

REVISITING PHARMACY MORIANEN: REVEALING FIRST TRACES OF ELEMENTAL SILICON IN A LABORATORY ENVIRONMENT

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Introduction

In a previous work in collaboration with National Museum of Art, the present author performed Raman analysis of pigments used by the 17th-century painter, Elias Brenner (1647-1717). Brenner published a book in 1680 in which he gave samples and names in three languages (Swedish, Latin, and French) of 30 different pigments he used in his work as a miniature painter. Three copies of this book could be found and were analyzed with Raman spectroscopy and other techniques (work still in progress). A first report was published in 2006 (1).

Since it is believed that artists of those days mainly bought their pigment material in pharmacies, alternatively producing many themselves, it is tempting to investigate findings of vessels from pharmacies of that time. Such an opportunity exists in this case, since the cellars of an old pharmacy were discovered during the construction of a garage for the Houses of Parliament in Stockholm in 1977. Written sources (2) clearly state that the Pharmacy Morianen was in operation at this site during the time 1670-1674. Then it was demolished to make space for a new stable for the king's horses. The idea emerged that it might be possible to find at least some of the sources of pigments by going through the traces of contents in the jars and vessels found. The operational period coincides well with Brenner's first years in Stockholm, where he arrived in 1673, so he could very well have been a customer at Morianen.

The owner and founder of Morianen is well known. His name was Christian Heræus (1643-1691), originally from Güstrow in Mecklenburg, Germany. He operated the pharmacy from its inauguration in 1670, during the time it was moved to another site, and up to 1678, when he left Stockholm for Leyden, where he took his doctorate degree in 1679. From 1671 to 1678 he was the court pharmacist for Queen Hedvig Eleonora.

Interesting for this investigation is also his employment by "Bergskollegium" as "chemicus." This organization had a neighboring house to the pharmacy, and Heræus's task was to find new uses for metals and minerals that were known and found during this time. He probably had a diversified chemical laboratory, to produce pharmaceutical products as well as to experiment with virtually anything. So the chemical activity in the pharmacy was not only related to medicine.

The findings from the pharmacy are relatively scarce. The cellars contain four rooms, which were almost empty since they were evacuated before the house was demolished. It was abandoned to give space for other buildings and moved to a new place (the pharmacy Morianen was in operation in different locations in Stockholm until 1971). Everything of value was of course taken away. The most interesting findings constitute a selection of some 50 more or less intact jars and vessels of glass and ceramic and some laboratory equipment like retorts, found in a latrine well at one side of the house. When or why they were deposited in the shaft is

impossible to know, but most likely it had been used as a waste bin. By means of modern techniques it may be possible to unravel what kind of activity was going on during that period.

In Ref. 2 a detailed description of shape and origin of some of these findings is given. Some analyses of contents were also made directly after excavation, mainly by means of X-ray diffraction and thermal analysis and reported by Wadsten (3). Some vessels contain insects, obviously collected for some medical reason; others remainders of syrup and raspberries, which were very often used as bases for drugs at that time. Subsequently, the findings have been stored at the premises of Stockholm Stadsmuseum for about 30 years.

This investigation was from the outset focused on finding traces of pigments that could have been sold to the artists, but some very interesting results were obtained that cannot have anything to do with making of pigments or producing pharmaceuticals. The fact that Heræus was also employed by "Bergskollegium" provides the opportunity for wide speculation as to what he might have been doing.

Techniques Used

Since the previously mentioned investigation of Brenner's pigments was performed with Raman spectroscopy, a nondestructive vibrational spectroscopy technique most commonly used with lasers in the visible spectral range, the same technique was used here. In addition some samples were analyzed with Fourier transform infrared (FTIR) spectroscopy, another well known technique.

The Raman instrument is a Renishaw InVia Reflex microspectrometer equipped with two lasers (514 nm and 785 nm), a deep depletion enhanced CCD detector, microscope objectives with different magnifications (x5 – x100), and also a white light video camera to observe the sample on the stage in the microscope. The laser spot can be monitored in the image and the point of analysis well defined. Photographs can also be taken of the samples.

