Deceptive Content: Unexpected Materials in Historical Bottles

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ABSTRACT

The apparent contents of bottles recovered from historical sites can mislead investigators in their search for the origin of the materials in question. Four examples from diverse locations demonstrate two important sources of "false" contents: material decomposition of glass and the reuse of containers. Chemical analysis of bottle contents reveal that low quality glass can, given the right circumstances, decompose to form secondary substances that could readily be mistaken for original contents. Bottle reuse is a more obvious cause of potential identification errors, yet one that is not commonly identified by archaeologists.

Introduction

Bottles and jars recovered from historical sites are of unique interest to investigators if some or all of the contents can be retrieved for further study. Sometimes the nature of these materials can be gleaned from the characteristics of the container—in ideal cases from embossing or surviving bottle labels. Frequently, however, chemical analysis must be used to determine, with a reasonable sense of certainty, what the material in question is—or, more likely, what it used to be.

One of the potential pitfalls in the identification-from-container scenario is that the material in the bottle at the time of its recovery is not necessarily the original contents. The work described here shows that chemical analysis of bottle contents can identify situations where what is in the bottle is at odds with the original product. Archaeologists have identified the reuse of bottles (Busch 1987), but less widely recognized is the repurposing of bottles, that is, a bottle that was originally sold containing one product but was subsequently used to store another. A further complication is that the container material itself may obfuscate the matter by playing a role in the chemical transformation of the contents, or even by producing a new material.

The descriptions below present examples of historical bottle contents with unforeseen origins, the identification of which required wary observation and a measure of chemical insight.

I. Pink Perfume Bottle

Background of Artifact

A small glass bottle (Figure 1) with an estimated volume of 50 ml was recovered from an 11-ft.-deep well at the Cyrus Jacobs-Uberuaga House in Boise, Idaho, in 2012 (Goodwin 2014). The word "Lundborg" was embossed on the bottle, and it was closed with a glass stopper that had sheared off and could not be removed. While being extensively cracked, it did hold about 15 ml of a clear liquid. A pink material coated the inside surface of the bottle, suggesting a remnant of the contents. Some of the coating had peeled off, producing pink flakes.

The Lundborg company, founded ca. 1850 in New York, exclusively produced perfumes (Perfume Intelligence Ltd. 2015) (Figure 2). It was taken over by Ladd & Coffin around 1890 and ceased production in the mid-1950s.

Procedures and Results

One of the cracked sections of the bottle glass was removed to expose the interior. The liquid inside was clear, colorless, odorless, and appeared to be aqueous. When spread on a surface and dried, it left a shiny, hard glaze that readily redissolved in water.

A quantity of the pink material was placed in a muffle furnace at 800°C for eight hours. This led to a 45% weight loss, but the pink color remained. The residue was not soluble in water or hydrochloric acid, but did dissolve in hydrofluoric acid. A sample of the pink material was dissolved in this acid and analyzed by atomic absorption spectrometry (AAS). It was found to have a manganese content of 0.075%.

Figure 1. Bottle I, Lundborg pink perfume bottle (piece broken out, showing pink flakes inside). (Photo by Tara Summer, 2013.)

