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# Mapping and Measurement of the Desalination Potential of Acetonitrile in Agar Gel on Marine Archaeologi- cal Copper Alloy Artefacts

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## Abstract

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The most commonly used methods for extracting chlorides from marine archaeological copper objects, sodium sesquicarbonate and deionized water soakings, while effective, can take a long amount of time to remove enough chlorides to stabilize the object. When objects need to be treated faster, alternative methods must be used.

In this thesis, multiple experimental treatments are performed on marine archaeological Swedish copper coins and plate monies in order to demonstrate the effectiveness of acetonitrile in extracting chlorides from copper over relatively short treatment durations. Acetonitrile will be used in conjunction with agar gel and an aluminium sheet in the treatment container, in order to give a visual indicator of the copper chlorides acetonitrile extracts from the object as they are drawn to the aluminium and start corroding it. Comparative tests will be performed with gels containing sodium sesquicarbonate and water. In addition to the visual examination of the results and humidity chamber tests that will show if the objects continue to actively corrode when exposed to environments with high relative humidities, chloride level analysis is performed when possible. Furthermore, the treated coins will be analysed with a scanning electron microscope (SEM) and compared to untreated coins.

Although clear quantitative data of the results of the experiments proved difficult to obtain, the aluminium sheets demonstrated the effectiveness of acetonitrile clearly, as they already started to show signs of corrosion after 24 hours, compared to the sesquicarbonate and water that failed to significantly corrode the aluminium in 27 days. In addition to the potential this treatment has for mapping chloride concentrations as shown with the treatment of a plate money, it clearly indicates the effectiveness of acetonitrile when compared to the other methods.

Keywords: marine archaeological copper, acetonitrile, desalination, agar gel, localized corrosion, plate money

## Tiivistelmä

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Yleisimmin käytetyt menetelmät kloridien poistamiseksi meriarkeologisista kupariesineistä, natriumseskvikarbonaatti ja deionisoitu vesi, ovat tehokkaita, mutta niitä käytäessä kloridien poisto sille tasolle että esine stabiloituu vie kauan. Kun esineet on käsiteltävä nopeammin, on käytettävä vaihtoehtoisia menetelmiä.

Tässä tutkielmassa suoritetaan useita kokeellisia käsittelyjä meriarkeologisille ruotsalaisille kuparikolikoille ja ploatuille, joilla demonstroidaan asetonitriilin tehokkuus kloridien poistamisessa kuparista suhteellisen lyhyellä käsittelyajalla. Asetonitriiliä käytetään yhdessä agar-geelin ja alumiinilevyn kanssa käsittelyastiassa, jotta saadaan visuaalinen indikaattori kupariklorideista, jotka asetonitriili irrottaa esineestä, kun ne tarttuvat alumiiniin ja alkavat korrodoida sitä. Vertailukokeita tehdään natriumseskvikarbonaattia ja vettä sisältävillä geeleillä ja liuoksilla. Tulosten visuaalisen tarkastelun ja kosteuskammiotestien lisäksi, jotka osoittavat, jatkavatko esineet aktiivista korroosiota kun ne altistetaan korkeaa suhteellista kosteutta sisältäville ympäristöille, tehdään mahdollisuuksien mukaan kloridipitoisuusanalyysi. Lisäksi käsitellyt kolikot analysoidaan pyyhkäisyelektronimikroskoopilla (Scanning Electron Microscope, SEM) ja verrataan käsittelemättömiin kolikoihin.

Vaikka selkeitä kvantitatiivisia tietoja kokeiden tuloksista oli vaikea saada, alumiinilevyt osoittivat selvästi asetonitriilin tehokkuuden, sillä ne alkoivat osoittaa korroosion merkkejä jo 24 tunnin kuluttua, kun taas seskvikarbonaatti ja vesi eivät korrodoineet alumiinia merkittävästi edes 27 päivässä. Sen lisäksi, että tällä käsittelyllä voidaan kartoittaa kloridikonsentraatioita, kuten ploatun käsittely osoitti, se osoittaa selvästi asetonitriilin tehokkuuden muihin menetelmiin verrattuna.

Avainsanat:	Meriarkeologien kupari, asetonitriili, suolanpoisto, agar-geeli, paikallinen korroosio, ploatu
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Tämän opinnäytetyön alkuperä on tarkastettu Turnitin Originality Check -ohjelmalla.

1	Introduction	1
2	Copper as a metal	3
2.1	Copper and it's alloys	3
2.2	The corrosion of copper	3
3	Treatment methods for marine archaeological copper	5
3.1	Sesquicarbonate and water	5
3.2	Benzotriazole (BTA)	6
3.3	Subcritical treatment	6
3.4	Electrolysis	7
3.5	Acetonitrile	8
4	Background for the Länsitonnttu archaeological finds	10
4.1	Plate money & coins	10
4.1.1	History of plate money in Sweden	13
4.2	History and excavation of the Länsitonnttu finds	13
4.3	Prior conservation	15
5	Conservation and analysis methods	16
5.1	Acetonitrile gel treatment	16
5.1.1	Agar gel	17
5.2	Testing and treatment plan	19
5.3	Humidity chamber tests	20
5.4	Chloride level measurements	20
5.5	Comparative tests	21
5.6	SEM analysis	23
6	Conservation and experiments	23
6.1	Preparation of objects	23
6.2	X-ray fluorescence measurements	26
6.3	Preparation of treatments	27
6.4	First treatment of coins	29
6.5	Second treatment of coins	33
6.6	Third treatment of coins	37
6.7	Comparative gel tests	39

6.8	Comparative solution tests	41
6.9	Treatment of the plate money	42
6.10	SEM analysis	49
7	Results and discussion	50
7.1	Chloride measurements	50
7.2	SEM analysis results	52
7.3	Aluminium and mapping	58
7.4	Effectiveness of the gel	59
7.5	Washing the gel	60
7.6	Samples	61
7.7	Future research	62
8	Conclusions	62
	References	65
	Appendices	68
	SEM analysis graphs	68
	Report of the Länsitonttu finds (in finnish)	79

# 1 Introduction

Metal objects are common finds at marine archaeological sites. While the treatment methods for treating archaeological metals of various types are numerous and widely studied, desalination is a crucial part of the stabilizing process that is often overlooked (Lois et al. 2019, 19). Chloride ions left on copper objects after treatment are directly responsible for the main form of destructive corrosion of copper, bronze disease (Pearson 1988, 233). While artefacts composed of copper alloys are still common in marine archaeological finds, the desalination methods for copper are even less widely studied than the methods for iron (Diego et al 2020, 19). While the main reason for this is most likely that iron objects are the most common type of metal artefacts, another reason might be that copper in itself is less reactive, being more noble, and on the surface often appears to require less stabilization than iron (Macleod 1987, 25). If the requirement for desalination is overlooked in this manner, this can lead to objects that were deemed to be stable starting to show symptoms of bronze disease later in storage.

Most common methods for the desalination treatment of copper alloys are long washing treatments of the object in solutions such as sodium sesquicarbonate or deionized water, among others. While sesquicarbonate has been deemed fairly effective in removing chloride ions, the treatment process is often very long. In most cases, the long treatment times are seen as acceptable, since the method typically is eventually effective, does not require much active monitoring or work, and the used solution, while not entirely non-toxic due to the eventual dissolved copper, is far less harmful or hazardous to the environment than some of the alternative chemicals. However, for museums or institutions with large amounts of objects requiring treatment, the long waiting periods can create a problem.

Objects typically require multiple treatments or a change of solutions for enough chlorides to be removed to stabilize the object. This, however, multiplies the

risks created by these treatments. This could be circumvented by locating the unstable areas of the object and focusing treatment to the most critically unstable locations.

Acetonitrile has been demonstrated in selected experiments to be effective and rapid at extracting chlorides from copper. However, it hasn't been widely used in practice, and while its effectiveness has been researched to some extent, its modern applications are limited.

In this thesis, a novel idea for both treating an object and using the treatment to locate corroded areas of the object, proposed by Dr. Ian MacLeod, will be tested. In the method, acetonitrile will be used in conjunction with agar gel on the object, and the areas where chloride ions are extracted in large amounts are located and mapped by using an aluminium sheet placed on the gel and observing the locations of active Cl<sup>-</sup>-driven corrosion through cementation of Cu(I) on and potential corrosion of the aluminium sheet by released Cl<sup>-</sup>.

The purpose of this test is to demonstrate the effectiveness of acetonitrile in extracting copper chloride (CuCl, also known as nantokite). As copper chloride is normally imperceptible, the aluminium sheet with the help of the gel will give a visual indicator of its mobilization and presence.

Tests using this method will be performed on sample objects. The selected samples are taken from a set of Swedish copper coins and plate monies recovered from the archipelago of Helsinki, Finland in 2009. The objects are placed in the gel treatment for varying durations, after which their stability will be tested in a humidity chamber. At the same time, observations of the Cu(I) cementation and the corrosion of the aluminium sheet will be made, which will then be compared to the signs of bronze disease on objects both prior to and after treatment (if any).

## 2 Copper as a metal

### 2.1 Copper and its alloys

Copper has been historically alloyed with many different metals. These include tin (bronze), zinc (brass), lead, antimony, nickel and arsenic (Craddock 1995, 93).

When exposed to oxygen, copper forms a layer of patina. This patina is composed of Copper (I) oxide ( $\text{Cu}_2\text{O}$ ) or Copper (II) oxide ( $\text{CuO}$ ), and typically includes other compounds that affect the patina's colour and appearance, such as malachite ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ) (Paterakis 2013). Contrary to most other metals, the patina formed on copper is often considered aesthetically pleasing and even integral to the appearance of the object. This means that in many cases when treating copper objects, the patina is left as is. This often results in preference to treatment methods that do not destroy the compounds forming copper's patina or discolour it.

### 2.2 The corrosion of copper

The most typical form of active copper corrosion is the so-called bronze disease. This is the result of copper reacting with oxygen in the presence of chloride ions.

Typically, the copper oxide patina protects the underlying metal well, resulting in a very slow corrosion rate in copper alloys. However, if chloride ions are also present, the patina layer can start to fail, and copper can start reacting with the chloride ions. Sometimes this only results in a layer of blue-green copper (II) hydroxy chloride patina, but often it can lead to the chloride ions penetrating the copper oxide layer and forming a layer of cuprous chloride ( $\text{CuCl}$ ), also known as nantokite in its mineral form, underneath it. Bronze disease forms when the cuprous chloride undergoes an oxidative hydrolysis reaction with its surroundings and forms copper chloride ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ) as well as free copper(II) chloride.



This then also recycles the chlorides released by hydrolysis, which in turn again reacts the uncorroded metal in a new cycle of corrosion when the object is left exposed to moisture and oxygen (Abu-Baker 2023, 39). This reaction starts “pitting” the metal surface as more and more of the metallic copper is consumed by the reaction and exposing in turn more metallic copper. Eventually this process can destroy the whole object if left untreated. (Scott 1990, MacLeod 1981)

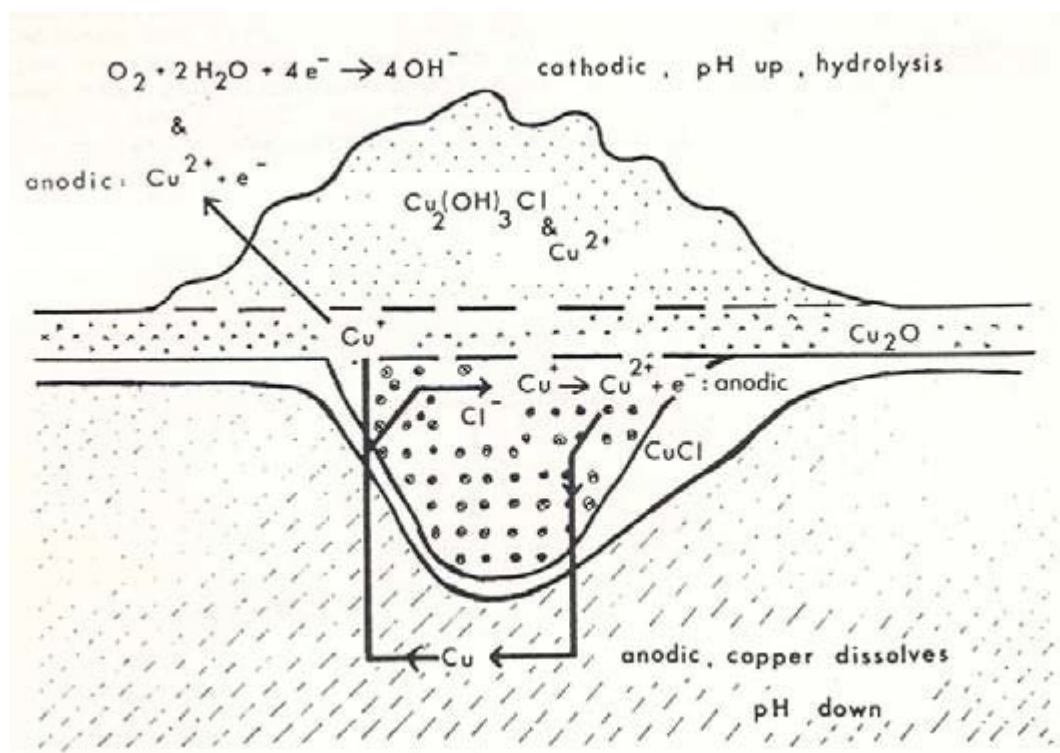


Figure 1: Schematic representation of the major oxidation and reduction reactions involved in Bronze Disease (MacLeod 1981, 19)

In terrestrial archaeological finds the bronze disease typically only appears as small, pitted spots (a schematic of this is represented in figure 1), and the treatments are less interventive and localized, such as mechanical cleaning and using corrosion inhibitors such as benzotriazole (BTA). Other treatments can include localized application of  $Ag_2O$  (Silver (I) oxide) directly at the cleaned corrosion site. However, as marine archaeological artefacts are virtually always in contact with large amounts of chlorides in the surrounding seawater, most often the areas suffering from bronze disease on the object are very large, if not encompassing the whole patina. (Pearson 1988, 232-233)

### 3 Treatment methods for marine archaeological copper

#### 3.1 Sesquicarbonate and water

Perhaps the most common method to treat bronze disease in marine archaeological copper objects is soaking them in a sodium sesquicarbonate ( $\text{Na}_3\text{H}(\text{CO}_3)_2$ ) solution (MacLeod 1987, 26). The sesquicarbonate reacts with copper (II) chloride in the object and breaks it down into harmless compounds, thus stabilizing the object over a period of time (Pearson 1988, 234).