The FTIR is an IlluminatIR from Smiths Detection, mounted on a Leica microscope with a white light video camera for sample observation and photography. The instrument is equipped with both all reflective (ARO) and an attenuated total reflection (ATR) objective, but here only ATR was used.

Results on Fibers and Insects

Many objects contain fibers. It is difficult to say whether these are original fibers or whether they have come into the vessels during the centuries or even after excavation. The most common fiber is actually a typical cellulose fiber; one example of an FTIR spectrum is shown in Figure 1. This spectrum compares very well with one of fibers from modern pine wood. Another common fiber is that from an animal, and in Fig. 2, one example is compared with a modern fiber from a horse and also with a spectrum from an old fur hair taken from the battle horse Streiff, belonging to King Gustav II Adolf (who died with him at the battle of Lützen, November 6, 1632). This horse was returned to Sweden and is now conserved and displayed at Livrustkammaren, Stockholm Castle. It is easy to imagine that these fibers have been embedded in the King's stable during the centuries following the demolition of the pharmacy. Horses' walking on the floor of pine plank is the probable source.

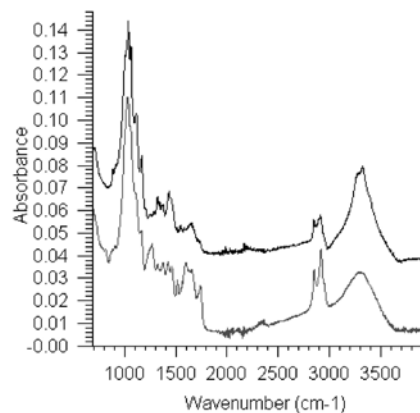


Figure 1. Fiber 1 commonly found in the vessels (upper), and as reference, a fiber from a modern pine tree (lower)

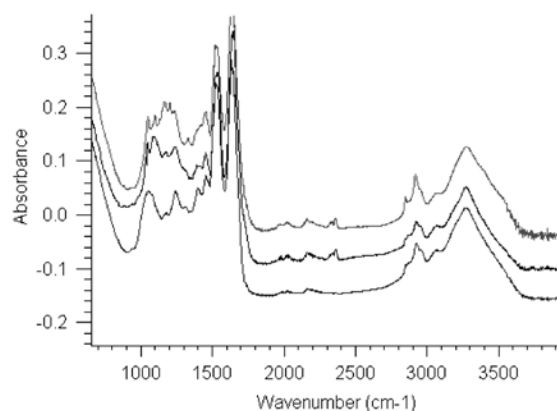


Figure 2. Fiber 2 commonly found in the vessels (middle), and as references, a fiber from a modern horse's fur (lower) and a spectrum from an old horse Streiff (upper).

Other common findings analyzed with FTIR are parts and fragments of insects. These can of course have been collected for pharmaceutical usage. This is certainly the case for one closed jar with dry, intact beetles, which was discovered in 1977; and since this particular insect did not have a name, it was dubbed “Kyrkogårdsbagge” by Wadsten (3). Other more commonly occurring findings in this investigation are much more fragmented and more probably remains of dead insects that have accumulated in the cellars during the centuries, rather than collected for pharmaceutical usage. In general, all artifacts are covered by a layer of dust, and spectra of common minerals like feldspars stem from this dirt layer. No examples are shown. The only finding that possibly could have been the remains of a pigment container is a fragmented ceramic jar, with a lump consisting of hematite mixed with charcoal (carbon). Fig. 3 shows the spectra of the sample and reference.