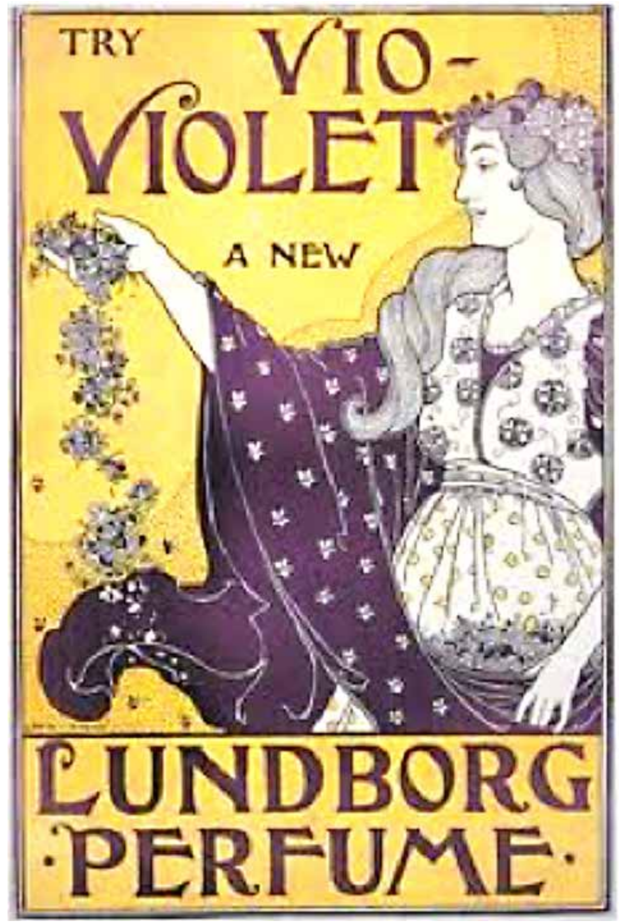

Figure 2. Lundborg advertisement, early 20th century. (Reproduced with permission from Attic Paper Vintage Ads.)

A 0.1103-g sample of colorless glass from the bottle was placed in a ball mill with zinc oxide and lithium carbonate and reduced to a fine powder. This was fused in a platinum crucible by means of a gas torch and dissolved in hydrochloric acid. The resulting solution was analyzed by AAS, showing that the glass had a sodium content of 15.8% and an iron content of 0.5%. A semiquantitative determination showed that the sodium content of the liquid in the bottle was high.

Discussion and Conclusions

The high sodium content of the bottle glass identified it as a low-quality glass of considerable hygroscopicity (Matson 1949). In moist environments such glass tends to take up water and decompose by flaking. In the present case, the pink layer on the inside surface of the bottle was initially assumed to be a dried remnant of the original contents. However, the fact that it appeared not to be organic and dissolved only in hydrofluoric acid suggested otherwise. Furthermore, it is known that Lundborg only sold perfumes, which are materials that usually do not leave a solid remnant. The fullness of the chemical evidence suggested that the pink solid and the viscous liquid in the bottle were decomposition products of the glass itself.

The 45% weight loss of the pink solid upon heating was ascribed to the loss of water taken up by the glass. The pink color of the inner glass layer was ascribed to manganese, which was added to the glass as a decolorizing agent (Lindsey 2014a). This is common practice with glass that contains iron, which would give it a greenish hue. Many manganese (II) compounds are pink, and chemical transformation of the original manganese decolorizer can result in pink coloration of the glass. This should not be confused with the photochemical process that is known to turn some glasses purple. In the present case, the inner layer of the hygroscopic glass took up water, mobilizing the constituents and allowing them to react. In addition, during this hydration sodium silicate (a soluble silicate, also known as water glass) leached into the water in the bottle, forming a viscous solution. The glaze that formed when this solution was evaporated was due to the drying of this silicate onto the surface. No trace was found of the original perfume in the bottle.

II. Amber Medicine Bottle with White Contents

Background of Artifact

The item was a circular brown medicine bottle, about 5 in. tall. It was recovered from a dump site in Nampa, Idaho. It arrived for analysis in broken condition and was coated with a white solid on the inside surface (Figure 3). The number “8” was embossed on the base, but there were no further distinguishing marks.

Procedures and Results

The white solid in the bottle was partially soluble in hydrochloric acid—evolving carbon dioxide—and the solution turned a light yellow color. The sample fully dissolved with the addition of hydrofluoric acid. When it was put in a flame it did not burn, but turned the flame orange. AAS showed that the material contained 15% sodium, as well as some iron. The infrared (IR) spectrum (Figure 4) showed no organic material. The peak at 1029 cm^{-1} indicated the presence of silicate, and the 1409 cm^{-1} peak was probably due to carbonate. Part of the sample was put into a muffle furnace at 800°C for seven hours, resulting in a 19% weight loss.

Discussion and Conclusions

The evolution of carbon dioxide upon addition of hydrochloric acid to the white material indicated the presence of carbonate, which was further confirmed by the IR spectrum. The high-temperature weight loss of the sample was probably due to some loss of water (IR peak at 3400 cm^{-1} on Figure 4), as well as the decomposition of carbonate to oxide with loss of carbon dioxide. The yellow color indicated iron, which was confirmed by AAS. Complete sample dissolution upon addition of hydrofluoric acid pointed to the presence of silicates, which was confirmed by IR as well. The orange flame produced by the sample indicated sodium, which was confirmed by AAS.

As regards the appearance of the white solid, it was noted that it adhered firmly to the glass surface, following all contours, and that it could be detached in large flakes (see Figure 3). In addition, it was noted that the material covered the entire inside surface, up to the very rim of the bottle. This last observation made it unlikely that the white material was a remnant of liquid contents that had dried onto the surface. For that, the bottle would have to have been brimful and undisturbed for a long period—an unlikely occurrence considering that it was found without a closure.

