The Use of Total Reflection X-Ray Fluorescence in an Underwater Archaeology Case Study

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ABSTRACT

This paper demonstrates the applicability of total reflection x-ray fluorescence (TXRF) as a powerful analytical tool for discovering the composition of the liquid inside a bottle found in the HMS *Swift*, a British warship which sank off Patagonia in 1770. In order to characterize the contents of the bottle, a microsample was submitted for TXRF determination. The collected spectrum clearly showed the presence of chloride (Cl) and mercury (Hg) signals which were quantified using gallium (Ga) as an internal standard. After quantification, results perfectly match mercurous chloride (Hg_2Cl_2), a compound which has historically had several pharmacological applications.

Introduction

The knowledge of archaeological objects in terms of their chemical composition and/or physical properties is mandatory for a better understanding of the technologies used in the past, and of requirements for suitable conservation procedures. From a broader perspective, this type of study addresses questions concerning the history of technology and of civilization in general. The tools that the archaeometry field needs in order to achieve successful results are mostly analytical techniques.

Since 1997 the underwater archaeology team of the Argentinean National Institute of Anthropology has conducted archaeological excavations of and research on the shipwreck of HMS *Swift*, a British Royal Navy warship which sank off the southeast coast of Patagonia, Argentina, in 1770 (Elkin et al. 2007). By 2006 the excavation of a significant portion of the officers' quarters above the main deck was completed. One find of particular archaeological significance was a small cylindrical glass bottle, still closed with a cork, containing an unidentified whitish substance and air (Figure 1). This bottle was found inside a compartmented wooden chest together with assorted items which appear to be personal belongings of one or more of the officers.

In order to discover the composition of the liquid inside the bottle, the application of total reflection x-ray fluorescence (TXRF) was proposed. TXRF is a proven microanalytical instrumental technique for elemental analysis in liquid media (Klockenkämper 1997). Only a small sample is required. It is deposited onto an extremely polished surface on which total reflection takes place after the sample dries. No additional preparation is necessary. For quantitative purposes, the internal standard method was applied in order to compensate for instrumental variations and inhomogeneities of the applied film of sample material. The main advantage of this technique over other analytical methods is the very small amount of sample required for quantification, which does not need any preparation and does not generate any additional wastes. These particulars are extremely important when analyses of highly toxic elements are conducted.

Principles of the TXRF Method

TXRF is an instrumental analytical method for the simultaneous determination of elements down to concentrations of one part per billion. It is a microanalytical tool for the analysis of small sample amounts placed on a flat carrier, for contaminants on flat sample surfaces, and analysis of stratified near-surface layers. The physical principles of TXRF and its instrumental state of development have been described in detail in the literature (Prange 1989; Aiginger 1991; Klockenkämper 1997).

The method was first described in 1971 by Yoneda and Horiuchi (1971). It was further developed by Aiginger and Wobrauschek (1974), and after the final construction of a compact system by Knoth and Schwenke (1978), TXRF has become a routine method of analysis.

In the TXRF procedure the sample is placed in the form of a thin layer on a sample carrier with a smooth surface, where it is excited to x-ray fluorescence. This is achieved

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Figure 1. Bottle found in the excavation of HMS Swift, sunk in 1770. (Photo from the National Institute of Anthropology, Argentina, 2005.)

by letting a primary beam hit the sample carrier at an angle of a few minutes of arc, from which it is totally reflected, thus causing effective excitation of the sample on the carrier. The x radiation emitted by the sample can be detected by energy dispersive spectrometers. Advantages of the method are extremely rapid qualitative information of the sample composition (about one minute), absolute limits of detection as low as the picogram range, absence of matrix effects, simultaneous determination of approximately 30 elements, simple quantification by the addition of a single standard reference element, and requirement of a minimal amount of sample in the µg or µl range.

The field of application of the refined method of ultratrace and ultramicroanalysis by TXRF is broad. It can be used to analyze liquids (solutions or dispersions), airborne particulates, sediments, soils, dust particles, pigments and paintings, inks, fine roots and hairs (after decomposition), metal and mineral powders, biological materials, etc.

Methodology

A sample of the liquid suspension inside the HMS *Swift* bottle was taken for chemical inspection in order to obtain qualitative information. The results showed the presence of mercury, among other elements. The presence of mercury posed a problem because TXRF requires placement of the sample on the reflector as a dry thin film, yet metallic mercury and its derivative compounds volatilize at low temperatures, typically 70 to 85° C in most cases. The metal, its chlorides, and mercury (II) oxides volatilize at around 75° C due to their low vapor pressure, whereas mercury nitrates decompose by heat at around 70° C (Lide 1999).

