Microchemical Journal 95 (2010) 227–234

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Application of a multi-analytical toolset to a 16th century ointment: Identification as lead plaster mixed with beeswax

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ARTICLE INFO

Article history:
Received 2 December 2009
Accepted 7 December 2009
Available online 16 December 2009

Keywords:
Ointment
Archaeological residue analysis
Chromatography
Mass spectrometry
Infrared spectroscopy
X-ray technique

ABSTRACT

During archaeological excavations of the Castle of Middelburg (Belgium), a 16th century ceramic vessel containing a greasy substance was found. A wide range of chemical techniques was applied on what was presumed to be an ointment to reveal its nature and function. The organic fraction, constituting about 24 wt.%, was analyzed by chromatography and mass spectrometry and consists of beeswax next to smaller amounts of a triglyceride lipid source. Infrared analyses indicated the presence of calcium carboxylate soaps. The inorganic ingredients represent about 30% of the total mass. While calcium, lead and iron were detected by elemental analysis, X-ray diffraction revealed calcium sulfate (gypsum) and lead sulfate as major minerals. Detailed study by X-ray photoelectron spectroscopy confirmed the presence of lead as a divalent species. Altogether, these results point to a medicinal formulation of a lead plaster, used for treating bruises, mixed with beeswax, which was added for easy application on the skin. It is further assumed that lead carboxylates, originally present in the sample, reacted with gypsum, resulting in the formation of calcium carboxylates and lead sulfate. Gypsum could have been added to whiten or to strengthen the plaster. Hence, the analyses confirm the presumed medicinal nature of the find and add it to the list of very rare finds of preserved historical ointments.

1. Introduction

Ancient cosmetics and medicinal preparations provide an interesting study object. They witness the cultural habits and scientific knowledge of historical civilizations. These preparations are manifold in their composition, comprising a lipid base and minerals to which diverse vegetal and animal products can be added for their odoriferous, medicinal or texture-determining properties.

In exceptional cases, archaeologists have the opportunity to excavate an ancient vessel still containing its original content. For example, analysis of Egyptian make-up powders, recovered from their original containers, showed that they contained apart from natural minerals also synthetic compounds. In this way it was proven that the Egyptians knew the practice of wet chemistry already from 2000 BC [1,2]. Another rare archaeological find was a small tin canister containing a white cream dated to the Roman era. Evershed et al. found that it consisted of a ruminant fat that had been mixed with starch and SnO_2 to prepare a cosmetic balm [3]. The reconstruction of this formulation led to a white cream having a pleasant texture when rubbed onto the skin. Probably Roman women used this emulsion as a cosmetic foundation layer. Using synchrotron FTIR microscopy, Cotte et al. analyzed an ancient Egyptian cosmetic preserved in a reed container [4]. They could observe that the core of the particles consisted of lead soaps, while phosgenite ($Pb_2CO_3Cl_2$) was discovered at the surface. As they could not prove whether the lead soaps were formed during the production of the cosmetic or afterwards during preservation, they set up a kinetic study of oil saponification by lead salts, with the conclusion that the reaction can be significantly accelerated by heating and adding water [5]. Another study reports the chemical investigation of the contents of 44 objects, found in the barber–surgeon's cabin of King Henry VIII's prestigious battle-ship the Mary-Rose [6]. Most of the ointment samples contained a rosin oil or pine resins, some of which were mixed with beeswax. A few samples contained inorganic material like sulphur, zinc or lead compounds

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0026-265X/$ – see front matter
doi:10.1016/j.microc.2009.12.005

which were in some cases mixed with a vegetal oil. Another group of ointments consisted of animal fat blended with a lead-based compound. Finally, an Etruscan ointment was characterized by Fourier transform infrared (FTIR) spectroscopy and gas chromatography-mass spectrometry [7]. It was found that a vegetal oil was used as a lipid base, to which scented compounds, like mastic and pine resin, were added.