The observations described above point to the likelihood that the white material was an exudate from the glass. As described for the perfume bottle above, sodium glass is hygroscopic and, given sufficient time and the right

Figure 3. Three views of bottle II, broken amber medicine bottle. (Photos by Sidney Hunter, 2014.)

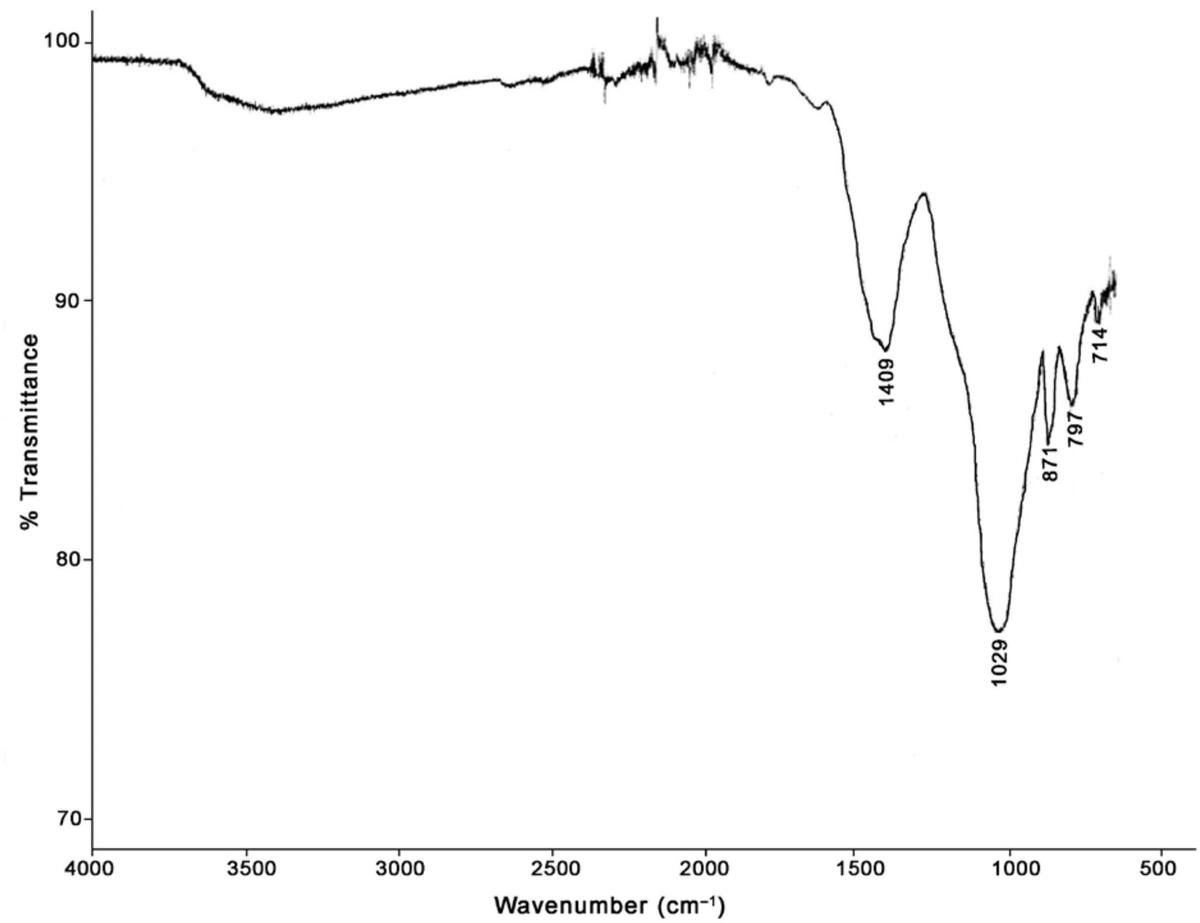

Figure 4. IR spectrum of white material in bottle II, amber medicine bottle. (Graphic by Sidney Hunter, 2014.)

moist environment, will take up water and mobilize its constituents: sodium, silicates, calcium, carbonates, iron, etc., which tend to migrate to the wet surface. Soda-lime glass contains sodium carbonate, lime, dolomite, silicon dioxide, some fining agents, and iron oxide (for brown or green bottles).