In order to retain the mercury compounds during the drying process, a chemical strategy was developed. It consisted of forming a chelated coordination complex by capture of positively charged metal Hg^{2+} ions inside a relatively large organic molecule. In this case, ethylenediaminetetracetic acid (EDTA) is well recognized as an effective trapping agent for metal cations due to excellent electronic and sterically sequestering properties (Mathew et al. 1993; Sillanpää and Oikari 1996; Canário et al. 2004; Liu et al. 2006). As an example, chelating capture of a metallic ion made by nitrogen and oxygen atoms of the EDTA molecule is shown in Figure 2. In this way, removal of the metal (in this case mercury) from this very stable complex is avoided.

Materials

For this experiment mercury (II) nitrate was obtained from Merck and ethylenediaminetetracetic acid (EDTA) disodic

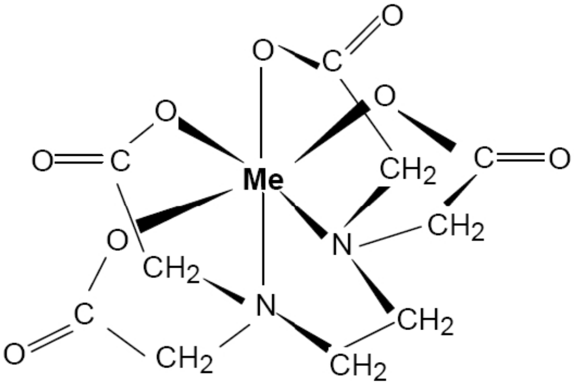

Figure 2. Schematic of a metallic ion (Me) trapped inside an EDTA molecule to form a chelate. (Diagram by authors, 2008.)

salt was obtained from Carlo Erba. Standard solutions of mercury (II), gallium (III), and natrium chloride used for the calibration of the TXRF spectra were prepared by appropriate dilution of stock solutions of Tritrisol Merck (1000 µg/mL). Deionized distilled water obtained from Millipore Milli-Q equipment (resistivity = 18.0 MΩ cm) was employed in all tests.

Standard and Sample Solutions

A series of standard solutions of mercury in the 1 to 5 µg/mL range were prepared by adding the chelating complex agent EDTA in a 10^{-2} molar concentration, followed by homogenization for five minutes. In all cases, 10 µL of the gallium internal standard solution (1000 µg/mL) was added to 1 mL of each sample. In the case of the sample coming from the bottle, 1 mL was treated with 100 µL of 10^{-2} molar EDTA and 10 µL of gallium internal standard solution (1000 µg/mL). For measurements, 10 µL of prepared solution was deposited on quartz reflectors and dried under an infrared lamp.

Instrumentation

For TXRF measurements, an x-ray fluorescence spectrometer composed of a Philips generator equipped with a fine-focus molybdenum x-ray tube was employed. Total reflection was achieved by a TXRF module designed by the Atominstitut der Österreichischen Universitäten (Wobrauschek and Kregsamer 1989). The acquisition data system consisted of an ORTEC fast amplifier and an ORTEC multichannel analyzer (MCA) associated with a Maestro-32 emulator computational program. For x-ray detection, a Canberra silicon-lithium detector with a beryllium window (80 mm^2 area, 0.008 mm thickness) and a 160 eV FWHM (full width at half maximum) for 5.9 keV was used.

Excitation conditions were 50 kV and 30 mA, and the acquisition time for each spectrum was 200 seconds. For spectra deconvolution and quantitative analysis the AXIL program was employed (Van Espen and He 1989). For quantification, a gallium (III) internal standard was selected due to compatibility with the study system (Klockenkämper 1997).

Calibration curves were represented in Cartesian coordinates (x, y) where x was the Hg concentration and y was the ratio between the intensities of Hg Lα and Ga Kα lines. All the measurements were made in air.

Results and Discussion

The collected spectrum shown in Figure 3 clearly demonstrates the presence of chloride and mercury signals, which were quantified using the gallium peak as an internal standard. After quantification, results matched perfectly with the compound mercurous chloride (Hg_2Cl_2).

Mercury was used for centuries for medicinal purposes in order to treat different diseases. Amongst its supposed therapeutic functions was the treatment of venereal syphilis, a disease which reached epidemic proportions in Europe in the late 15th century. Mercury was used in various ways to combat syphilis: as ointments, in urethral injections, in fumigation, in steam baths, or orally in salts such as calomel (Maehle 1999; Barrio 2000; Vergara Mardones 2002).