The method is fairly effective and simple to perform and monitor but has its downsides. The treatment times are long, and in many cases the objects need to be soaked well over a year before the treatment has a desired effect. The long treatment time enhances the other downsides of the method, mainly that the sesquicarbonate reacts with the corrosion layer and form bluish-green sodium copper carbonates, changing the colour of the patina. Furthermore, due to the long treatment, the solution needs to be changed multiple times, potentially making its usage costly especially in the case of larger objects. Of course, the treatment time itself doesn't mean that the treatment requires much work, as the objects only require periodic checking. For conservators working with a large amount of copper objects this can be problematic, however, due to often too limited laboratory and storage space at most facilities. Furthermore, on objects that need to be stabilized rapidly (for an exhibition, for example), the long treatment time is not suitable. (Drayman-Weisser 1987, 105-108)

It should also be noted that due to the relatively low amounts of chlorides that are released into the solution, the measuring methods must be fairly accurate when monitoring the chloride amounts. Typically, volumetric chloride titrations which rely on colour changes in indicator strips are not sensitive enough but potentiometric titrations using an Ag/AgCl electrode are. This increases the amount of time and effort required for accurate monitoring. (Pearson 1988, 234)

Treatments in water on the other hand can even cause damage in the objects. Trace amounts of iron, lead and zinc in the object can release chlorides into the water, speeding up its corrosion (Pearson 1988, 235). Furthermore, the effectiveness of water has been deemed even slower than that of sesquicarbonate (MacLeod 1987); The Swedish copper coins and plate monies used in the tests in this thesis, which will be discussed in more depth later, were previously treated with water for nearly 5 years and were still not stabilized.

### 3.2 Benzotriazole (BTA)

Benzotriazole or BTA ( $C_6H_5N_3$ ) has been used as a corrosion inhibitor for archaeological copper for some time, being first used in 1967 (Golfomitsou & Merkel 2004, 345). Treatment is usually performed by soaking objects in an aqueous BTA solution after chloride removal. The BTA forms a film on top of the copper, which acts as a retardant for the dissolution of the copper, as well as acting as a barrier to stop oxygen reduction on the metal surface (Faltenmeyer 1995, 45-46). This prevents or at least significantly slows down the bronze disease, thus stabilizing the object.

Recently, however, the use of BTA has gradually diminished after it has become apparent that it is carcinogenic, in addition to potentially having multiple other negative health effects (Hartwig 2020, 3-5). This is especially harmful if it is used on a copper object with large amounts of bronze disease which it would fail to completely protect, as the copper chloride produced by the corrosion process would form into a fine dust in dry conditions, which could be easy to accidentally inhale when handling such an object.

### 3.3 Subcritical treatment

Subcritical treatment processes involve similar aqueous solutions as the more commonly used methods, but instead of simply soaking the objects in it, the solution is placed in a pressurized chamber, which allows water to be heated well above its room-temperature boiling point of 100 °C while remaining in liquid

form. This significantly decreases the solution's viscosity and surface tension, allowing it to penetrate into the object and thus diffuse chloride ions far more efficiently. The method has been successfully used on iron since 2003 (Drews et al 2004) but hasn't been used with copper as extensively.

To date, studies have shown that while the method is very effective in removing chlorides from copper alloy objects undergoing active corrosion, further research is required to establish optimal parameters for copper alloy artefacts, particularly bearing in mind the effect on the alloying elements, as well as the aesthetic characteristics of many copper alloy objects. Furthermore, the treatment requires the usage of a large and expensive pressurised subcritical treatment equipment, so its use is limited to places where such a system is available. (Näsänen 2018, MacLeod & Näsänen 2023)

### 3.4 Electrolysis

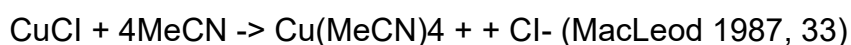
A common method in treating non-marine archaeological metal finds is electrolysis. While most often used for ferrous objects, the method can be used for copper and other metals as well. It is performed by passing a direct electrical current through the object and an ionic solution. The process involves establishing a galvanic cell, in which the metal object being treated acts as the cathode, and a selected metal sheet or piece serves as the electron donor or the anode is connected to the positive terminal (Zierden, i.a.). In the case of iron objects, the metal used for the anode is typically acid-proof steel, while with copper the anode should also be copper (Rodgers 2004, 114). In the treatment process, chloride ions are drawn from the object into the anode, thus stabilising the object. (Lacoudre et al 1991, 11; Meyer-Roudet et al 1999, 114-115)

A typical set-up for electrolysis on small items is inexpensive and the materials are readily available: A battery or a variable voltage DC power supply, connector cables, and a plastic tub form the basis of the treatment system, sodium carbonate (baking / washing soda) dissolved into deionized water acts as the

ionic solution, and a sheet of metal acts as the anode. The process can, however, take long; typically, lower currents are recommended for more fragile objects, which then leads to longer treatment times. Usually, however, small copper objects can be stabilized in a few days. The method is, however, unsuitable for the most corroded and fragile marine archaeological artefacts as it can easily break them. (Zierden i.a.)

### 3.5 Acetonitrile

The subject of this thesis, acetonitrile (also known as Methyl Cyanide, abbreviated as MeCN), has seen fairly low popularity in usage, despite the promising results from the few existing experiments. In the tests that have been done, treatment in an acetonitrile solution has been shown to provide results much faster than sesquicarbonate or distilled water. Acetonitrile stabilizes copper by reacting with copper chlorides (CuCl), forming harmless compounds in the following reaction:



In MacLeod's *Lively* experiment, which compared different treatment methods using sheathing tracks from a shipwreck as samples, the aqueous acetonitrile solution used had released 79 ppm chloride after two hours, when the sesquicarbonate and water solutions only had from 2 to 6 chloride ppm. However, in this test, after 26 treatment hours the stronger sesquicarbonate solution (5 wt%) provided similar results than acetonitrile, and after a prolonged treatment the amount of chlorides outranked the acetonitrile. However, it was noted that the reason for the sesquicarbonate solution's high chloride rates was at least in part because of it reacting with the compounds of the patina instead of removing the chlorides directly from the object. For this reason these scores are not fully comparable. (MacLeod, 1987)

Note that, while BTA doesn't actively extract chlorides from copper per se, it does compete with the chloride ions for active spots in the alloy, and as it gradually replaces the chloride ions some chlorides would eventually be released to

the solution. According to Ian MacLeod, this is one of the reasons it was used in the chloride removal comparison experiment.

In a similar treatment comparison test performed by Uminski and Guidetti, acetonitrile treatment appeared to be the most effective treatment methods from the ones tested. The test used artificially corroded copper sheets as samples, and compared water, benzotriazole, AMT (5-amino-2-mercapto-1,3,4-thiadiazole), sodium carbonate and sodium bicarbonate treatments. (Uminski & Guidetti 1995)

Despite these apparently promising results, acetonitrile has been used very little in museums if at all. Despite its apparent effectiveness, the treatment method has its drawbacks, which might be at least a part of the reason for this. Longer treatment times can cause changes in the colour of the patina. When soaked in a solution for more than six weeks, black copper (II) oxide can start to form, darkening the object (MacLeod 1987, 33). This is due to the much higher solubility of dissolved oxygen in 50% acetonitrile water mixtures, compared with water.

In addition, the acetonitrile solution itself is moderately toxic as well as highly flammable (Carl Roth 2021). Coupled with the fact that acetonitrile vaporizes quickly in room temperature, this means that a well-ventilated workstation and airtight containers are required. These can be a logistical and a budgetary problem for some, alongside the obvious safety issues, especially if there are no adequate working environments to handle toxic solutions. Small amounts of acetonitrile can be disposed of by leaving them to evaporate in a fume closet if it is available, but larger amounts of acetonitrile waste need to be collected and delivered to the appropriate waste management facilities.

Despite these drawbacks, the rapidness of the method and the affordability of the required chemicals could potentially make this treatment method invaluable for museums and other institutions with a limited budget and a large number of objects that require treatment. On many objects where the patina is deemed too

important to risk the method might not be found suitable, but on objects where the change in colour is considered less of an issue, the short treatment time can make it the preferred method.

## **4 Background for the Länsitonttu archaeological finds**

### **4.1 Plate money & coins**

The test samples that will be used to test the acetonitrile treatment method are a set of Swedish copper plate monies (plåtmynt in Swedish, ploomu in Finnish; Figure 2), as well as copper coins which were found in the same location.



Figure 2: One of the plate monies

The monies in question were recovered near a skerry named Länsitonttu in the Helsinki archipelago in 2009. They are dated to be from the earlier half of the 18th century (1710-1740). They belong in the collection of the Maritime Museum of Finland, located in Kotka, which operates under the Finnish National Museum.

The plate monies were in what appeared to be the remains of a chest, alongside a trove of 700 or so coins. The coins were assumed to be in a sack, as there are remnants of cloth around them. Due to the heavy corrosion, many of the plate monies have pieces of wood, cloth and the smaller coins stuck on them, and many of them were attached to each other.



The plate monies were treated shortly after their discovery by soaking them in deionized water for approximately five years. After this they were soaked in a BTA solution for five months, and then coated with multiple coats of Paraloid B-72. However, it was assumed that these treatments were not enough to stabilize the objects and they still contain chloride ions. This assumption is reinforced by the facts that in the previous conservation reports the conservator suggested that the objects are most likely still unstable, and that the objects, especially the smaller coins have shown signs of degradation in storage, evident from the green stains on the paper pouches they have been stored in that have been caused by bronze disease.

Luckily from this experiment's point of view, at least one plate money was stored separately for an unknown reason and was never treated in any way. This means that it does not have the Paraloid B72 coating or the BTA and has heavily degraded while in storage, showing large areas where bronze disease has affected it. Both these factors, while naturally catastrophic to the condition of the object itself, make it the most suitable sample from the ones available for the treatment.

It can be assumed that the Paraloid B-72 coating will interfere with the acetone-trile treatment test and will have to be removed. This will be done by soaking them in acetone for a period of time. Typically, after this a humidity chamber test would have to be performed to observe if the objects still contain chloride ions as assumed, but the objects have already shown signs of corrosion in storage after the prior treatments so it is not necessary in this case. For most of the tests, the smaller coins will be used instead of the plate money, as they already show clear signs of active bronze disease and are much easier to handle and require far less treatment solution per object.

The samples are assumed to be composed of fairly pure copper, as virtually all Swedish plate money and copper coins were made of unalloyed copper as previously mentioned. However, due to the processing methods, they are expected

to include minor impurities. An XRF measurement will be taken of the samples before treatment to determine their accurate composition.

#### 4.1.1 History of plate money in Sweden

Copper plate money was used in Sweden from the year 1644 all the way to the year 1777, although their minting was halted in the 1750s. As Sweden had large natural deposits of copper (producing at the time approximately 2/3rds of Europe's copper) but little gold or silver, it was deemed that Sweden would use the "copper standard" as their method of currency alongside the silver standard, in an attempt to control the value of copper to Sweden's advantage. Naturally the value of copper is lower than that of silver, so instead of a normal sized coin, a "coin" would be a heavy minted copper plate weighing several kilograms, depending on its value. The plate monies had four stamps, one in each corner, and one in the middle denominating its value. They were cumbersome to use and transport, which eventually led to Sweden being the first country in Europe to adopt the use of banknotes, which were used as certificates of value for plate monies deposited in the bank. (Stryker 2016; Swedish Coppers 2016)

#### 4.2 History and excavation of the Länsitonttu finds

Finnish Heritage Agency first heard about the plate monies in Länsitonttu in 1977 when a diver delivered two of them to the agency and told them where they had been found. One of the monies was redeemed for the National Museum's collection, and one was left to the diver.

Much later in 2005 another diver similarly brought two plate monies to the National Museum, which he told were from the same location, and told that they also saw coins at the location.

This find activated the National Museum to make surveys in the area. During the next years multiple dives were conducted by the marine archeological unit and associated civilians to locate the finds, until in 2009 they were located with

a ROV diving robot. The images taken by the ROV showed approximately 15 plate monies and an unknown amount of coins.

Due to the high diving traffic in the area potentially threatening their safety as well as the National Museum's interest to take the finds into their collection, it was decided that they would be excavated.

The excavation took place on 16.6.2009. At the excavation, the finds were relocated using the same ROV diving robot and left at the seabed next to the finds. This way the divers were easily able to locate it following an attached cable. On the first dive the finds and the surrounding area were photographed and documented. The finds, which were two bundles of plate monies and a large number of coins, were in what appeared to be inside the remains of a canvas bag and were surrounded by the remains of a wooden box or a chest. One separate plate money was located roughly two metres from the finds. The diver who located the finds in 2005 recalls that this plate money was located with the others at the time – it is unknown if it had been moved or why.

Then, a second dive was conducted to excavate the finds. The plate monies were loaded by divers into a basket lowered from the boat, and then lifted up. The smaller coins were collected into a box and brought up by the divers. After this the sediment was lightly moved to locate any potential buried objects as well as to determine the size of the wooden box. No further finds were located aside from one coin found slightly off from the dig site.

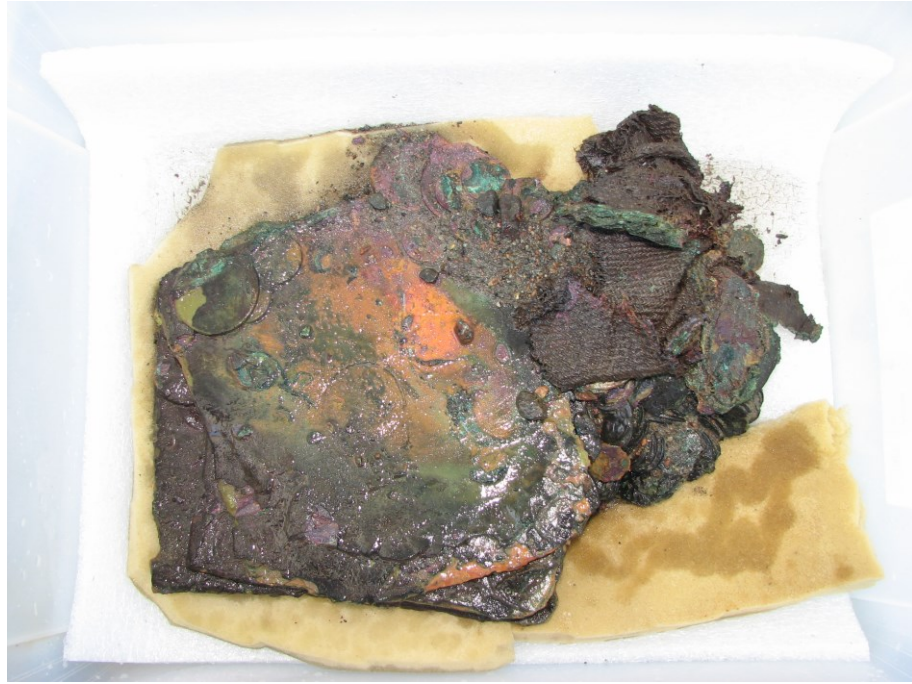


Figure 3: Some of the plate monies and coins as well as wood and fiber fragments stuck together, just after excavation. (Photograph credit: Finnish Heritage Agency)

The original report of the excavation, written in Finnish, can be found in appendix 2.