Moisture appeared to have been trapped in the bottle and over time the elements leached out and precipitated on the moist inside surface, primarily as carbonates and silicates. These materials are all white, and being formed on the surface, adhered firmly to it, up into the neck of the bottle. Again, this is a case where the apparent bottle contents were actually a decay product of the glass itself. Unlike the decomposition products of the Lundborg perfume flask, however, those of the medicine bottle were not pink. The reason for this lies in the color of the glass: manganese is added for decolorization, and with an amber bottle there obviously is no call for this. There was no evidence regarding the original bottle contents.

III. Liquor Bottle with Indeterminate Contents

Background of Artifact

The item was recovered by the Idaho Power Company at a historical trash scatter in Elmore County, Idaho. It was a colorless glass bottle with a volume of about 250 ml and a rusted screw cap (Figure 5a). It was embossed with the words “FULL ½ PINT” on the side and “15” on the base. There were several pieces of a red-brown material with crystalline appearance inside the sealed bottle (Figure 5b).

Figure 5. Bottle III, liquor bottle: (*a*) full view of half-pint liquor bottle, (*b*) brown material from inside bottle. (Photos by Elizabeth Harman, 2014.)

Procedures and Results

On close examination, the contents were a translucent red-brown material with irregular faces (i.e., not crystalline). The contents did not dissolve in water or methanol, although the latter caused dispersion. The melting range was 160–180ºC. In a muffle furnace at 800ºC (for eight hours) the sample was almost completely consumed. The IR spectrum (Figure 6) showed evidence of oxygen-hydrogen, carbon-hydrogen, and carbon-oxygen bonds. When placed in a flame, the sample melted and caught fire. The Benedict test for reducing sugars gave a very weakly positive result. Qualitative AAS measurements showed traces of calcium, copper, and iron. The material did not have a sweet taste.

A piece of the material was submerged in water in a small test tube for two days; the test tube was then placed in a boiling water bath, which caused the material to soften to a gel-like consistency. When removed from the hot water, it solidified again.

Discussions and Conclusions

The bottle's form and embossing indicated that it originally contained a half-pint of liquor, possibly whiskey. Containers of this type were manufactured from the 1890s through 1920 (Lindsey 2014b). No evidence of alcohol was found in the bottle. The behavior of the material in the bottle indicated that it was probably an animal glue (Koob 1998). Such collagen glues, made from bones, hooves, or hides, were widely used in furniture making. They had the advantage that they could be softened by heating, thereby allowing for the ungluing of joint surfaces.

This is an example of reuse of a container for purposes wholly unrelated to its original contents. Why the glue was placed in a whiskey bottle could not be determined, but it may be suggested that a relatively small, portable container with a good screw cap could conveniently be used by a carpenter who needed to have a supply of glue close at hand.

IV. Beer Bottle

Background of Artifact

The bottle was recovered from the Market Street Chinatown site in San Jose, California. The Chinatown that

