the nineteenth century, but it was still incorporated into a variety of products well into the early twentieth century. Interestingly, some of these had cosmetic and medicinal applications. An example of a cosmetically used mercury compound was provided by a sample of Gouraud's Oriental Cream recovered from a project in Sandpoint, Idaho (Figure 1). The material, an off-white creamy substance, turned out to be mercurous chloride (Hg_2Cl_2, aka calomel), which was advertised as a facial cream (Figure 2). It was touted for imparting a "pearly glow" to the user's skin, as well as removing unsightly blemishes. Curiously, it was noted in the advertising that the product was *tasted* to ensure that it was *properly made*. Around the middle of the nineteenth century, calomel was also taken internally as a cure against diseases ranging from cancer to ingrown toenails. Although calomel is not acutely toxic, it is recommended that archaeologists dealing with suspected samples handle it carefully. Exposure, especially ingestion, can lead to mercury poisoning.

A second example of mercury in archaeological samples is mercuric sulfide (HgS, aka cinnabar). The sample comes from a medicine vial excavated in the 1980s as part of the Market Street Chinatown project in San Jose, California (von Wandruszka et al. 2014; Figure 3). Such vials are quite commonly recovered archaeologically. The red mineral in the vial is the common ore of mercury, and it continues to find wide use in traditional Chinese medicine (TCM) as an antibacterial agent (von Wandruszka and Warner 2021). Although potentially more poisonous than calomel, its toxicity is limited by its low solubility in stomach acid. Archaeologists are most likely to find the material in medicine vials like the one shown in Figure 3. However, the same material is also often contained in *yinni*, the stamp ink used to seal documents in China for thousands of years. Again, archaeologists should minimize exposure to the material, especially breathing its dust.

PHOSPHORUS

Phosphorus (P) is an essential part of living systems, but many phosphorus compounds are deadly poisons. Historical archaeologists excavating sites associated with agricultural establishments or hospitals should be especially leery of materials that were used

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FIGURE 2. Gouraud's advertisement (*Salt Lake Tribune*, August 26, 1908, p. 11).

as rodenticides. Some of the most effective ones contain phosphorus, and many of those are acutely toxic to humans. One of the most pernicious of these is sodium dihydrogen phosphide, $NaPH_2$. This is an off-white to light-yellow material that is kept in a sealed ampule (Figure 4) because it spontaneously reacts with moisture in the atmosphere according to this reaction:

$$NaPH_2 + H_2O \rightarrow PH_3 + NaOH$$

PH_3 is phosphine, a highly toxic gas that kills mice and rats, but it is also very dangerous to humans. One mode of action for an operator is to carry a quantity of solid $NaPH_2$ in a sealed container, open it in a locale such as the hold of a ship or a grain-storage facility, and immediately leave the venue. Upon opening, the material continuously reacts with the moisture in the air, emitting foul-smelling PH_3 (garlic/fish odor) until it is depleted.

The sealed ampule with $NaPH_2$ shown in Figure 4 was recovered from the site of a hospital/morgue in New England, where it was presumably used to keep the vermin population down. Project archaeologists actually recovered two of these ampules. Upon identification of the contents, we notified the lab manager of the significant health risks and provided detailed guidance on how to dispose of the other ampule. Archaeologists who come across an artifact of this general appearance should be extremely careful not to accidentally break or open it. If it needs to be opened, this should be done in a good chemical hood.

Other phosphides were also used to generate PH_3 and kill rodents. A prime example is aluminum phosphide (AlP), which reacts with water as follows:

$$2AlP + 6H_2O \rightarrow Al_2O_3.3H_2O + 2PH_3$$

AlP has been (and still is, in some parts of the world) distributed in tablet form, in which the phosphide is combined with inert excipients such as silicates. Although the mode of action is, in

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FIGURE 3. Medicine vial from Market Street Chinatown, San Jose, California (photo by Ray von Wandruszka).

FIGURE 4. Ampule recovered from morgue/hospital in New England (photo by Ray von Wandruszka).

principle, similar to that of a pure phosphide, it proceeds much more slowly. Figure 5 shows a sample of such tablets that were sent to our laboratory from a school site in St. Augustine, Florida. The tablets were not found in a sealed container, and they had long since "outgassed"—that is, they had lost all phosphorus. Because of this, they presented no danger. It is, however, conceivable that tablets in a tightly closed container could still produce PH_3 when exposed to the atmosphere.