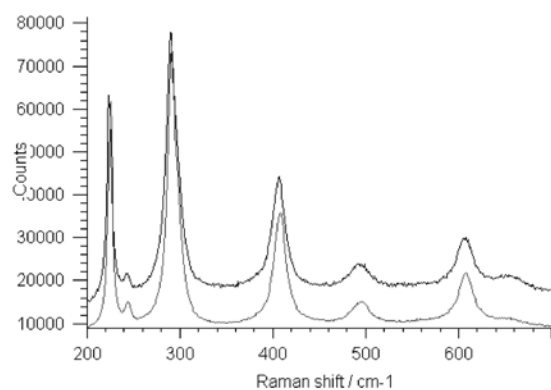


Figure 3. Sample from ceramic vessel 533 (lower) and reference Hematite, Fe_2O_3 (upper).

S, Si, Hg, As, and C: Elements and Compounds

Another wide and open ceramic jar has fine small crystals of pure sulfur scattered over the surface. Fig. 4 and 5 show a white light picture of the crystals and the Raman spectrum, together with a modern reference spectrum. Sulfur has been used in both medicine and chemistry – and alchemy! – for very long time.

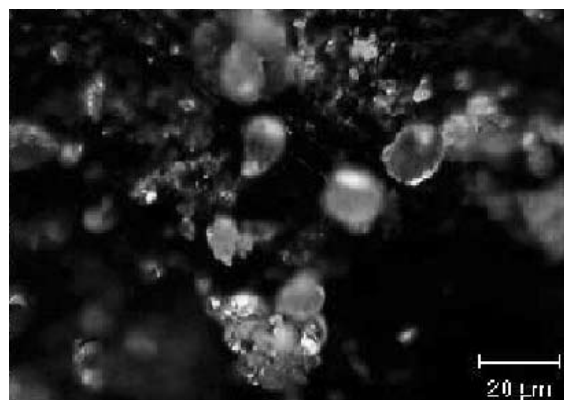


Figure 4. White light picture of crystals in vessel 19907.

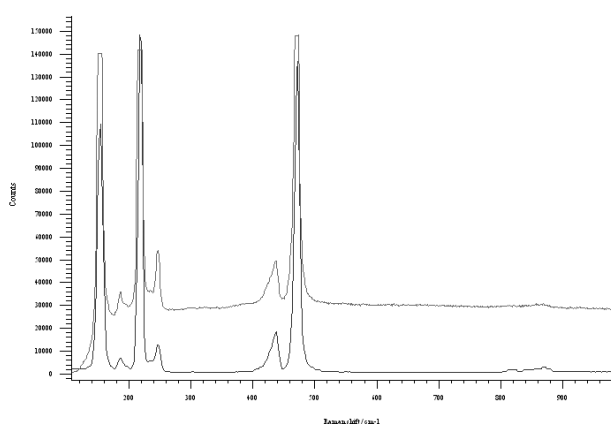


Figure 5. Spectra of crystals in vessel 19907 (upper) and reference Sulfur (lower).

The most interesting and puzzling finding is part of a retort—a vessel with an Erlenmeyer-like design and a narrow tube that projects almost horizontally. (A picture of this artifact, named 457 in this investigation, is given on page 353 in Ref. 2.) This vessel was typically used as early distillation equipment. Heating the content in the vessel and then condensing the reaction products in the cooling tube allowed for some separation. This particular finding of glass is a part of the cooling tube. It has a very narrow hole, about 2-3 mm in diameter, and thick walls. The length is approximately 180 mm. First discovered in the tube were droplets of metallic mercury, easily recognized by their luster and shape (see Fig. 6). Some compounds of Hg have also formed (see Fig. 7a and 7b). The spectrum in Fig. 7a is from $HgCl$, commonly named calomel. The spectrum in Fig. 7b is similar to imiterite, a compound of Ag_2HgS , with just a single peak at 281 cm^{-1} (ruff id R080014).



Figure 6. White light picture of a droplet of Hg in 457.