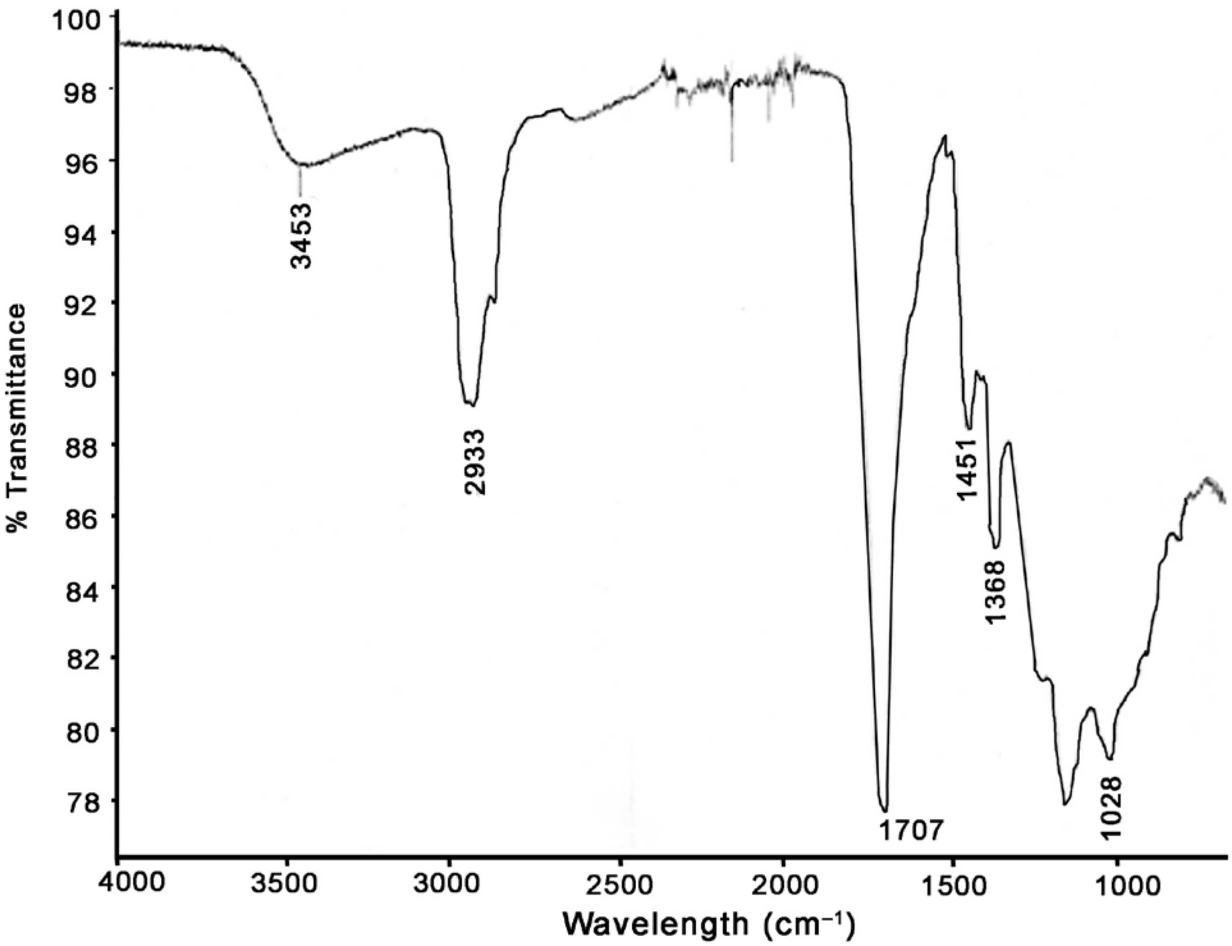

Figure 6. IR spectrum of contents from bottle III, liquor bottle. (Graphic by Elizabeth Harman, 2014.)

existed at this location flourished in the second half of the 19th century, but was destroyed by an arson fire in 1887 (Market Street Chinatown Archaeological Project 2014). The bottle was made of brown glass (Figure 7a), quart size, and embossed with "San Jose Bottling Co. C Maurer." It was stoppered with a lightning-type closure, which was rusted in place and stamped in red with "San Jose Bottling Co" (Figure 7b). A 4.3-cm depth of a viscous liquid with waxy white solid chunks was present in the bottle.

The San Jose Bottling Co., run by C. Maurer, was the primary bottling company in the San Francisco Bay Area from the early 1800s to the early 1900s. Prior to 1890 it was required that bottling companies be kept separate from the brewery that produced the contents. The C. Maurer bottling company was the primary bottler for the Fredericksburg Brewing Company during the late 1800s. This firm was a major brewer of lager beer during that period (Brewerygems.com 2011).

Procedures and Results

The stopper was in good condition and kept the bottle tightly closed. The liquid inside was initially thought to be beer, but upon decanting it was noted that it was viscous and had an odor of grease. A sample was placed in a Bunsen flame and found to burn brightly and completely. A sample of the solid waxy material was also burned with the same result. An IR spectrum was taken of both the liquid (Figure 8) and the solid and showed that the substances were primarily composed of hydrocarbons with a carboxylic acid peak at 1710 cm^{-1}. The spectrum was compared to those of bacon grease, coconut oil, and canola oil, and it