A third path by which potentially dangerous phosphorus can make its way into the world of archaeology is via hypophosphites. These are a suite of compounds (e.g., KH_2PO_2, potassium dihydrogen hypophosphite) that were sold in syrup form in the nineteenth and early twentieth centuries (Figure 6). They were part of a larger "patent medicine era" and were frequently accompanied by outrageous names and claims (Young 1961).

Hypophosphites can also form phosphine gas, but not in reaction with water. Instead, they disproportionate, especially at raised

FIGURE 5. Outgassed pills from St. Augustine, Florida (photo by Ray von Wandruszka).

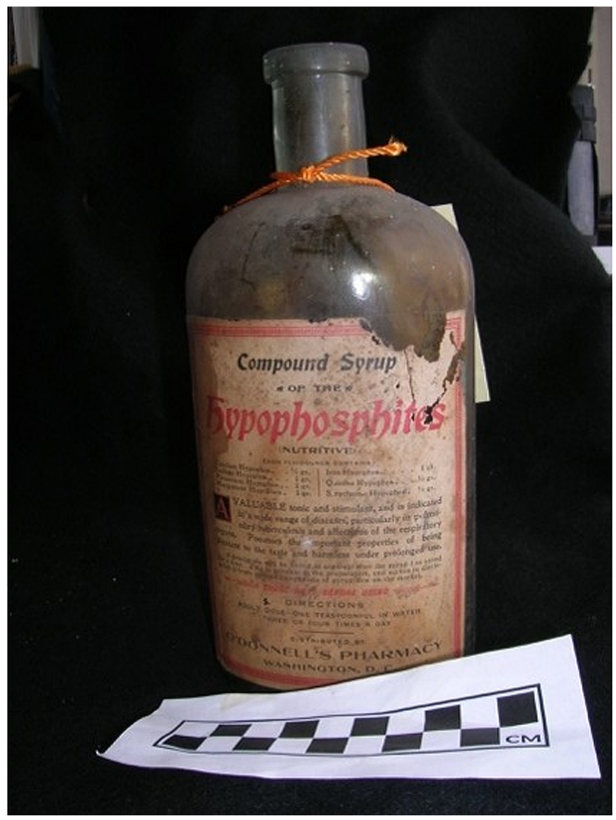

FIGURE 6. Pharmacy bottle from Washington, DC (photo by Ray von Wandruszka).

temperatures:

$$2KH_2PO_2 \rightarrow PH_3 + K_2HPO_4$$

These compounds are somewhat less hazardous than the phosphides in an archaeological setting, but they should still be handled with caution. This is especially true for the example shown in Figure 6, because this syrup also contained strychnine (presumably as a stimulant), which is a notorious poison.

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ARSENIC

Until the 1920s, when it was discontinued, Kellogg produced an insect poison known as Ant Paste in Los Angeles, California (Figure 7). It was a sugary paste, laced with arsenic (As), that had a sordid history involving murder trials and that caused the death of two children who ingested it (Willis v. State, 37 Ala. App. 185, 66 So. 2d 753 [1953], https://cite.case.law/ala-app/37/185/1696781/). A distinguishing feature of the container was a "rattle cap," in which small shot pellets were placed in a hollow space in the lid, producing a rattling sound when the container was moved. Although this was meant to alert the user that the contents were poisonous, it may, in fact, have attracted the children.

A small, unlabeled jar of ant paste was submitted to our laboratory from an excavation originally conducted in 1969. The jar is part of the Yreka Chinatown collection housed at the California State Parks' State Archaeological Collections Research Facility in McClellan, California (Figure 8), and it contained a remnant of its original contents, including arsenic. It must be viewed as a hazardous compound.

FIGURE 8. Kellogg's Ant Paste jar from Yreka, California, Chinatown. Collection housed at the California Parks' State Archaeological Collections Research Facility (photo by Ray von Wandruszka).

FIGURE 7. Kellogg's Ant Paste advertisement (*San Antonio Express*, April 29, 1917, p. B8).