### 4.3 Prior conservation

After the objects were excavated, they were taken into the Finnish Maritime Museum's (which operates under the National Museum) collection and conserved.

The objects were desalinated by soaking in deionised water. The desalination started on 7.10.2010 and ended on 9.6.2015 (approximately 46 months). During the desalination the plate monies that had been stuck to each other were manually separated.

After the desalination, the objects were stabilized by soaking in a 2:1 BTA / deionised ethanol solution. The process was started on 9.6.2015 and ended on 10.11.2015 (5 months).

After this, the objects were coated with a 5% Paraloid B72 / acetone solution by spraying and brushing.

In the conservation report, the conservator noted that despite the BTA stabilisation treatment, it is possible that the objects are still unstable. At the time of writing, it is apparent that this was correct, as the coins especially have developed major signs of bronze disease after the BTA treatment. This can be seen from the green stains that have formed on the paper pouches the coins have been stored in (Figure 4).

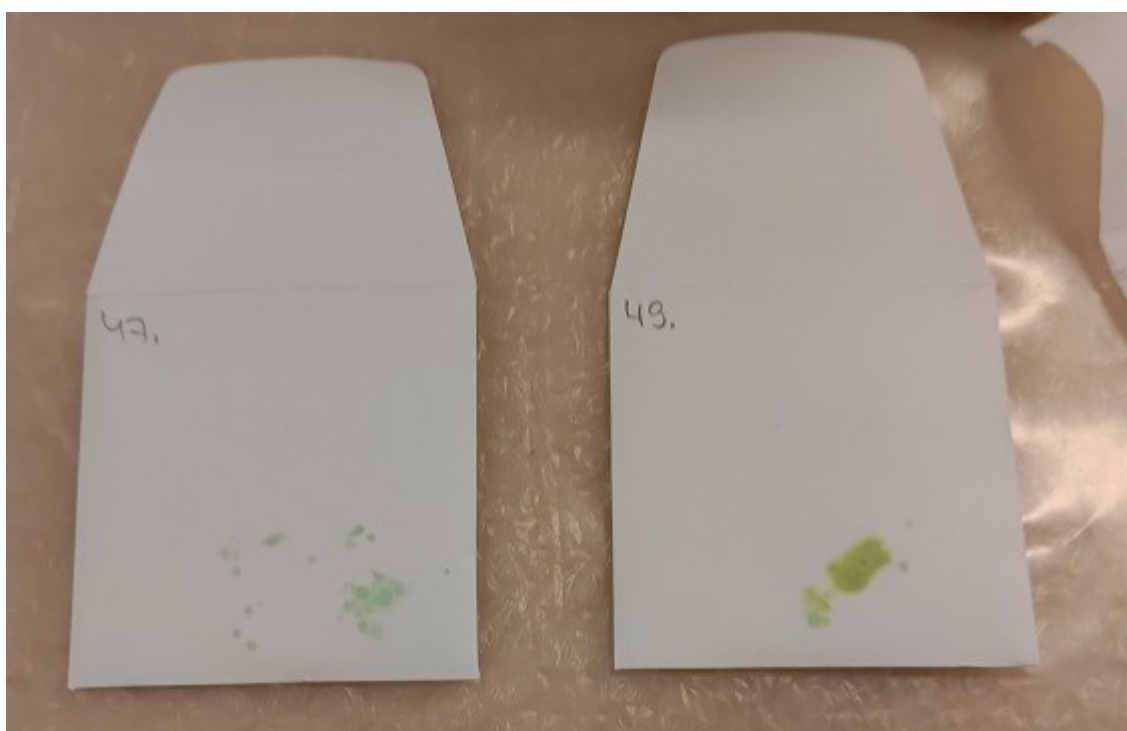


Figure 4: Paper pouches the coins were stored in, stained by discharge from bronze disease.

## 5 Conservation and analysis methods

### 5.1 Acetonitrile gel treatment

The purpose of testing the proposed method is to both gauge the effectiveness of acetonitrile as a treatment method, and to see if it can be used to pinpoint

localized chloride deposits in marine archaeological copper alloy objects in conjunction with agar gel.

The objects that will be treated are immersed in an agar gel that has been mixed with acetonitrile. The acetonitrile in the gel would then extract the chlorides in the object in the same manner as it would as an aqueous solution, but instead of the chlorides being drawn evenly into the solution, they would be drawn out in localized areas of the gel, concentrated around the areas of the objects that have the largest deposits of chlorides. An aluminium sheet would be placed on the gel, and over time the localized chlorides and mobilized copper(I) ions would react with the aluminium and start to corrode it. By looking at the areas where the aluminium sheet starts corroding first and comparing them to the object, it could then be determined which areas of the object contain most chlorides and thus are most likely to start exhibiting symptoms of bronze disease.

The main limitation of this method that is acknowledged before testing is the fact that it's only easily applicable on objects that are mostly two-dimensional, as the aluminium sheet has to be placed perpendicular to the surface of the object so that the chlorides start corroding it evenly. Coins and flat plates of copper are ideal objects for testing this method, which is why they were chosen.

### 5.1.1 Agar gel

Agar, or agarose is a gel derived from some red algae species, such as those of the *Gelidium* or *Gracilaria* families. It has been used in conservation of three-dimensional, often porous, objects as cleaning material. When used in this way, it acts both as a poulticing material as well as a solvent. As it dissolves the materials it does, it acts as a sponge and draws them out and away from the object, holding them within its gel matrix. Typically, agar has been used only as a solvent for water-soluble impurities, but when mixed with different chemicals it could be used for other materials as well. (Scott 2012)

These properties of the gel are what allows the use of the aluminium in this experiment to map out the locations of the chloride concentrations. When using an aqueous solution, the extracted chlorides would be left in the solution and be able to freely move, thus being drawn to the aluminium sheet evenly all around it. With gel, as the chlorides and complexed  $\text{Cu}^+$  ions are stored in the gel matrix and essentially held in place, they will then slowly move towards the aluminium sheet and come into contact with it first in areas they are extracted from in the largest amounts.

Objects can be immersed in agar gel in multiple different ways. The gel can be left to fully coagulate before placing it on the object, after which it can be cut into desired shapes, or it can be poured to surround the object while it's still in a liquid state and be left to coagulate around it (Scott 2012, 73). The second method is not, however, recommended for archaeological or otherwise highly porous objects, or to those that have a fragile surface, since the gel can in its liquid form penetrate fairly deep into the object and cause damage when it is peeled off (Giraud et al 2021, 77). A third method that has not been mentioned, which will be attempted in this research, is to "crush" the gel into a pulp, which can then be flattened against the object. Naturally this method is not suitable for fragile objects, and it will be performed only on the coins which appear to have a sturdy patina layer, and not on the plate monies that appear to at least partially have more fragile parts in their patina layer.

Preparation of agar gel is fairly simple; the powder is just mixed into water, and then the solution is heated close to 100 degrees Celsius. The gel will then solidify as it cools to room temperature. The gel can be prepared on a heating plate or in a microwave; in this test it will be done in a microwave. The acetonitrile, or any other solvent or solution that would be mixed with the gel, can be mixed with it after it is heated but before it cools, so solvent is mixed evenly with the gel as it solidifies.

## 5.2 Testing and treatment plan

Before the treatment tests, naturally the objects need to be thoroughly documented. At least photographs that show the corrosion spots on the objects, and the weight of the objects before the treatment are needed. Although it is assumed that the objects are composed of unalloyed copper, an analysis with a portable XRF scanner will be done to confirm this.

The old Paraloid B-72 coating on the objects applied after the prior treatment will have to be removed, as it most likely would hinder the gel's ability to penetrate the object's surface. This is done by soaking them in acetone for a period of time, following a washing in acetone and then water. The BTA applied to the objects will be mostly removed by this process as well, and according to Ian MacLeod, any remaining residual BTA will be neutralized by the acetonitrile.

All of the gel treatments will follow a similar form. The gel (agar gel with 50% acetonitrile) will be placed on the bottom of a container. The object, which is either a coin or a plate money, will be then placed on the gel. Another layer of gel is then placed on top of it. Finally, the aluminium sheet used to map the chloride and copper concentrations will be placed on top. Each coin will use approximately 100g of gel, but the amount of gel required for the plate monies is naturally much larger. This will be determined later when a suitable container is prepared for them.

The aqueous acetonitrile that will be mixed in with the gel and used for the treatments has to be deoxygenated. Otherwise, the oxygen in the solvent will produce a blackish tenorite (CuO) patina that is undesired. The deoxygenation will be done in an ultrasonic cleaner. The ultrasonic cleaner has a degas option, which will separate gases mixed with liquids placed in it.

First, a single set of three coins will be placed in the gel for one day. The results of this treatment will determine the duration of the future tests. While the optimistic hope is that the objects would be somewhat stabilized in one day, this is



not expected, and most likely they will require longer treatment times. However, the aluminium sheets could have some markings on them just after one day.

### 5.3 Humidity chamber tests

To find out if the objects contain chlorides in the amounts enough to cause further corrosion after treatment, they will be placed in a humidity chamber. After 24 hours of being in a 100 % RH environment, visible signs of greenish white powdery corrosion product caused by bronze disease should appear, if the corrosion is still active. However, they can and will be left to the humidity chamber for up to five days if signs will not appear in the first 24 hours in order to simulate the issues associated with prolonged storage at high relative humidities.

Normally, if using for example artificially corroded objects or objects with no visible signs of bronze disease, the objects should be held in a humidity chamber before treatment as well, to pinpoint the locations where most active corrosion would appear. This, however, is not necessary in this test, as the objects already show major signs of active corrosion that have appeared during being in storage.

### 5.4 Chloride level measurements

Normally, when using aqueous liquid treatment solutions, samples would be taken periodically from the treatment solutions and then the chloride levels of those samples would be measured to see the gradual effectiveness of the treatment. However, this is not possible when treating with a gel. Because of this, the chloride levels of each treatment gel as a whole will be measured after the treatment. (Fontaine et al. 2022)

The commonly used titration measurement methods can be challenging or ineffective to use depending on the solidity of the gel. One method of measuring the chloride levels from a gel has been an XRF scan (Fontaine et al. 2022). However, this would most likely require an XRF scanner with a filter to allow it to detect chlorides to a reliable degree. While such a filter is not available to use for

this study, a measurement will nevertheless be taken with a normal portable XRF scanner to see if any chlorides are detected in the gel. The unreliability of these results will be noted.

The gels can also be attempted to be re-heated, which will liquify them again. After this the titration measurements can be attempted. One possible problem for this is that the heated gel can solidify quickly if just a small sample is used.

A third method proposed by MacLeod is to dissolve the gel in an acid solution, after which the resulting liquid would be suitable for a titration measurement (after sufficient neutralization).

While they don't provide any quantitative data, the corrosion of the aluminium sheets will also provide some information about the chloride levels. Comparing the resulting sheets of each test will at least indicate which of the gels has a higher amount of chlorides than others, as those aluminium sheets would have corroded more.

Finally, it should be noted that as the chlorides are released unevenly into the gel, all of the previously mentioned measurement methods performed on the gel will be unreliable to a degree. While the gels will be attempted to be mixed in order to make the amount of chlorides even all around the gel, the complete success of this can not be validated and is not expected.

The titration sticks used are Hach Quantab Titrators for Chloride Low Range (30-600 ppm) (0.005-0.1% as NaCl) and High Range (300-6000 ppm) (0.005-0.1% as NaCl).

## 5.5 Comparative tests

Multiple comparative tests will be made as well, to provide more ways to compare the results of the acetonitrile gel treatment if the measuring of chlorides becomes an issue.

First, two more sets of three gel treatments will be done. The first will be made using a gel containing sodium sesquicarbonate, and the second will be just the agar gel (equal to a water soaking treatment). The main reason for these tests will be to compare the marks left on the aluminium sheets, observing how fast they appear compared to the acetonitrile and how large they will be. This will already give a visual indication of the acetonitrile gels' effectiveness compared to other solutions.

The second comparative tests will be three sets of three aqueous solutions. The first set will be an acetonitrile solution (50%), the second will be a sesquicarbonate solution (2%) and the third one will be water. The purpose of these tests is to provide ways to compare the chloride levels of these three types of treatment solutions in case the chloride measurements of the gels provide to be difficult. With these tests, as they are aqueous, periodical samples can also be taken to observe the increase rate of the amounts of chlorides in the solutions over a period of time. These tests will also have an aluminium sheet placed in the solution in a similar manner to the gel treatments. This is to both give a way to visualize the difference in the effects of the solutions, and to demonstrate the localized mapping chloride spot mapping capabilities of the gel tests, as it is expected that the chlorides will react with the aluminium sheet evenly in the aqueous solutions instead of as localised spots.

At this stage it is undetermined how long these tests will run; most likely that will be as long as time allows, which will be perhaps a month. The water treatment especially is unlikely to provide any significant results over just a few days, so the longer these tests can be let to run the better.

Furthermore, at least the sodium sesquicarbonate gels and solutions are expected to be fairly alkaline, which will interfere with the titration tests. The pH of these will have to be neutralised in order to obtain any results.

## 5.6 SEM analysis

A selection of the copper coins will be analysed using a scanning electron microscope (SEM) after the treatments. This will be done at the University of Turku.

Both treated and untreated (or water-treated) coins will be scanned from several spots. Main interests would be to look at pitted spots on both a treated and apparently stabilized coin to compare the amounts of chlorides on each. The assumption is that with an apparently stabilized object, the amount of visible chlorides should be much lower than on an object that is still visibly unstable. The SEM analysis will also show any impurities present on the surface of the object and can be used to analyze any irregularities that would appear during or after the treatment (unexpected colour changes on the object's surface or patina, for example).

## 6 Conservation and experiments

### 6.1 Preparation of objects

The sample preparation process began by selecting plate monies and coins from the ones available. The three plate monies with the most signs of bronze disease were selected. While none of them seemed to have visibly active corrosion (green powdery discharge, visible active pitting), they were all heavily corroded. Originally, the intent was to perform the treatment on these three plate monies, but because of time and resource limitations, they were left unused, and in the end just the one previously untreated plate money (Figure 5) described previously was treated.



Figure 5: The previously untreated plate money before treatment, showing heavy signs of bronze disease.

The coins were selected from amongst the largest, with ones that showed the heaviest active corrosion. Most of the larger coins were clearly heavily affected by bronze disease, with visible green powdery residue and pitting (Figure 6).



Figure 6: One of the coins before treatment, with signs of bronze disease.