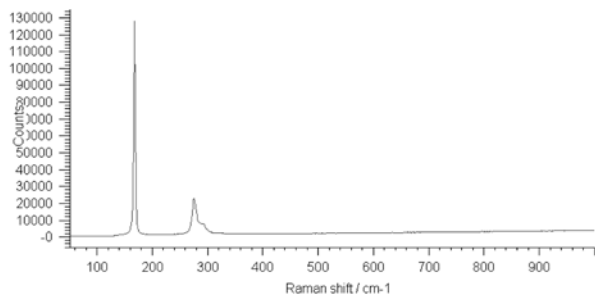


Figure 7a. Peaks at 166 cm^{-1} and a double peak at 274 and 286 cm^{-1} , identified as calomel.

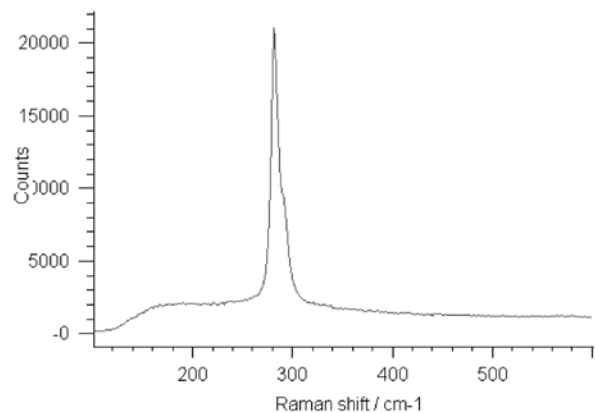


Figure 7b. Double peaks at 282 and 291 cm^{-1} .

The Raman analysis revealed many more interesting things. There are pure crystals of arsenic inside the tube. In Fig. 8, a spectrum of As is compared to that of a modern reference material.

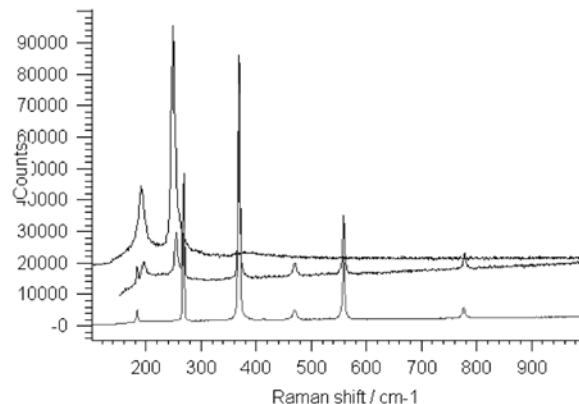


Figure 8. Newly cut surface of As reference (upper), oxidized outer surface of reference sample (middle) and spectrum from the finding, vessel 457 (lower).

The upper spectrum is from a clean, newly cut surface of elemental As. The spectrum in the middle is from the oxidized surface of this modern sample. The lower spectrum is from the finding in the retort. One can see that the oxidation peaks have grown higher than those in the other spectra, indicating that this is indeed an old sample. It seems as if elemental As has sublimed at a position along the tube, where the temperature allowed this to happen, and then later was oxidized.

In the tube there are also two bones from a fish's spinal cord. These are most certainly from herring (4), a common fish that was a very basic food at that time.

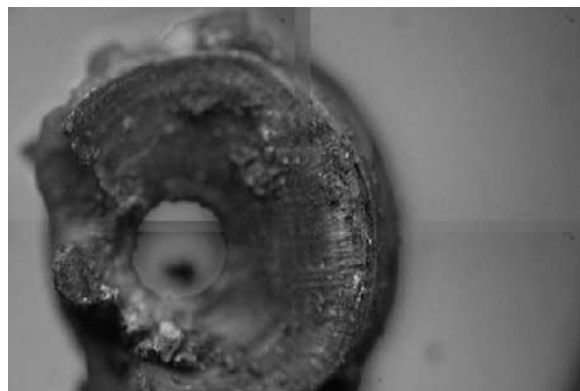


Figure 9. White light picture of a fish bone, spinal cord of herring. Magnification $\times 5$.