Calomel or mercurous chloride, known in 18th-century England as *mercurius sublimatus dulcis*, *mercurius dulces*, or mild mercury (Eklund 1975), was also used for its antiseptic and diuretic properties (Vergara Mardones 2002). Side effects of mercury treatments, however, could include tooth loss; mouth, throat, and skin ulcerations; neurological damage; and even death (Harvard University 2008). In spite of that, mercury continued to be used well into the 20th century, when it was finally replaced by penicillin (Barrio 2000).

In relation to finding calomel on board the HMS *Swift*, historical documents indicate that the ship's surgeon's cabin was located on the port side of the stern below the main deck (National Maritime Museum 1762), but this area has not been excavated yet. As was stated before, the bottle was found in a cabin above the main deck and inside a wooden box which seems to have stored items belonging to one or more officers, but not necessarily the surgeon. The archaeological interpretation, therefore, is that the calomel bottle was taken on board the *Swift* mainly for personal use by one of the officers.

Comparable finds in other 18th-century shipwrecks are worth mentioning here. Analyses of the content of intact medicine bottles recovered from the American Revolution privateer *Defence* (1779) revealed, among other

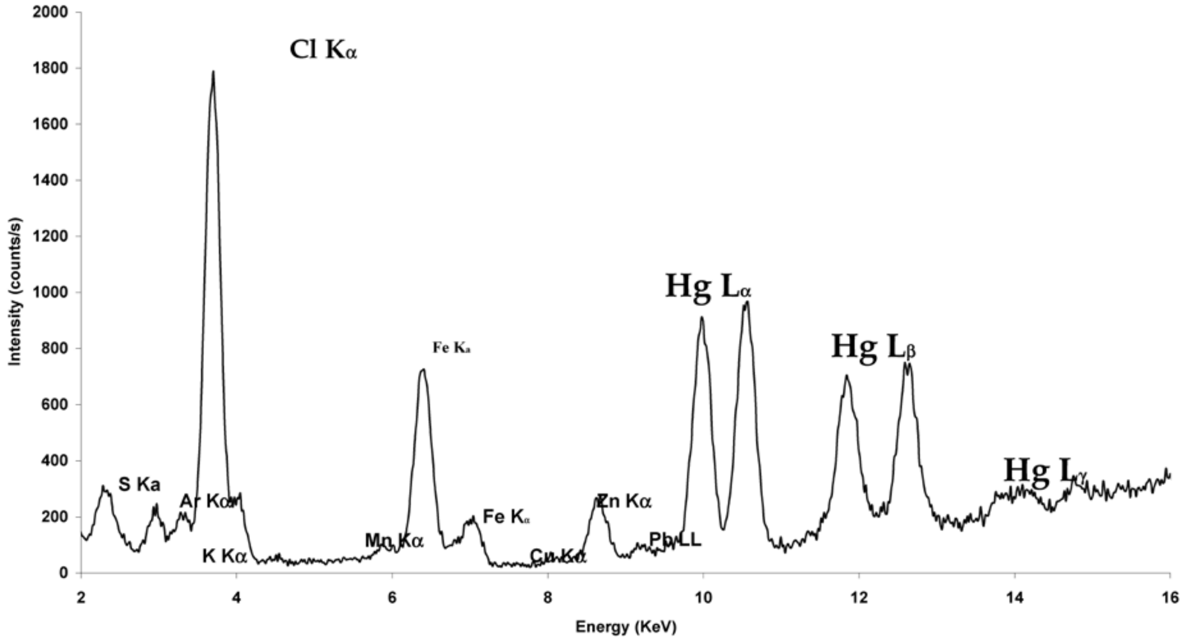

Figure 3. TXRF spectrum of the liquid found in the HMS Swift bottle. (Chart by authors, 2008.)

compounds, mercuric sulfide and mercuric oxide (Smith 1986:153; Erwin 1994). As for the HMS *Pandora* (1791), traces of mercury were found inside at least one small ceramic container. In addition, small glass bottles found on that wreck site, similar in size to the one described in this article, have been assigned to medicinal purposes, but no published reports are available on their actual contents (Campbell and Gesner 2000).

Conclusions

Finding evidence of medicinal substances is extremely rare in archaeological excavations, and the techniques used for their characterization and study must be carefully selected and applied. This article reveals the potential of TXRF spectrometry to study precious archaeological evidence, in this case shedding light on the medicinal resources on board an 18th-century warship.

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