It was deemed that the Paraloid B-72 layer placed in the prior treatments would most likely interfere with the treatment process too much or block it completely. For this reason, the selected objects were placed in an acetone bath to remove the layer. The BTA left in the objects, however, would be neutralized by the acetonitrile, so it wasn't deemed an issue.

The objects were placed in metal containers with airtight lids, on top of a metal support mesh so that they wouldn't touch the bottom of the container (Figure 7). Then acetone was poured into the container to cover the objects completely. The containers were then sealed, and the objects were soaked for 12 days. It should be noted that the soaking time was that long for scheduling reasons, and a shorter time probably would have sufficed.



Figure 7: The first 12 coins undergoing the Paraloid-B72 removal process.

After 12 days, the objects were removed from the acetone bath, and then rinsed with acetone. After the acetone evaporated, the objects appeared visually to be far less glossy, indicating that at least the surface layer of paraloid-B72 had been dissolved.

## 6.2 X-ray fluorescence measurements

The selected objects were analyzed using a portable X-ray fluorescence (XRF) scanner to determine what metal alloy they are composed of. The assumption was that they were made of unalloyed copper, as was this was typical of Swedish copper alloy coins and especially plate money of that time period.

All coins were analyzed at several spots on both sides of the coin, and the plate monies were analyzed at multiple different spots at both sides.

According to the analysis, all of the objects appeared to be composed of nearly pure copper (Figure 8). Some, but not all of the objects contained small amounts of silica (typically around 1% in the analyzed location, but sometimes up to 10%). As the coins still have soil on them that has been attached to the patina, this is assumed to be from locations where there is a noticeable amount of sand. All other metallic elements that appeared in the analysis (lead, zinc, silver, nickel) had amounts of one to two tenths of a percent or less. These can be attributed to minor impurities in the metal, impurities from the surroundings and the error margin of the measurement.

Nimi	Luokka	Päivämäärä	Kellonaika	Kesto		
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<b>Alkuaine</b>	Fe %	Co %	Ni %	Cu %	Zn %	Ag %
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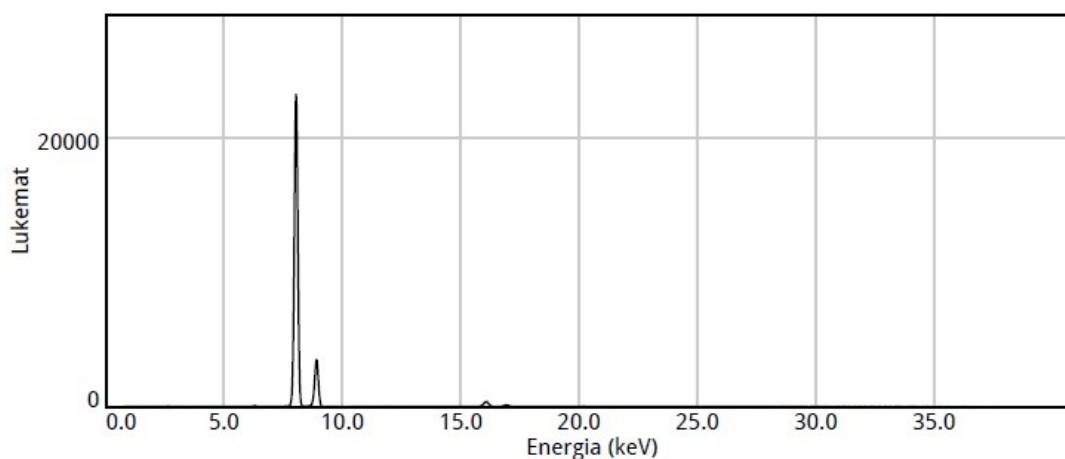


Figure 8: The XRF scan results of one of the coins. Most of the results are almost identical, with some showing small amounts of silica in addition.

The model of the portable scanner is Oxford Instruments Handheld X-MET7500, which was used in the 'Alloy' mode on the objects.

### 6.3 Preparation of treatments

The treatment of the coins was to be done in low glass jars, approximately 9 cm wide and 5 cm tall. During the whole process, the jars, as well as any containers for the chemicals as well as utensils were carefully washed with deionized water



and detergent (Farnos Pesetti Neutradish) to remove any chlorides or other impurities. While this is always required, it is of even more importance in the tests conducted here, as even small amounts of chlorides from an external source can interfere with the process.

The acetonitrile was mixed with deionized water (50%) in a glass bottle, and then deoxygenated in an ultrasonic cleaner (The model being Elma Elmasonic S 30 H) for approximately 10 minutes using the 'degas' mode on the cleaner, until the majority of the air bubbles rising from the solution were no longer visible (Figure 9).



Figure 9: The acetonitrile solution being deoxygenated in the ultrasonic cleaner. Note the rising air bubbles, indicating the gaseous oxygen is being separated from the solution.

The agar gel was then prepared. First a test batch was made; the powder (12g) was mixed with water (300ml) and prepared in a microwave. It was heated in

three 1-minute increments and stirred in between. The stirring ensures that the gel coagulates evenly, preventing gel explosions as evaporating water bubbles escape it. After this, it was placed in a refrigerator. After approximately 1 hour, the gel had coagulated. After this, the batch that would be used for the treatment was prepared in the same way, but instead of placing it in the fridge, the acetonitrile solution was mixed into it (300ml), and it was left to coagulate in room temperature overnight. The next day, the gel had coagulated, and it was heavily stirred to turn it into a slurry that could be used in the treatment.

#### 6.4 First treatment of coins

Approximately 50g of the gel was placed in the bottom of the glass jar, and a coin was placed on top. After this, the coin was covered with another 50g of gel, and an aluminium sheet was placed on top. The aluminium used was 0,03mm thick laboratory-grade aluminium foil sheet, cut into a circle the size of the glass jar. The jar was then placed in an airtight plastic bag and left overnight (Figure 10). This process was done three times, so it was used on three separate coins.

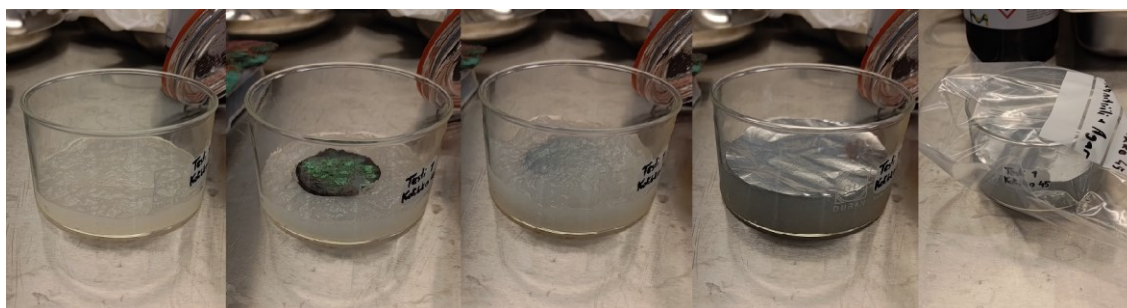


Figure 10: One of the coins being placed in the gel treatment.

After a day, the aluminium had already heavily corroded, indicating at least some amount of success in removing the chlorides (Figure 11). In the corrosion reaction on the aluminium, there is a combination of copper(I) ions cementing on its surface as well as aluminium corrosion induced by the released chloride ions. When the objects were removed from the gel, it was noticed that the patina of the objects had, however, visibly darkened, despite the deoxygenizing of the acetonitrile. While at first it was thought that this suggests that either the

deoxygenation process using the ultrasonic cleaner is not effective enough, or that the amount of oxygen in the solution cannot be lowered enough to prevent the reaction, afterwards it was realized that while the acetonitrile solution was deoxygenated, the water used in the gel was not. This was deemed the most likely reason for the darkening of the patina. For the next tests, the gel would also be deoxygenated.



Figure 11: Corroded aluminium sheet after 1 day.

After removing the objects from the gel, they were washed in hot water to remove the gel residue. Care was taken to ensure that the comparative position of the objects to the aluminium sheet was photographed and documented, so that any new corrosion products that would form on the surface of the object could be compared to the areas where most chlorides were attached to the aluminium. Especially with round coins, this was somewhat difficult and most likely

some errors occurred. With the test coins, this was not deemed a major issue as the actual mapping of the corrosion areas would not be performed on them, and it would be far easier to record the larger square-shaped plate monies' position. However, if this process were performed on coins, a better method for recording the relative position of the aluminium sheet and the coin should be devised.

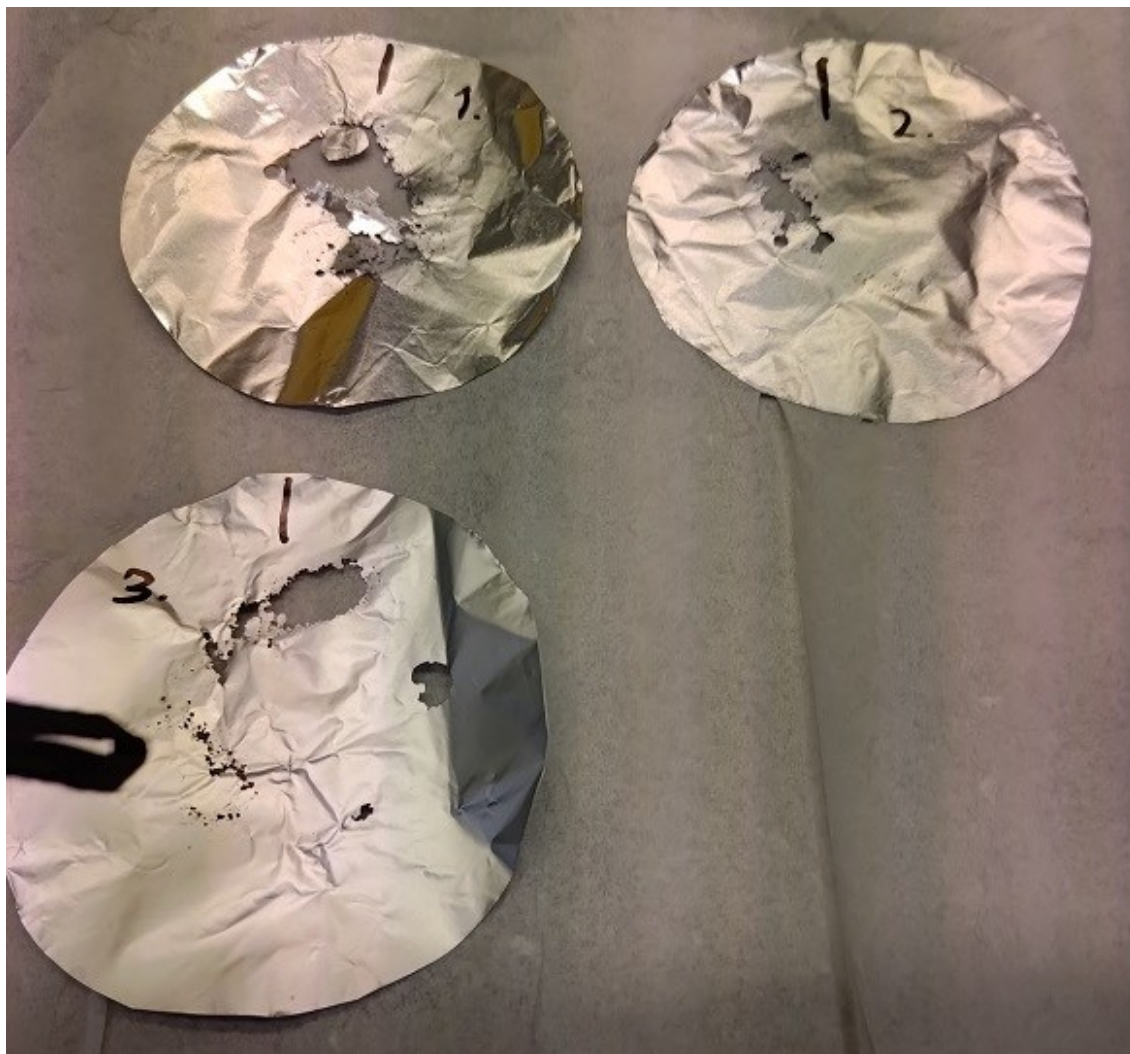


Figure 12: The aluminium sheets of the first three sets.

After this, the objects were placed in a humidity chamber to test the effectiveness of the treatment. After four days, the objects in the humidity chamber showed major signs of new pitting and green powdery discharge, indicating that the treatment time of one day is not enough (Figure 13). Although there was

never a full assumption that a one-day treatment could remove all the chlorides from an object and more time would most likely be required in any case, one reason for these results is the condition of the samples. While they on the surface display heavy signs of corrosion, the metal core of the objects is still fairly solid. If the samples would have been thoroughly corroded, the 'sponge-like' structure the corrosion would have left behind would have allowed the acetonitrile solution to penetrate to the object more effectively, thus speeding up the treatment time.



Figure 13: The first three coins after the humidity chamber, displaying fresh signs of bronze disease.

## 6.5 Second treatment of coins

While originally the plan was to gradually increase the treatment times until results were visible, the results of the first test indicated that the objects would most likely require more treatment time than just a few days. For this reason, it was decided that the next treatment would last for 9 days. If after this the objects would show no further signs of bronze disease after the humidity chamber test, a shorter treatment could be done in order to determine the required time more accurately, but if even 9 days was not enough, skipping the shorter treatments would save a lot of time from the project's already limited schedule.

The next test was prepared in the same manner as the first one, and three new coins were placed into the acetonitrile gel.

After nine days, the coins were removed from the gel and placed into a humidity chamber in the same manner as the previous ones. The aluminium sheets on these tests were thoroughly covered in holes and corrosion marks (Figure 14), one to the point that it had almost disintegrated into fragments. This result means that for longer treatment times it would most likely be better to use thicker aluminium sheets or multiple of them stacked on top of one another. On the other hand, however, signs of corrosion can be observed earlier with the thinner sheet without the need to remove it (which would risk changing its position).



Figure 14: Aluminium sheet of one of the coins from the second batch.

The coins had multiple light green stains on them after the treatment and the washing. It was observed that at the later stages of the treatment the gel had formed into an opaque light green slurry, assumedly from dissolved corrosion compounds. These marks were at this point assumed to most likely be just stains left behind by that gel that the washing didn't manage to remove. The stains could most likely be removed mechanically if needed. However, the colour of the stains was very similar to the colour of any signs of bronze disease that could form when the objects are in the humidity chamber, which means any changes will be harder to spot. They can, however, be compared to photos, so this wasn't deemed a major problem.

The objects were placed in a humidity chamber. After four days, two of the three coins showed no signs of any new bronze disease formations when compared to pictures taken before. This indicates that the 9 days of acetonitrile gel treatment removed enough chlorides to at least somewhat stabilize the objects.