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FIGURE 9. Patent medicine bottle from Missoula, Montana (photo by Ray von Wandruszka).

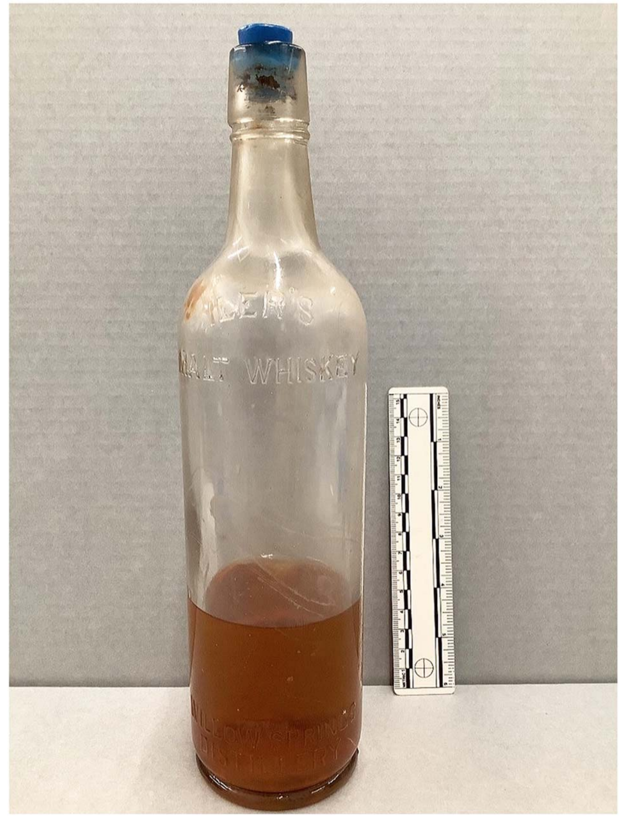

FIGURE 10. Iler's whiskey bottle from Washington State. Catalog number: 45SN409/2008/1278.1, Courtesy of the Burke Museum of Natural History and Culture, Seattle, Washington (photo by M. Caves).

PERCHLOROALKANES

A colorless glass medicine bottle with a square base containing a small amount of dark-brown sticky residue was submitted to our laboratory (Figure 9). It was recovered during property renovations of the still-standing "Cranky Sam" Public House in Missoula, Montana. Cranky Sam's was formerly associated with the city's red light district and Chinatown. The material in the bottle was found to contain hexacholoroethane (aka percholoroethane), a compound that was used as an anthelmintic in veterinary medicine.

In suspension with bentonite clay and water, it was used as a treatment for parasites in cattle and sheep until the 1940s. It was effective against common mature liver flukes but not against the larvae. Because of this, farmers had to frequently re-treat their livestock. In the 1920s, hexachloroethane was found to be toxic to humans and animals, primarily when it is absorbed through the skin. It is no longer produced in the United States.

URINE, NOT WHISKEY!

A sealed Iler's Malt Whiskey bottle with a remnant of a dark yellow liquid was recovered from a privy site in the state of Washington. It had been stored on the shelves of the Burke Museum in Seattle for approximately 15 years. A sample of this liquid, presumed to be whiskey, was submitted to our laboratory for analysis (Figure 10). It was found to be aqueous, with a notable content of potassium (K), phosphorus (P), and—especially—urea.

These findings left little doubt that the liquid in the whiskey bottle was in fact not a distillery product but urine. Although the bottle obviously had been repurposed as a urine receptacle, its deposition was, of course, consistent with the privy from which the artifact was recovered. One may speculate that the bottle was used as a vessel of convenience, in order to avoid a nighttime trip to the outhouse.

ODOROUS OIL

The final sample we discuss is a large mason jar with a wire bail, approximately three-quarters full with a thick, dark-brown liquid (Figure 11). It was recovered from a trapper's cabin in Southern Idaho, and it was introduced by the archaeologists as a scent, "brewed" to attract animals to traps. Although this may have been the purpose of the material, when the jar was unsealed, it gave off a most unpleasant, penetrating odor.