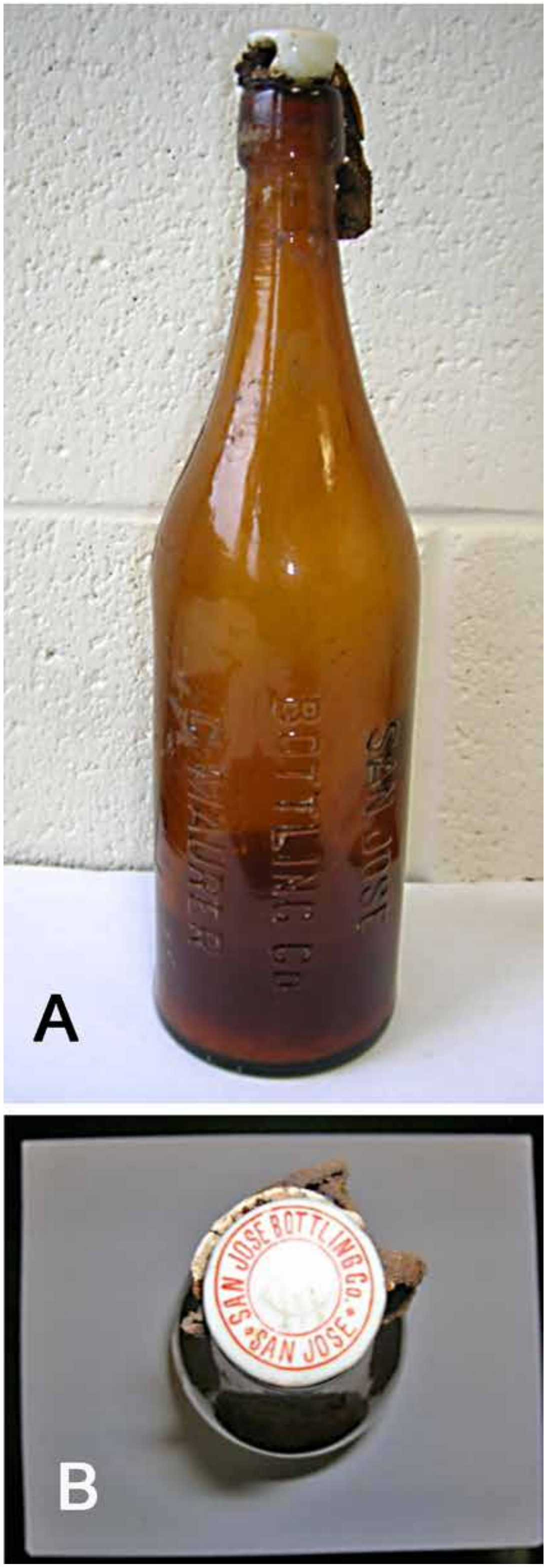

Figure 7. Bottle IV, beer bottle: (*a*) full view of San Jose Bottling Co. beer bottle, (*b*) flip-top bottle closure. (Photos by Tara Summer, 2013.)

was found that all were nearly identical with the exception of the acid peak. The iodine number of the unknown oil was determined to be 9.

Discussion and Conclusions

From the above analysis it was concluded that the contents of the beer bottle were not beer, but rather an oil. Most likely they were a vegetable oil, that is, an unsaturated material that comprised multiple carbon-carbon double bonds. This molecular structure renders the hydrocarbon chains of the oil geometrically "skewed" so that they cannot "line up" as would be required for a solid fat. It stands to reason that this was a liquid oil at room temperature, considering that keeping it in a beer bottle with a narrow neck would not be practical for a fat that may be liquid when hot (e.g., the drippings from a roast) but would solidify upon cooling.

This reasoning, however, leads to a conundrum: an unsaturated vegetable oil, a liquid, would typically have an iodine number much higher than 9. Also, the IR spectrum lacked the telltale alkene frequency around 1660 cm^{-1}. There was, however, a strong carboxylic acid peak at 1710 cm^{-1}. This suggested the following explanation: the oil was originally an unsaturated triglyceride, but prolonged exposure to air and moisture led to gradual oxidation and hydrolysis, which attacked both the carbon-carbon double bonds (i.e., the unsaturation) and the triglyceride ester bonds. In many instances this caused chain scission (especially at the double bond locations), producing shorter carbon chain segments. Oxidation of the esters produced the observed carboxylic acids. As a result of the shorter chain lengths, the oil, although by now much less unsaturated with an iodine number of only 9, remained a liquid. Not all hydrocarbon chains were cut short—some remained whole and formed the observed quantity of solid fat.

This beer bottle is another example of container reuse. It is not difficult to construct a scenario in a household where a resealable (lightning-type closure) beer bottle was used to store leftover cooking oil for later use.