However, on the third coin, one area had started to form a new green powdery spot (Figure 15).



Figure 15: The three coins from the second batch, before and after being in the humidity chamber. On closer examination, the area circled in red that was previously covered by the smaller coin developed fresh signs of bronze disease.

At this point, it was realized that perhaps the short washing in hot water after taking the objects out of the gel wasn't sufficient, and the residual chlorides could affect the humidity chamber tests. For this reason, the third coin that showed new signs of corrosion was washed by placing it in a vessel with running deionized water for two hours. This washing regime should remove most of



the remaining gel and chlorides from the object. After this, the corroded area of the object was mechanically cleaned, and it was placed again in the humidity chamber. However, after a few days it again showed new signs of corrosion, indicating insufficient washing was not the issue, at least in this case (Figure 16).



Figure 16: The third coin after being mechanically cleaned, before and after its second round in the humidity chamber. Note the new bronze disease symptoms in the mechanically cleaned area circled in red.

It should be noted that the third coin had one smaller coin originally attached to the area the new bronze disease appeared. During the treatment, however, the two coins had separated from each other. While at this time it wasn't realized, this most likely was the reason for the treatment not stabilizing the object as well, as the gel wasn't able to penetrate the area between the two coins until they were separated.

Despite the longer treatment time, this time the patina of the coins hadn't darkened. For this batch, as mentioned previously, the water used in making the agar gel was also deoxygenated. This apparently was enough to reduce the amount of oxygen in the treatment gel to the level that it didn't affect the colour of the patina.

## 6.6 Third treatment of coins

A third test was made with three coins to determine if an even longer treatment would be enough to completely prevent the appearance of new bronze disease symptoms. The treatment was performed in an identical manner to the previous one, but the treatment time was increased to 20 days.

After 20 days, the aluminium on the gel had almost completely corroded away on all three tests (Figure 17).

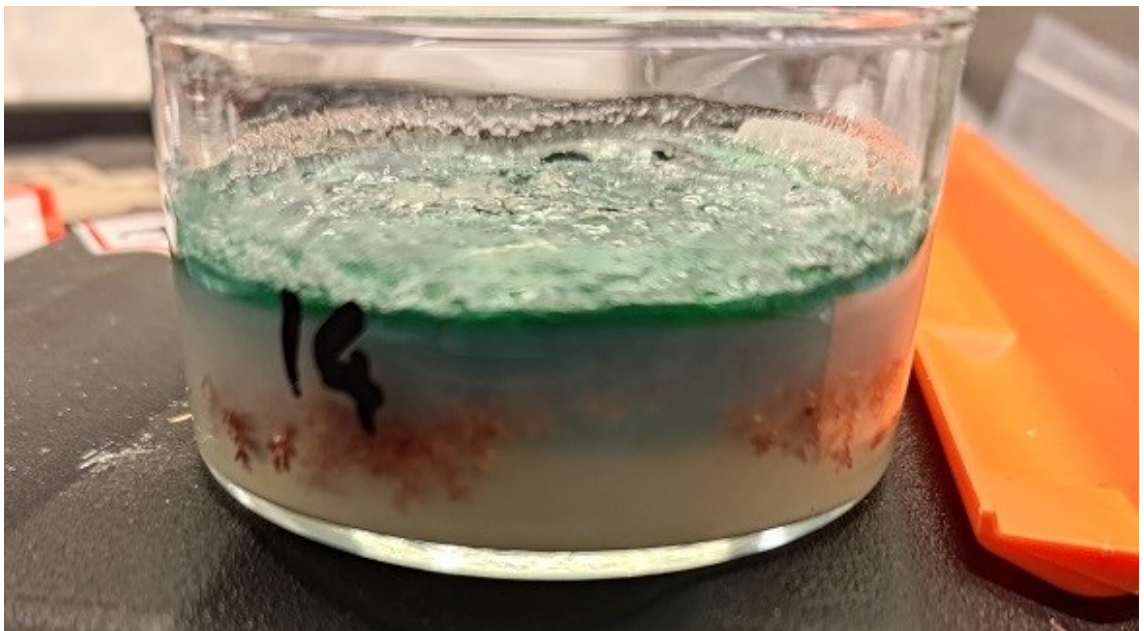


Figure 17: One of the coins from the third batch in the gel after 20 days. The aluminium on top of the gel has completely corroded away.

Again, after washing and the humidity chamber, two of the three coins had apparently stabilized and showed no new signs of bronze disease, but the third one was still clearly and heavily unstable (Figure 18). As the third coin again had smaller coins attached to it, this time it was realized that the reason for this most likely were the inaccessible chloride deposits between the coins.



Figure 18: The third coin from the third batch. The two smaller attached coins, as well as a piece of crusted patina detached during the treatment, revealing large actively corroding areas underneath them.

After the coins were taken out of the humidity chamber and left to dry, it was noticed that they developed a white-coloured coating on some areas of the surface (Figure 19). A similar white coating had appeared on some parts of the previously treated coins as well. Originally this was suspected to be dried out residual gel, but later the SEM analysis revealed this to be aluminium oxide in addition. According to Ian MacLeod, as the long treatment time caused the aluminium sheet to completely corrode away, aluminium was then able to migrate to the surface of the copper in larger amounts due to the electrochemical reactions similar to that when the copper chlorides migrate to the surface of the aluminium, as both the copper and the aluminium will have both anodic and cathodic areas. It is expected that this aluminum oxide coating is removable, which will be discussed in more detail later in the thesis.



Figure 19: White aluminium oxide coating on the coins.

## 6.7 Comparative gel tests

Two sets of three comparative tests were set up as well. For one, the agar gel was prepared using a sodium sesquicarbonate solution (2%), and for the second, just water. These two tests would be left untouched for a longer period of time, as it is expected that their effect will be much slower than that of the acetonitrile based on prior research. The aluminium on top of these test jars is inspected periodically for any signs of chlorides.

After one day of the comparative tests, there was a small visible mark left on the aluminium of one of the sesquicarbonate tests. The rest of the tests had very small dots, which possibly were also caused by the chlorides. With the acetonitrile tests, after this amount of time the aluminium sheets were already heavily corroded to the point of having multiple holes in them. This already suggests that acetonitrile is far more efficient in removing chlorides.

The tests were left to run for a total of 27 days (Figure 20), after which the coins were taken out of the gel and then washed and placed into a humidity chamber in the same manner as the coins previously treated with acetonitrile gel.



Figure 20: Comparative gel tests after 27 days. Most of the aluminum is in pristine condition with just small, darkened marks visible.

On all the six tests, the gel had been coloured slightly green, but not nearly as pronounced as the acetonitrile gel had. While these gels were still fairly translucent after 27 days, the acetonitrile gel that was used for 20 days had turned into a fully opaque green slurry. This is another sign of the short-term effectiveness of acetonitrile when compared to water or sesquicarbonate. The aluminium sheets of all the tests showed only minor marks at most on the top, and some of their undersides had been coloured slightly brown.

After the objects were removed from the humidity chamber, the coins treated with the water gel appeared to not have been stabilized at all, as all three had developed major signs of bronze disease. The coins treated with sesquicarbonate had fared a little better, but still had developed small spots of new bronze disease.

## 6.8 Comparative solution tests

Since it was anticipated that measuring the chloride levels from the gel treatments would be challenging, and because periodical samples couldn't be taken from the gels, three tests were performed using aqueous solutions to get more accurate data about acetonitrile's effectiveness in removing chlorides. Three sets of three coins were prepared and placed in containers with a solution. The three solutions used were water, sodium sesquicarbonate (2%) and acetonitrile (50%). A sheet of aluminium was placed in each container as well, to give a visual indicator of the effectiveness of the process (Figure 21).

Samples of the solutions were taken periodically. The chloride levels of these samples were then measured using chloride titration indicators to see the speed and effectiveness of each solution in removing chlorides. The tests ran for 20 days, after which the coins were removed from the solutions and placed in a humidity chamber.

It should be noted that water and sesquicarbonate typically require much longer treatment times to have a significant effect on an object's chloride amounts, so they were not expected to stabilize the objects at any amount in this time and were just used as a comparison to the acetonitrile.



Figure 21: One of the coins after the aqueous acetonitrile test. Note the even distribution of the corrosion and copper concentrations on the aluminium, compared to the localized spots with the gel treatment.

## 6.9 Treatment of the plate money

Finally, it was decided that the single plate money that was originally left untreated would be treated with the acetonitrile gel. Originally the plan was to treat three separate plate monies that were prepared beforehand, but due to their large size and the time and effort required, the schedule only allowed for the treatment of one. Thus, the lone previously untreated plate money was chosen.

The plate money was dry-cleaned with a brush (Figure 22). The lack of treatment had left it in a sorry state; the plate money had multiple major areas with large pitting and greenish powdery residue, as well as many larger pieces of copper that had started to flake off.



Figure 22: The plate money after careful dry-cleaning.

After dry-cleaning, the treatment container was prepared. A plastic container was lined with a plastic sheet, and the bottom was lined with aluminium sheets. While the coins only had the aluminium on the top side, for this treatment the aluminium was decided to be put on both sides of the object, as the areas containing concentrated chlorides would most likely be different depending on the side of the object. Plastic foam supports were then placed on the bottom. These would hold the plate money separate from the underlying aluminium in case the gel wouldn't be solid enough to support it (Figure 23).





Figure 23: The container for the treatment of the plate money, with aluminium sheets on the bottom. The gel is then poured in the container and the supporting foam pieces are placed.

The gel was then prepared and mixed with the acetonitrile. Although the method was previously mentioned not recommended for archaeological objects with fragile or porous surfaces, the gel was nevertheless poured on the bottom in a partially unsolidified state so that it could spread evenly. Approximately a one cm thick layer was made. The plate money was then placed on the supports, and another 1cm layer of gel was poured on top. Finally, the second aluminium sheet was placed on top of the gel (Figure 24).



Figure 24: The plate money is placed on the gel and the supports. Finally, gel is poured on top and covered with aluminium sheets.

The plate money was left in the gel treatment for 16 days in total. After the first day, corrosion marks already started to form on the aluminium. Eventually the aluminium was almost completely corroded away (Figure 25).



Figure 25: The aluminium sheets after 1 day, 7 days and 16 days of treatment respectively.

After the 16 days had passed, the plate money was removed from the gel (Figure 26). First, the small remaining pieces of aluminium were picked off from the top. Then a plastic spoon was used to scoop off the gel from the top. After this, the money was carefully lifted. The bottom layer of the gel had mostly stuck to the plate money, so this too was scooped off with a spoon.



Figure 26: The gel after treatment. The top layer of the gel had turned green-coloured (left) while the bottom layer had turned brown and remained attached to the plate money (right).

While the top layer of the gel had turned into a green slurry, the bottom layer had instead been coloured brownish-orange, which is consistent with formation of cuprite ( $\text{Cu}_2\text{O}$ ) as the copper(I) chlorides underwent hydrolysis. The differences in the gel in the top and bottom layer can possibly be attributed to different levels of oxygen, as oxygen wouldn't be able to effectively reach the bottom layer.

In an attempt to remove as much of the gel as possible, the plate money was then gently rinsed with hot water and cleaned with a soft brush. The surface of the patina had been left very fragile, so this had to be done carefully. Despite this cleaning, residual gel was still left on the plate money. Finally, it was left in a vessel with running deionized water for two hours, similarly to the coins previously.

Like the third set of coins treated with the acetonitrile gel, the plate money also had developed a white-coloured residue that became visible when it dried (Figure 27). As with the coins, the assumption was at this point that it was dried

residual gel that had been left on the surface of the object despite the washing, but later the SEM analysis revealed it to be aluminium oxide.

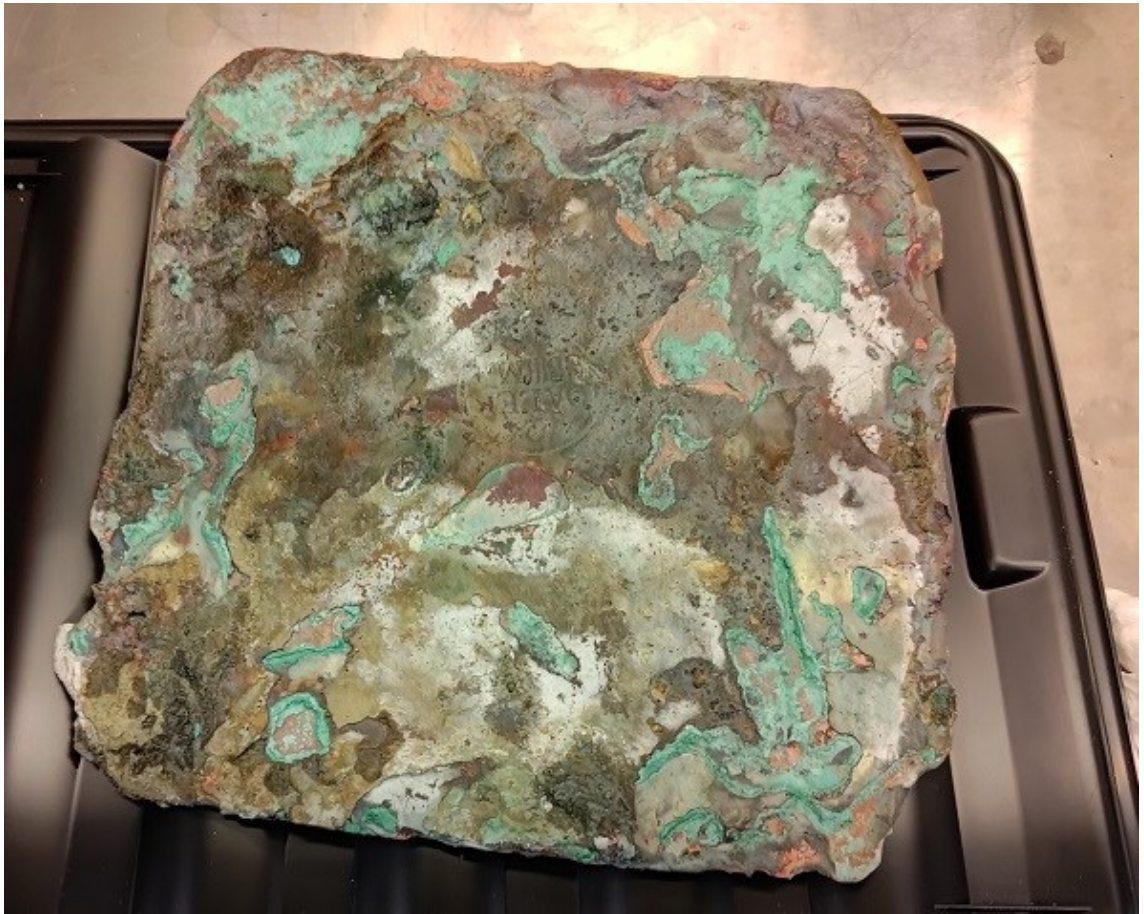


Figure 27: After drying, some areas of the plate money turned white-coloured due to the aluminium oxide.