On these bones there are small crystals of elemental silicon! Fig. 9 shows a white light image of one of the bones; Fig. 10 displays the shiny crystals, whose spectrum is shown in Fig. 11. It was also found that some silicon is strained: the main peak at 520 cm^{-1} has

shifted 3-5 wave numbers. The occurrence is really an unexpected finding; although silicon is a very common element in nature, it never exists in the pure elemental form, always as compounds such as silicates or quartz (5). There are, however, some examples of Si in solid solutions, for instance copper in ancient arrow heads of bronze, manufactured about 525 BC. It is probable that silica was unintentionally reduced in the smelting process and Si contaminated the alloy, where it hardened the product (6). Elemental silicon was produced and described as an element for the first time by Berzelius in 1823—more than 150 years later than the findings in Morianen (7)!



Figure 10. White light picture of metal inclusion in fish bone 457. Magnification x50.

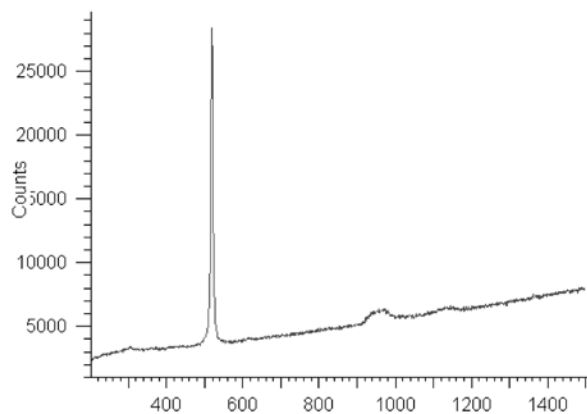


Figure 11. Spectrum of Si on the fish bone. Main peak at 515 cm^{-1} .

On the fish bones there are also small particles of pure carbon; one spectrum is shown in Fig. 12.

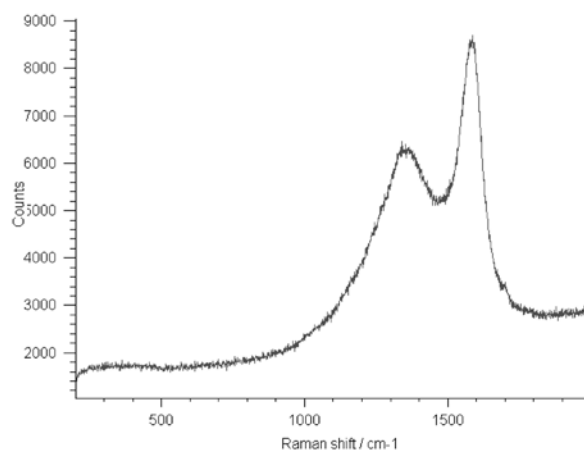


Figure 12. Carbon spectrum from particulates on the fish bones.

There are also small white crystals on the fish bone that have not been clearly identified (see spectra in Fig. 13). These are taken on different occasions and from different spots, but the relative intensities among the peaks are almost the same. If the spectrum comes from a mixed compound, these relations would most probably not have been reproduced. The best fit from reference libraries is therefore mullit ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) common in glass. The peaks below 700 cm^{-1} are similar to rutile, TiO_2 , but the peaks at higher wave numbers do not fit. (Rutile was not known in 17th-century Sweden).

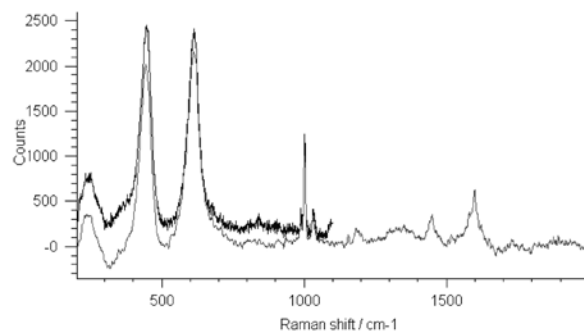


Figure 13. Two examples of spectra of the white crystals on the fish bone in vessel 457.