The present study investigates the nature of a greasy material preserved in its original ceramic container, which was found during the excavations at the Castle of Middelburg (Maldegem, province of East-Flanders, Belgium) at the border with The Netherlands and close to Bruges. The castle and the city of Middelburg played an important role during the late-Medieval and early-Modern period and were often the scene of fierce battle, especially during the Religious Wars of the late 16th–early 17th century. At that time, the castle of Middelburg had become an important military anchor-point in the Spanish–Dutch Wars. Two garderobe-chutes of the castle, filled up ca. 1600 AD, contained a large amount of material culture and paleo-ecological remains of military origin and even revealed an exceptionally large amount of gallipots, identical in form and fabric to the one from which the sample described below originates. This unusual find was interpreted as the material proof of the presence of a military-surgeon cabinet at the castle during the late 16th century [8]. It is indeed to be expected that armies engaged in constant battle brought along their own surgeons and encamped them with the troops at the headquarters.

The find of a presumed medicinal container can be placed in a wider scientific context historically as well as chemically and raises therefore some important questions. A prime question was to elucidate the initial nature and function of the greasy material, more precisely to find out if it was an ointment as was suggested by the form of the container. If this is indeed the case, the next question would be its formulation and way of preparation. Another point of interest was to reveal whether it was intended for cosmetic or medicinal purpose, for instance in treating wounded soldiers.

2. Material and methods

2.1. The sample and its find context

The container with the preserved content (Fig. 1) was found at the base of the bottom layer of the castle moat at 2.5 m below actual surface (ca. 10.5 m below actual sea-level) in permanent waterlogged conditions. The matrix of the sediment in which it was buried consisted of highly organic clay mud of ca. 50 cm thick, containing many other archaeological objects dating from the late 16th and early 17th century AD. This layer was sealed by ca. 2 m of debris from the castle, dumped in the moat during the destruction of the site (ca. 1750). The container in which the sample was found is typologically known as a *gallipot* or *albarello*, a ceramic vessel form which was originally intended to contain salves or ointments [9]. Typo-chronologically and based on the find context, the form can be dated in the second half of the 16th, early 17th century.

Fig. 1. The *albarello* from the castle of Middelburg.

2.2. Chromatographic analyses

Standard lipid analyses are described in detail in previous works [10,11]. In brief, 0.5 g of the sample was submitted to Soxtec extraction using chloroform/methanol (2:1 v/v) as solvent mixture. An internal standard (*n*-heptadecane) was added to each extract. The dried extract was subjected to transesterification by treatment with methanolic KOH during 3 min at room temperature. This procedure is sufficient for transforming the triglycerides to fatty acid methyl esters (FAMEs), which were then analyzed on a polar phase gas chromatograph (PP-GC) and on a gas chromatograph combustion isotope ratio mass spectrometer (GC-C-IRMS). A second dried extract was used to prepare FAMEs from both triglycerides and free fatty acids using boron trifluoride and MeOH before analysis on a PP-GC. A third lipid extract was silylated with *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (97%) (MSTFA) before analysis on a gas chromatograph with mass spectrometer (GC-MS). Peak assignments were made on the basis of retention times of reference compounds, relative elution times from literature, mass spectral libraries (NIST 2.0), and interpretation of the mass spectra. A non-derivatized lipid extract was analyzed on a liquid chromatograph with mass spectrometer (LC-MS) with atmospheric pressure chemical ionization (APCI).

2.3. Fourier transform infrared spectroscopy

Attenuated-total-reflectance Fourier transform infrared spectroscopy (ATR-FTIR) analysis was performed on a Bruker IFS66 FTIR spectrometer equipped with a liquid nitrogen cooled mercury–cadmium–telluride detector. The resulting spectrum is obtained from the average of 256 interferograms collected at a nominal resolution of 2 cm^{-1}. The sample compartment was continuously purged with dry air in order to minimize the spectral contribution of atmospheric water. The internal reflection element was a germanium ATR plate with an aperture angle of 45° yielding 25 internal reflections. A small amount of dried subsample was deposited directly