Before being placed into the humidity chamber, a small, corroded area was mechanically cleaned of any corrosion products to make it easier to notice any new corrosion forming in the area. After 5 days of being in the humidity chamber, the object appeared not to have formed any major new signs of bronze disease. The area that was mechanically cleaned hadn't developed any new signs of bronze disease (Figure 28).



Figure 28: The mechanically cleaned spot before the cleaning, after the cleaning and after being in the humidity chamber for 5 days.

However, as the corrosion products in the large pitted areas were not removed, determining the formation of any new bronze disease was difficult. For this reason, a larger area was mechanically cleaned, and the object was placed into the humidity chamber again.

After the second time in the humidity chamber, the results were mixed. While the mechanically cleaned areas hadn't developed any new corrosion (Figure 29), the areas surrounding them that were now exposed after the mechanical cleaning had. Apparently, chloride deposits were still left under the patina surface which the gel wasn't able to reach, and now that the surrounding areas were cleaned of corrosion products, the humidity was able to reach these chloride deposits and they started to corrode. This process caused the patina surrounding the cleaned area to become very brittle as well, as the layer containing chlorides under it had started to increase in volume due to the active corrosion and the formation of copper chloride.



Figure 29: The second, larger mechanically cleaned area before the cleaning, after the cleaning and after being in the humidity chamber. No new visible new bronze disease appeared in the area itself, but the patina especially in the red circled area had become very brittle.

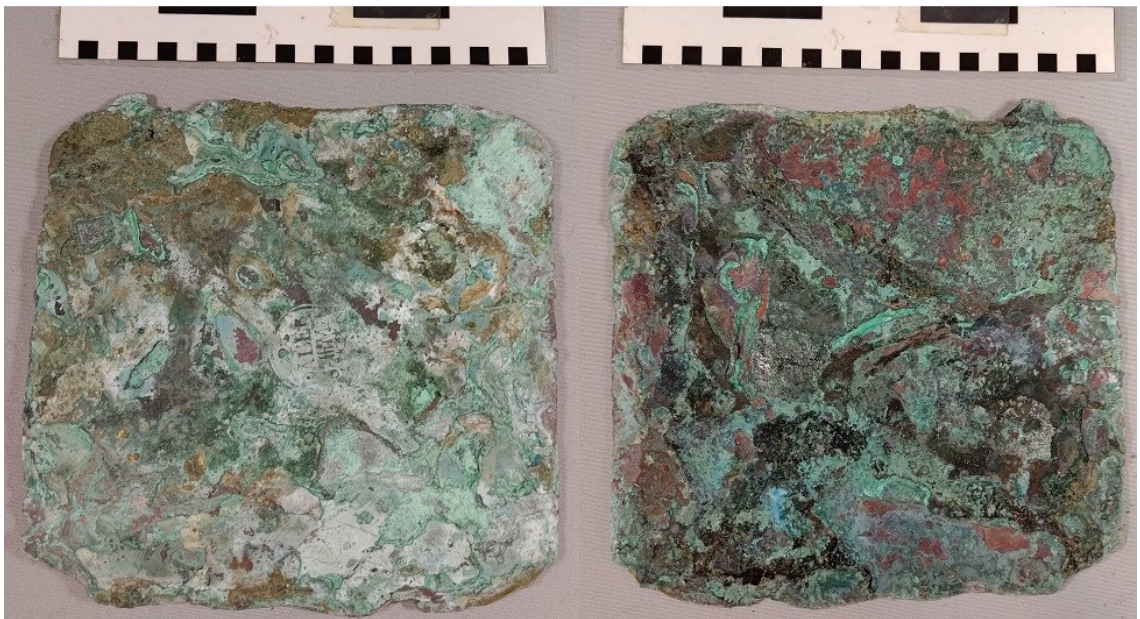


Figure 30: The final appearance of the plate money (both sides).

### 6.10 SEM analysis

After the treatments, five coins were selected to be analyzed with a SEM (scanning electron microscope). First, two coins that were treated in acetonitrile gel for nine days were selected. One of them was cleaned of any residual gel and corrosion products mechanically, while the second was the one that still had

active bronze disease after the treatment. Then two coins that were treated with the acetonitrile gel for 20 days were selected. Both of these coins had formed the unknown, white-coloured layer on the surface, the composition of which would be determined by the SEM. One of these coins was boiled in water beforehand to remove as much of the residual gel as possible, and to see if this would remove the white-coloured layer (which it didn't). The fifth coin was one that was treated in the comparative tests with the gel containing just water, and still had active bronze disease.

Due to time limitations, only three of these samples were analyzed. Analysis was taken from pitted spots of both a coin that was deemed stabilized as well as one of the unstable coins, the metal surface of the coins, and the white-coloured layer. Furthermore, in preparation for a potential future experiment briefly described later, the coins were analyzed with a higher power output to see if any of them had iron impurities in them.

## **7 Results and discussion**

### **7.1 Chloride measurements**

While it is apparent that the acetonitrile gel treatments, especially those that lasted for longer, removed large amounts of chlorides compared to the water and sesquicarbonate treatments, determining the exact amounts (i.e. quantification of the chloride extraction processes) proved challenging, and the results were left partially inconclusive.

While the titration measurement sticks did provide results with some of the gels, particularly those that had been left in a slightly more liquid form, they didn't provide any results at all with the other gels. The aqueous solutions, however, did provide results that appear to be accurate.

While an XRF scan was performed on the gels, unfortunately it wasn't accurate enough to detect chloride without the specific filter required, which was not

available for this study. This most likely would have been the most accurate method if there would have been access to such a filter during the study. However, it should be noted that a scan with a portable XRF unit still doesn't provide definitive quantitative data and only reports on the surfaces that are presented to the sensing head, not the whole object.

Nevertheless, while the exact rates are not determined, it's clear that acetonitrile is far more effective in removing chlorides with short treatments than water or sesquicarbonate. This can be visually determined from the aluminium sheets used in the treatments. Even with the first treatment that lasted just for 24 hours, the aluminium had visibly started to corrode from because of the copper chlorides, whereas in both the aqueous and gel treatments involving sesquicarbonate and water, the aluminium sheets were left with just a few minor marks even after 27 days of treatment.

Table 1: Chloride levels of the gel tests

Test batch	Treatment time	Coin	Chloride (PPM)
First acetonitrile gel	1 day	1	1140
First acetonitrile gel	1 day	2	1234
First acetonitrile gel	1 day	3	972
Second acetonitrile gel	9 days	1	Inconclusive
Second acetonitrile gel	9 days	2	Inconclusive
Second acetonitrile gel	9 days	3	Inconclusive
Third acetonitrile gel	20 days	1	431
Third acetonitrile gel	20 days	2	Inconclusive
Third acetonitrile gel	20 days	3	1053
Plate money	16 days		5159
Water gel	27 days	1	Inconclusive
Water gel	27 days	2	Inconclusive
Water gel	27 days	3	Inconclusive
Sesquicarbonate gel	27 days	1	Inconclusive
Sesquicarbonate gel	27 days	2	Inconclusive
Sesquicarbonate gel	27 days	3	Inconclusive



Table 2: Chloride levels of the aqueous solution tests

Test batch	Coin	Sample 1 Cl ppm	Sample 2 Cl ppm	Sample 3 Cl ppm	Sample 4 Cl ppm
Water	1	<30	30	72	150
Water	2	<30	<30	<30	>30
Water	3	<30	<30	<30	>30
Sesquicarbonate	1	<30	<30	<30	>30
Sesquicarbonate	2	<30	<30	<30	>30
Sesquicarbonate	3	<30	<30	<30	>30
Acetonitrile	1	607	>607	>607	>607
Acetonitrile	2	349	>607	>607	>607
Acetonitrile	3	81	81	91	91

Note the low results of the third acetonitrile solution when compared to the two others. During the process it was noticed that the aluminium in the third container didn't have any corrosion or copper concretions (seen in figure 20) in it like the two others. As the solution in the third container was mixed separately, it can be assumed that a careless mistake happened during this process, and either far too little acetonitrile ended up in the solution, or that in place of acetonitrile, water was mixed in instead.

## 7.2 SEM analysis results

Due to time limitations, only three coins out of the five selected were analyzed. The most significant results are detailed here. Elemental spectrum graphs for the circled locations in the pictures can be found in Appendix 1.

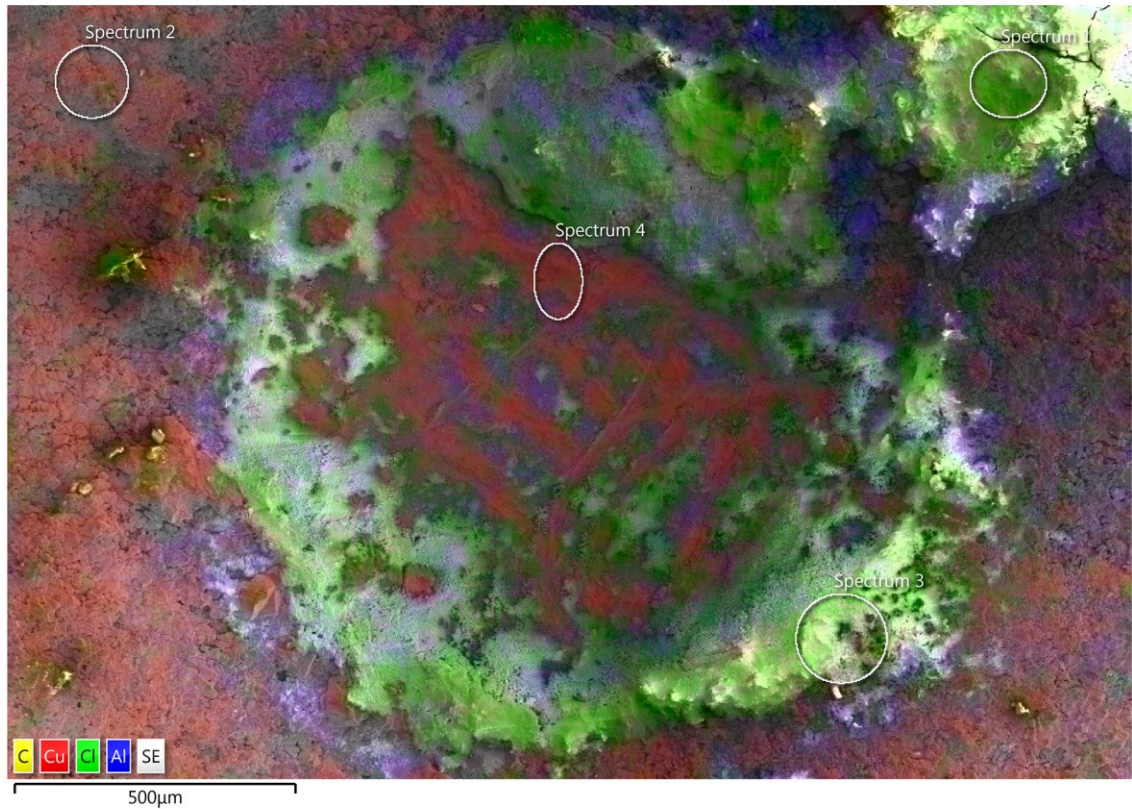


Figure 31: Small bronze disease pit on the coin that was in the gel treatment for 9 days and was mechanically cleaned (57).

First, a coin that was in the gel treatment for 9 days and was then mechanically cleaned afterwards was analyzed. In figure 31, a small pit caused by bronze disease on the coin can be seen.

The areas with remnants of the copper chlorides created by bronze disease are highlighted in green. These appear to be mostly concentrated around the pit, as expected, but there's also a small deposit next to the pit (Spectrum 1). The metal surface (Spectrum 2) and the cleaned bottom of the pit (Spectrum 4) have no significant amounts of chloride. It should be noted that there appear to be remnants of aluminum from the corroded sheets on this coin as well (highlighted in blue), but not in the same amounts as on the coins that were treated for 20 days.

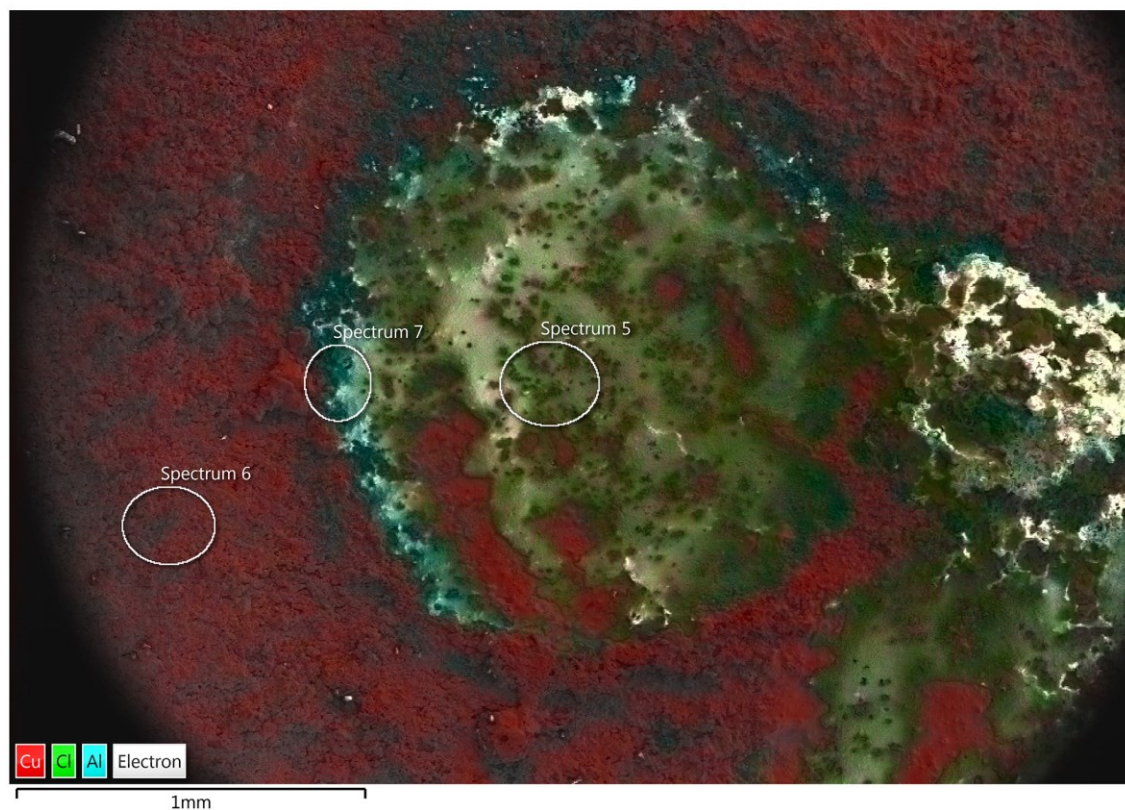


Figure 32: Another pit on the same coin (57)

Figure 32 displays a second pit on the same coin that had not been cleaned as well. While the chloride levels in the matching areas are close to those on figure 30, the bottom of the pit is mostly covered in copper chlorides.