Finally, in this sample there are also traces of quartz, again being present on the fish bone pieces and on the surface of charcoal particles (see Fig. 14).

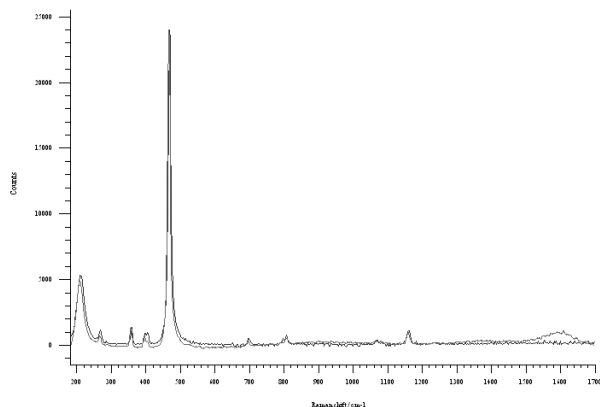


Figure 14. Spectra from particles on the fish bone (lower at low wave numbers), similar to reference spectrum of quartz (upper at low wave numbers).

What was Heræus Doing?!

As mentioned, the first successful synthesis and description of elemental silicon were done by Berzelius and published first in a letter to the French Academy of Science, where it was read by M. Dulong, and later printed in Ref. 7. The element Si was not known before 1823.

The pharmacist, chemist—alchemist—Heræus was obviously experimenting wildly. In the glass vessel, (source of quartz, mullite?) item 457, he must have mixed mercury, arsenic, salt (NaCl?), fish bones, and other organic materials like charcoal. Then he must have raised the temperature relatively high. (It has been reported by Wadsten (3) that traces of “probing” analysis, i.e. analysis at high temperatures to decide purity of noble metals, were found in the pharmacy). What reactions occurred, and how could they lead to formation of elemental silicon? In the early attempts to reduce silica by Berzelius and others, many routes were tried. Even electrolytic methods were used (8), and later on during the 19th century also high temperature reactions between silica and carbon in electric arc furnaces. Berzelius, however, mentions processes applying “ordinary chemical agents,” as he expressed it in an even earlier article (9). In a work by Davy as early as 1808, silica (in his glass vessel) reacted by chance with potassium to form a brown powder (10). Davy did not realize that this probably was silicon. The full understanding of the reaction was given by Berzelius in the referenced paper (7). In his work Berzelius used SiF₄ gas, which was treated with potassium. This did not require very high temperatures (in

Berzelius words “heated by a spirit lamp”). In the retort from pharmacy Morianen there are large amounts of Hg and also calomel. Is it possible that salt, NaCl (commonly used to preserve fish), had reacted with the mercury, and then in addition to calomel an amalgam between sodium and mercury might have formed? Amalgams do not have Raman spectra, so remainders of this would not show up in these analyses. On the assumption that this could happen, elemental sodium could perhaps have the same reducing effect on silica as potassium, described in the referenced old papers. In fact, Oersted published as early as 1825 a paper in which he described reduction of silicon chloride by sodium amalgam (11). Both the amalgam and metallic mercury in the retort of course evaporate at low temperatures and sublime along the cooling tube. This could have provided a transportation reaction and brought the sodium in contact with silica.

Arsenic also evaporates and sublimates (sublimation temperature 616° C (12)); and since it probably did not react during the process, it indicates that the environment should have been reducing. (It was oxidized later in air over the course of 300 years). The presence of large amounts of elemental carbon also indicates a reducing atmosphere.

Christian Heræus was obviously aiming at something completely different, and he would not have had the capability to find or analyze the small pieces of Si in this reaction vessel, even if it had not been broken and thrown away in the latrine well. Once formed, the Si is very stable; and it is no wonder that it has survived for 350 years in a protective environment. But this property of Si is well known to all current chemists, as a result of the intense research on Si since the 1960s.

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