It was established that the liquid was not aqueous (i.e., not brewed), but rather an organic (carbon based) material. It showed

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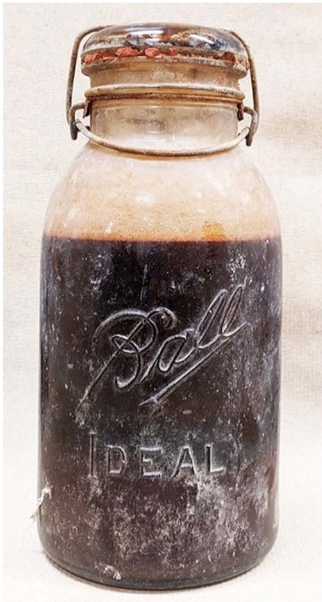

FIGURE 11. Mason jar with trapper's "scent" from southern Idaho (photo by Ray von Wandruszka).

signs of extensive oxidation, which accounted for the foul smell and strongly suggested that this was a rancid natural oil. Oxidative decay of this kind primarily happens with (poly)unsaturated oils, which may be of plant nature, but could, in view of the trapper's setting, also be animal oils. Mink oil and neat's-foot oil are cases in point. Whether the oil was originally produced to attract animals to traps or to treat their hides after tanning remains an open question.

CONCLUSION

Collections managers are all too familiar with the problem of inadequate funding to curate collections. This is particularly the case with historical collections. The volume and variety of materials recovered is generally substantial, and all too frequently, curation budgets are not sufficient to process the materials fully (Sullivan and Childs 2019:81–83). One consequence of this is that objects get put on the shelves without curation staff being fully aware of what they have. In most cases, this is not a concern. Indeed, many a thesis has been produced on collections that have been sitting on repository shelves (at the University of Idaho, approximately 50% of our theses are collections based). However, as our work has demonstrated, not fully knowing what is on our shelves can lead to problems. A broken ampule of phosphide or a leaking bottle of 100-year-old urine may only lead to a nasty cleanup job, but it could be much worse. A lack of understanding of the contents of containers that "still have stuff in them" can be an unrecognized health risk for lab staff.

It is not a realistic expectation for repositories to immediately check all of their collections for bottles that may have bits of residue in them (illustrated in Figure 9). Indeed, there are probably hundreds, if not thousands, of containers of this kind on repository shelves, and the cost of testing such materials would be prohibitive (in a commercial lab setting, we estimate that the cost would be about $5,000 per artifact). However, collections managers can take some small steps to manage the possible health implications presented by such containers.

A first step is for repositories to make a point of identifying when they have containers with contents in them—although it is not enough simply to have contents noted in the comments section of a site catalogue. Instead, we suggest that repositories keep separate listings of such items and post those lists in lab workspaces with the appropriate OSHA Safety data sheet. This way, all personnel could at least (1) be aware that there are items that are not the typical empty bottles and (2) know where these objects are located. We also suggest that lab managers include some focused instructions about dealing with these artifacts. This could be as simple as instructing lab technicians not to open any sealed containers they encounter and to contact their supervisor for specific processing instructions when they encounter containers that contain obvious residue. Related to this point, lab managers should have contact information available for their local hazardous-materials disposal agencies. Finally, when practical, it is important to have container contents tested by analytical chemists so that one knows what one has, can make informed decisions about curating these items, and perhaps take appropriate steps to dispose of the contents, if necessary.

What we want to achieve with these recommendations is some reasonable awareness of, and responses to, an issue that many collections managers and lab personnel do not think about (we also note that field techs should be given training on how to properly handle artifacts with contents in them). As we have demonstrated, there are clearly items sitting on repository shelves that can be quite nasty: the arsenic in Kellogg's Ant Paste had been sitting on a shelf for about 50 years. An important step is simply to become aware that such items are in collections. Being mindful of the possible health implications of such containers should be a small but significant reminder for all lab personnel.

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Data Availability Statement

All reports on the chemical analysis of materials reported on in this article are available in the Department of Chemistry, University of Idaho.

Competing Interests

The authors declare none.

NOTES

1. Apologies if the title offends, but it can be a challenge getting people to read collections-focused articles.
2. We do this work free of charge, and we are always looking for interesting samples. If you have samples to test, please contact us.

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