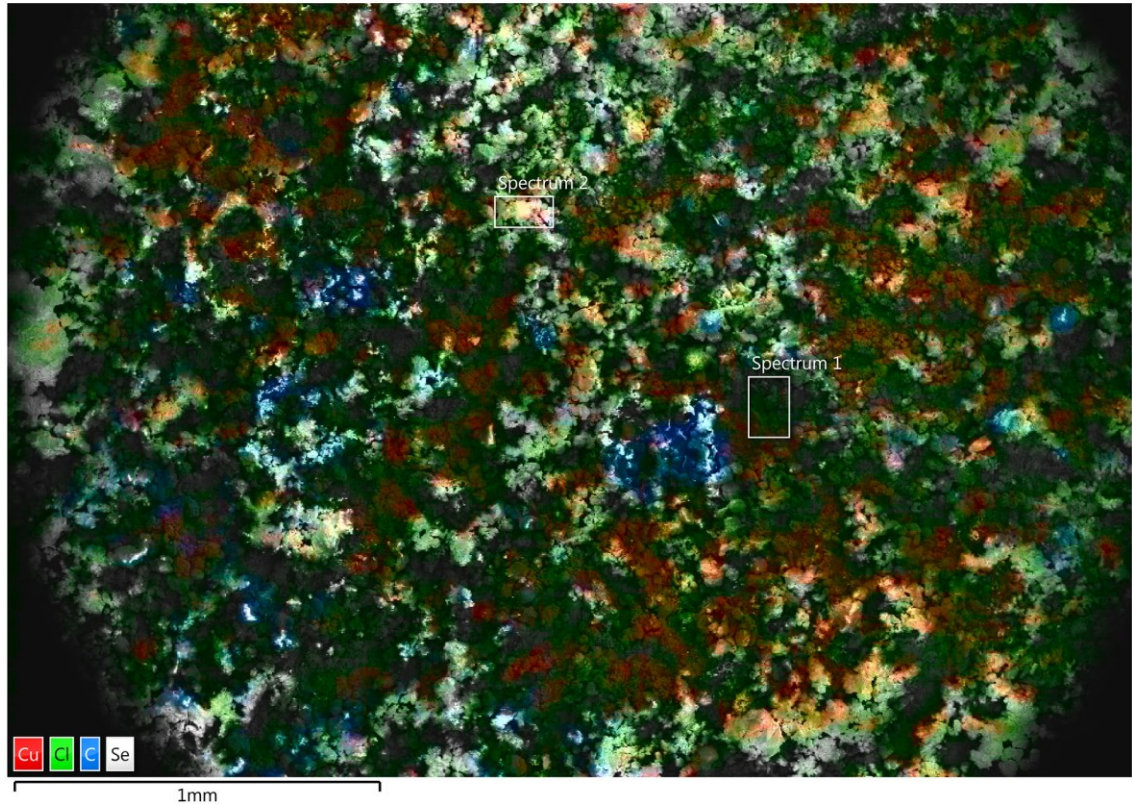


Figure 33: Area with active bronze disease in a coin treated with water (63)

Next a coin that was used in one of the comparative tests and was treated with just water gel was analyzed. Figure 33 displays a section of a larger area actively undergoing corrosion. While the chloride levels in the selected areas (Spectrums 1 and 2 in figure 33) are close to the same levels as the copper chloride concentrations that can be seen in figures 31 and 32, this mostly tells us only that the concentrations are of roughly the same thickness. Visually from these images it can, however, be determined that the condition the area displayed in figure 33 is vastly different to that of the previous ones, as copper can be barely seen at all under the chloride layer.

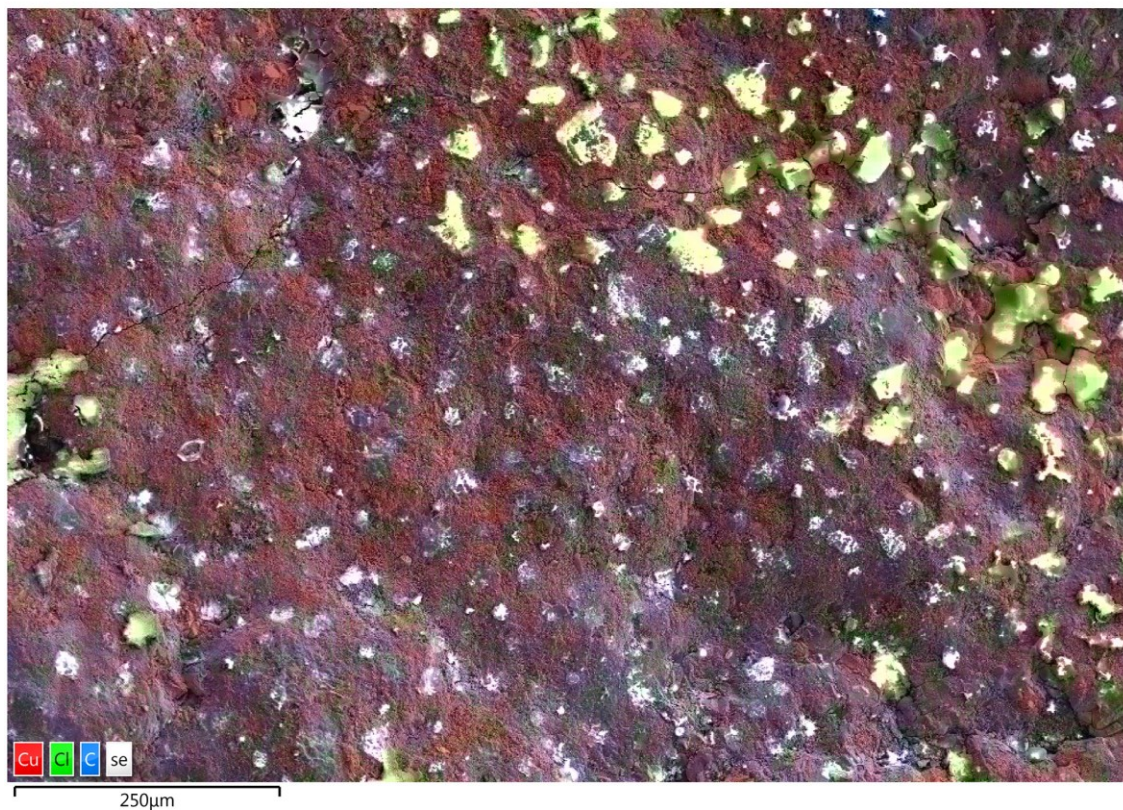


Figure 34: Metal surface on the same coin treated with water, apparently displaying large amounts of chloride deposits.

Figure 34 depicts a section of the metal surface on the same coin. This area, as many others on this coin, showed large amounts of small concentrations of chloride (shown in yellowish green). These appear to be partially inside the metallic surface, suggesting that they are not remnants of the gel. This is another indicator that the treatment with water was not effective enough to affect chloride concentrations like these.

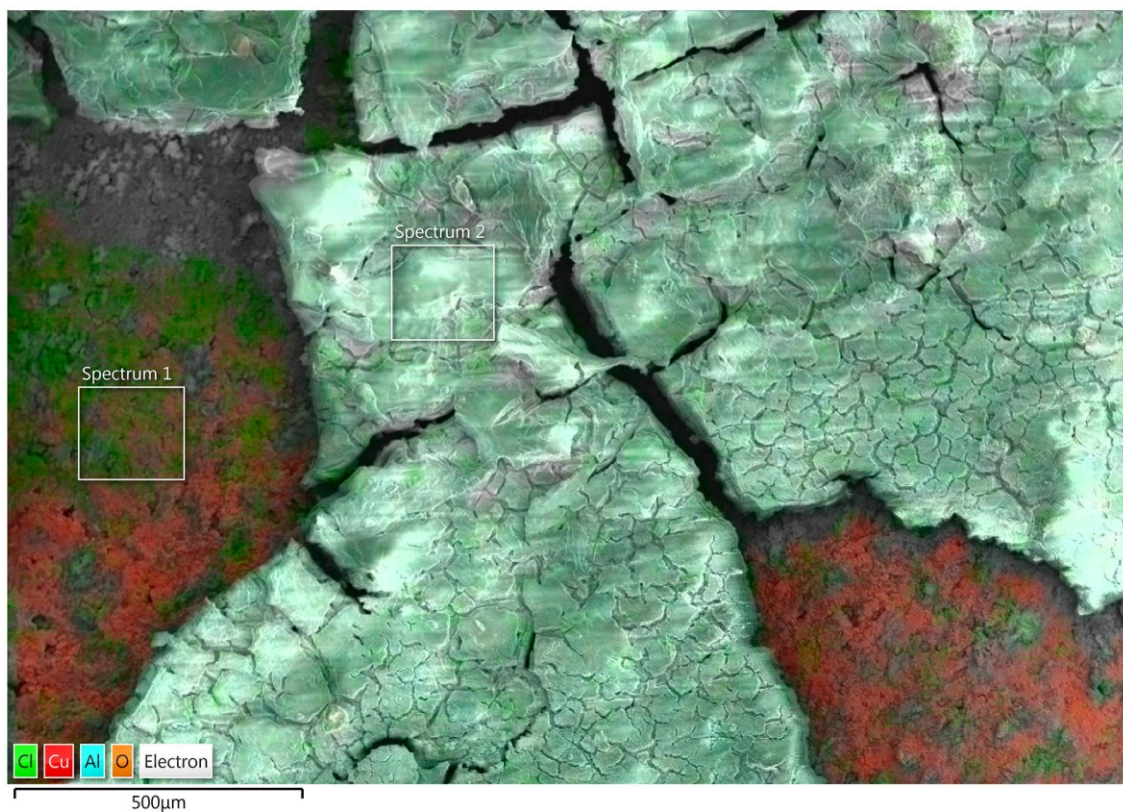


Figure 35: Aluminium oxide on the surface of one of the coins that was treated in acetonitrile gel for 20 days (68). The minor and major cracks are typical of a matrix that was once a gel-like product that has undergone dehydration.

Finally, a coin that was treated in the acetonitrile gel for 20 days was analyzed. The main interest point was the white-coloured coating that developed on the coin, the composition of which was unknown prior to this analysis (although it was suspected to be the dried-out residual gel). One such area is displayed in figure 35.

The white-coloured area (spectrum 2 in figure 35) appears to be composed mostly of oxygen, aluminium and chloride. In addition, Ian MacLeod pointed out that the crackled texture is typical of a gel that has undergone dehydration. Thus, it is fairly apparent that the white-coloured coating is a mixture of aluminium oxide from the corroded aluminum sheet and dried-out gel containing chlorides extracted from the object.

It should be noted that this coin was boiled previously in an attempt to remove the residual gel; apparently even this was not sufficient enough to remove the thin aluminum-infused layer encrusted on the surface.

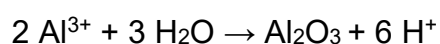
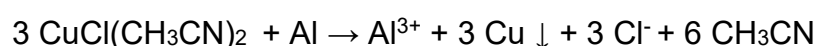
The SEM-system used was Thermo Scientificin Apreo S -model with a field emission based electron source. The EDS-detector was Oxford Ultim Max, with a SDD (Silicon Drift Detector)-detector.

### 7.3 Aluminium and mapping

Using the aluminium sheets in the acetonitrile gel appears to be a fairly effective method to pinpoint areas on copper objects that have larger amounts of chlorides. On all the acetonitrile gel treatments, the aluminium sheet started to visibly corrode after 24 hours, and the spots where the corrosion started to first form appeared to correlate with the areas on the objects that already had visible bronze disease on them.

However, using the aluminium sheets with the treatments did cause some problems. If the treatments run longer, the sheets corrode too much, leaving behind no recognizable spots. In the treatments that ran the longest, the sheets had completely corroded away, and had mixed with the gel. This had resulted in the objects developing a partial white-coloured aluminium oxide coating.

However, it should be remembered that the main reason for the presence of aluminium in the treatment and the reaction of the metal with solubilised CuCl was only being used as an indication of the effectiveness of extraction of nan-tokite and it is not envisaged that proper treatments of copper alloy objects will be done in the presence of aluminium sheets. The chemical reactions associated with the formation of the corrosion reactions are shown below.



Thus, the dissolution of the aluminium foils is due to the cementation reaction of copper on aluminium (Power & Ritchie 1976). The large difference in the standard reduction potentials for aluminium and copper provide the driving force for this type of specialised corrosion reaction.

Trace amounts of aluminium was also left even on the objects that didn't visibly show the white aluminium oxide and were treated for shorter times. The coins that were in treatment for 9 days had noticeable amounts of aluminium on their surface according to the SEM analysis, even though their colour hadn't changed. While the aluminium is most likely removable (Ian MacLeod proposed using EDTA to remove it, but the project ran out of time before this could be attempted), this nevertheless creates an unnecessary step in the process, creating both more work and potentially causing damage to the object.

For these reasons, if the method is used to map the object's chloride amounts, the treatment should be performed for just a few days. This time should be short enough so that the aluminium sheets would indicate clearly the most corroded areas. After this, the object should either be removed from the gel and treated with a different method, or if the gel treatment should run for longer the aluminium sheets should be removed. This would minimize the amount of aluminium that is released into the gel and on the object.

#### 7.4 Effectiveness of the gel

When observing the results of the treatments, it became apparent that the gel is too viscous to be able to penetrate everywhere on the object. In the case of the coins where multiple smaller coins were attached on the object, the space left between them had been left mostly unaffected by the acetonitrile. When these were then placed into the humidity chamber, the humidity was able to penetrate between the coins, accelerating the formation of bronze disease. The crystallization of chlorides then forced the coins apart, exposing the area completely and accelerated the process even further.



On the plate money, a similar effect could be observed after it was placed into the humidity chamber the second time after the mechanical removal of the corrosion products in an area. The area between the surface patina layer and the metallic copper hadn't been affected by the treatment at least to the same extent as the exposed corroded areas, and now that the surrounding corrosion was removed, humidity was able to penetrate in between the layers and accelerate the corrosion, causing it to break the surface patina in some of the areas surrounding the cleaned spot.

On the other hand, coins that didn't have similar areas where there was a significant amount of chlorides between the patina and the metallic copper, or that didn't have smaller coins attached, the treatment seemed to have stabilized all the areas that were previously affected by bronze disease.