Conclusion

The cases presented above highlight one of the ancillary benefits of taking the time to analyze the contents of ar-

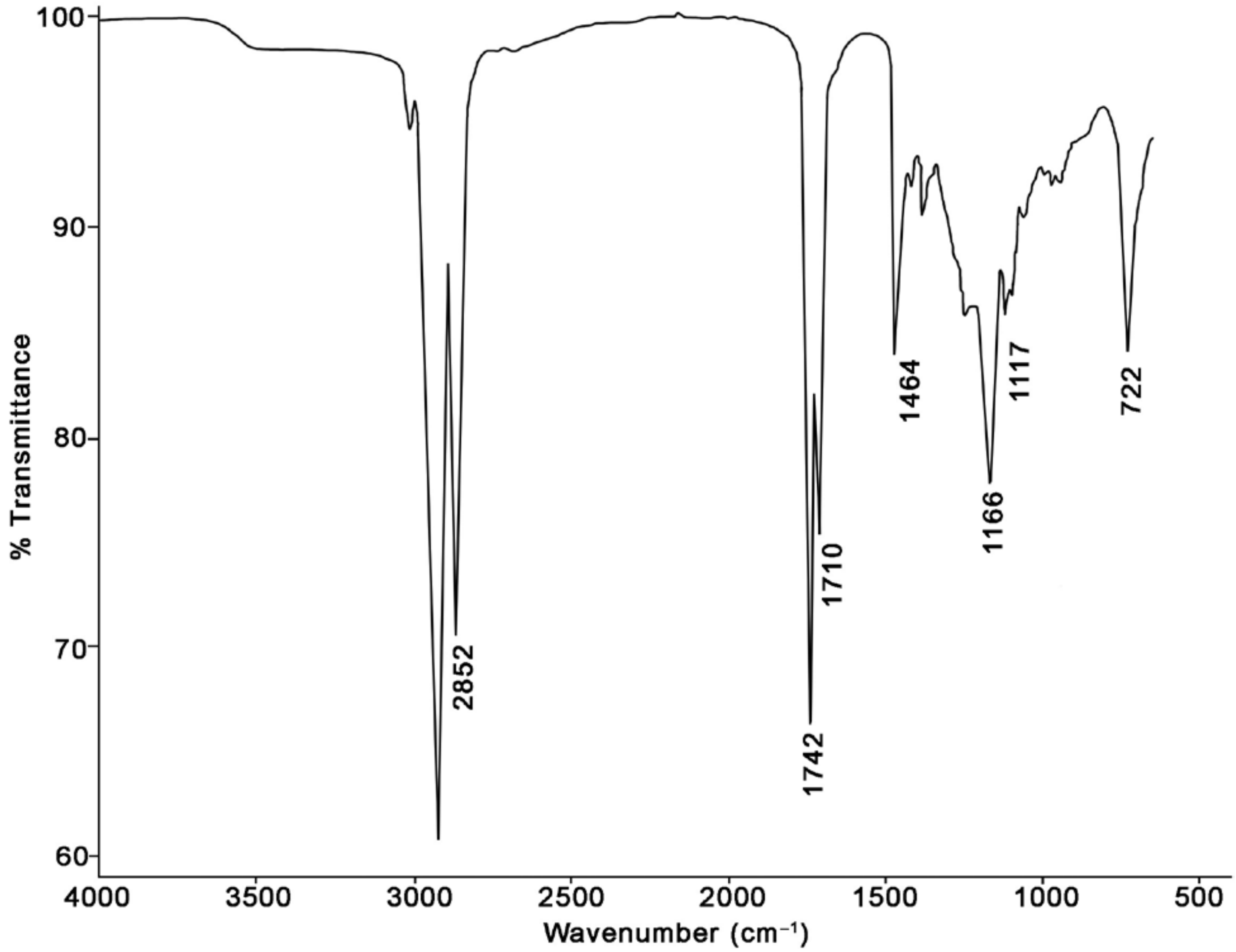

Figure 8. IR spectrum of liquid in bottle IV, beer bottle. (Graphic by Tara Summer, 2013.)

chaeologically recovered bottles. In many cases such work can yield more or less expected results (Spinner et al. 2011) but this work highlights other outcomes. In the case of the Lundborg bottle and the medicine bottle we see what are effectively "false positives," or bottles that seemingly still have their original contents but, in fact, are just showing the natural decay of glass. The other two bottles open the door to exploring the largely unreported behavior of reusing bottles to store products that are quite different from what they were originally intended to hold. It is behavior that archaeologists are undoubtedly aware of but have not documented with any regularity.

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