## 7.5 Washing the gel

Washing the gel away from the object proved to be more difficult than expected. Despite multiple different methods of washing that were attempted, residual gel still remained on most of the objects. Attempts were made to wash the objects in both cold and hot water, keep them under running cold water for several hours, gently brushing under hot water and even boiling. Only the boiling attempt seemed to remove the visible gel from the one object it was attempted on, but several others, including the plate money, were left with residual gel, and while most of it was mechanically removed, small amounts still remained that eventually dried out on the object.

While boiling for approximately 30 minutes appeared to work on one of the coins, the SEM analysis revealed that the white-coloured coating developed on the coin most likely was at least partially composed of the remnants of the gel, indicating that even this was not sufficient in removing all of it. Furthermore, it was performed on a coin with no apparently fragile patina. It obviously is not a suitable method of washing for objects with fragile surfaces. An idea that could perhaps have worked would have been to keep the object under running hot

water for an extended period of time, but this was not carried out due to time constraints.

If a similar treatment with gels is attempted in the future, a sufficient washing method needs to be devised. It should be noted, however, that current research does not indicate that the dried gel poses a risk to the object (Scott 2012, 74).

Furthermore, the use of the gel in the treatment was to show that selective mobilization of nantokite took place in the 50% acetonitrile solution and the aluminium was present to indicate that copper chloride was mobilized. When obtaining this type of information isn't necessary, an aqueous acetonitrile solution should typically be preferred.

## 7.6 Samples

When the project started, the objects selected as the samples seemed perfect candidates. After all, they were all of the same metallic composition and had all been in the same conditions. Nevertheless, during the project it was noted that there were significant differences in the object's conditions. While they were all taken from the same archaeological find, their random placement at the seabed nevertheless resulted in some coins apparently having much larger chloride amounts in them than others. Furthermore, some of the samples chosen had smaller coins attached to them and some didn't, which resulted in larger chloride deposits left between the coins which were not as accessible to the gel.

While to attain more reliable results artificially corroded pieces of copper that all have evenly corroded in a controlled environment should have been used instead, nevertheless for this study the samples chosen were the only option because of time constraints; the timetable allocated for the study wouldn't have accommodated the time needed to artificially corrode samples to the point that they would have been usable. Another problem with artificial samples would have been the even distribution of chlorides around the object, as one of the test's main points was to pinpoint localized chloride deposits, which wouldn't have existed in artificial samples.

## 7.7 Future research

The original idea Ian MacLeod had was that he suspected iron impurities in the copper might sometimes correlate with the chloride concentrations in the metal. To determine this one could use a thiocyanate gel on the object in a similar way to the acetonitrile gel, after the object has already been treated with the acetonitrile gel and the chloride concentration spots have been located. The thiocyanate would show any iron impurities in the object, as the gel would turn reddish brown in the areas the impurities would be in. These results could be then compared to the results from the acetonitrile gel treatment to see if there is any correlation with the locations of the iron impurities and the chloride concentration spots, which could indicate that the two are related.

Originally, the intention was to perform this test if time allowed, as it requires objects that have been treated with the acetonitrile gel and thus have their chloride concentration locations known. However, as these objects apparently didn't contain any iron impurities, according to the XRF analysis and the SEM analysis, this would have most likely provided no results and was thus left out.

## 8 Conclusions

At the beginning of the paper, it was stated that a sodium sesquicarbonate soaking had perhaps been established as the "normal" method to extract corrosion-causing chlorides from marine archaeological copper artefacts. Despite this, the method does exhibit some problems, the most pertinent being the long duration of the treatments. When a rapid treatment is required because of schedule or storage place limitations, or when an object is being exhibited soon and needs to be stabilized before that, an acetonitrile treatment could provide to be a viable alternative, as demonstrated by existing research.

The acetonitrile gel experiments that were described provided another demonstration of its effectiveness at extracting chlorides from copper. Multiple treatments using acetonitrile gel were performed on Swedish copper coins and a

plate money, which were all part of an archaeological find recovered from the archipelago of Helsinki in 2009. The coins had only been treated with a soaking in water and a BTA infusion beforehand, and had actively corroded while in storage, so they were excellent subjects for these tests. In addition to the acetonitrile gel treatment, multiple comparative tests were also made, in which coins were treated with solutions and gels containing water, sodium sesquicarbonate and acetonitrile.

The acetonitrile gel tests were done with an aluminum sheet placed on top of the gel. As the gel extracted the copper and chlorides from the object, they would then concentrate on the aluminium sheet and start to corrode it. The purpose of this was to be a visual indicator of the changes happening in the object and the amounts of copper and chloride ions that were extracted. This proved to be an effective method, as even after one day the aluminium sheet started to show signs of corrosion and copper concretions. The comparative tests using water and sesquicarbonate, on the other hand, didn't affect the aluminium sheets to this degree.

While acquiring quantitative information about the chloride levels of the gels after the treatments proved challenging, some results were able to be gained with titration sticks. Furthermore, an analysis on the treated coins was performed using a SEM, in which visible amounts of chloride on the surfaces of coins were compared. Both of these analysis methods indicated that acetonitrile had removed chlorides in a noticeable larger amount than a water- or sesquicarbonate treatment had, as the acetonitrile gels and solutions contained much more chlorides than the water- or sesquicarbonate counterparts, and the SEM analysis showed much more visible chlorides on the surface of water- and sesquicarbonate treated coins than on the surface of acetonitrile-treated coins.

Using the acetonitrile in gel form did cause some problems, however. The gel wasn't able to penetrate everywhere on the object, which resulted in chloride deposits being left on some of the coins with thick crust or patina layers, or ones with smaller coins attached to them. This then resulted in those coins starting to

actively corrode as they were exposed to humidity. Furthermore, the gel proved difficult to wash off the objects, and some residual gel remained on all of them. On the objects that were in treatment the longest, the aluminum had completely corroded away and mixed into the gel, resulting in an aluminum oxide layer being stuck to the object's surface.

However, as the gel and aluminum's main purpose was to give a clear visual indicator of acetonitrile's chloride extraction potential, these problems wouldn't occur when an object would simply be treated with an aqueous acetonitrile solution. While there could be applications for the gel treatment as a tool to map chloride concentrations on objects, in most cases a treatment with aqueous acetonitrile would be preferable. While in the end the tests weren't able to provide quantitative data about the amounts of chlorides that were extracted and not all of the coins used in the tests were stabilized due to the problems mentioned, the results make it clear that acetonitrile is far more effective in extracting chlorides from copper than water or sesquicarbonate treatments, and its use should warrant for more research in the future.

Finally, I would like to thank Liisa Näsänen from the National Museum of Finland as well as Ian MacLeod for their immense help and guidance during this project. Furthermore, I'd like to thank Elisa Ahverdov from the National Museum of Finland for helping with the project, especially in practical matters, at multiple occasions, Sari Granroth from the University of Turku for performing the SEM analysis and making it possible, and the staff from Metropolia's conservation study program, especially my supervisors Heikki Häyhä and Kirsi Perkiömäki.

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## Appendices

### SEM analysis graphs

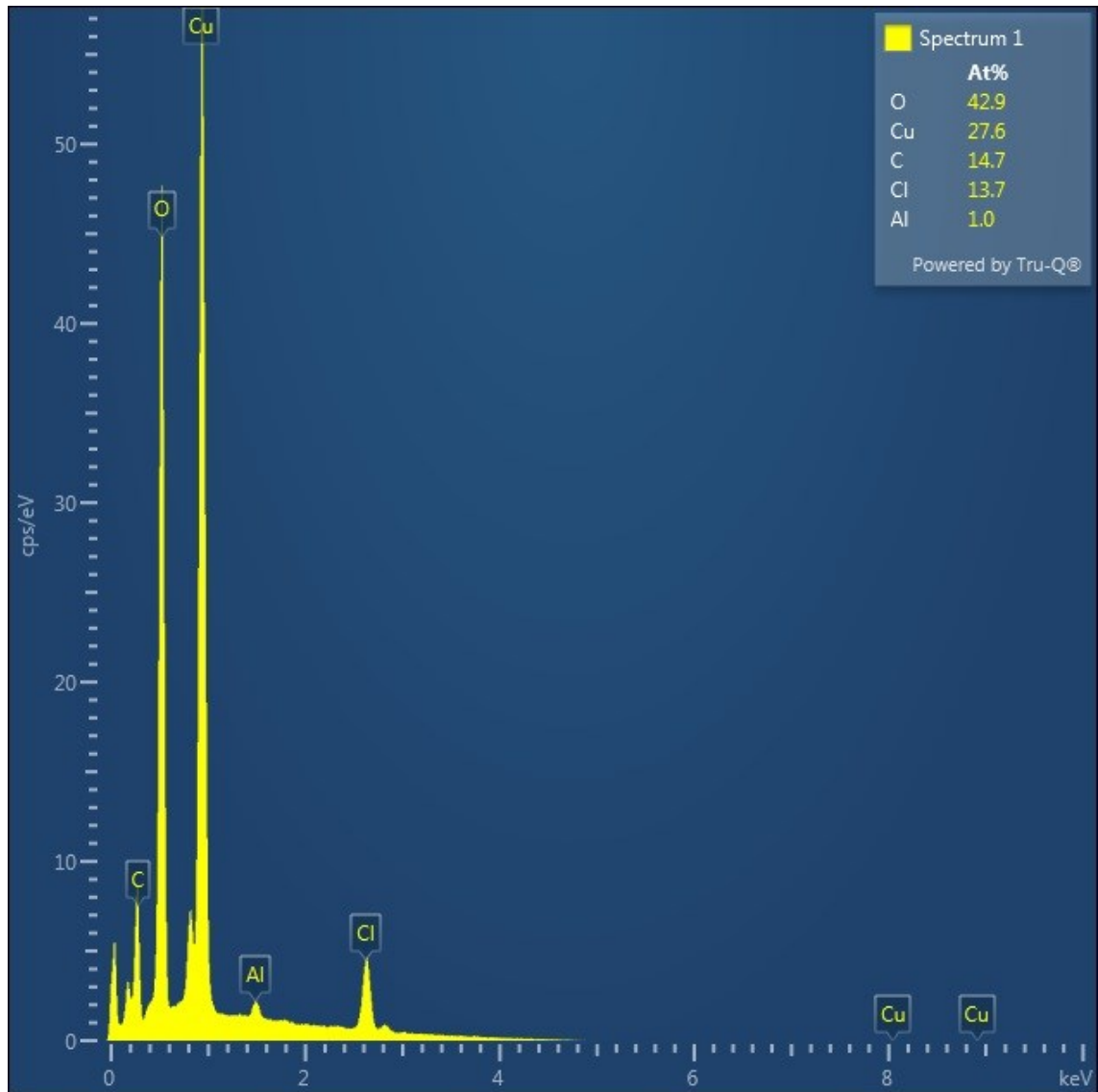


Figure 36: Spectrum 1 from Figure 30

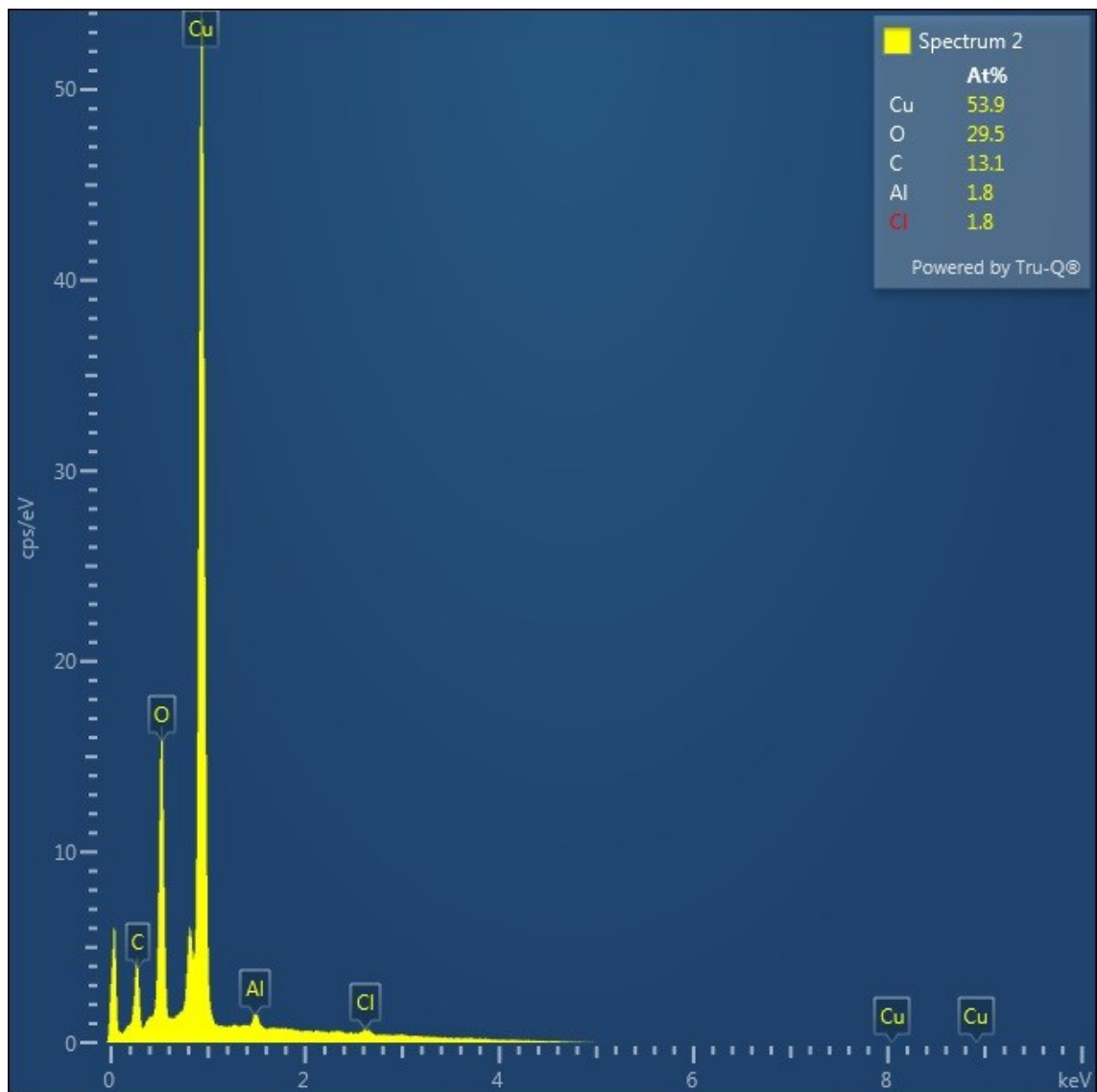


Figure 37: Spectrum 2 from Figure 30

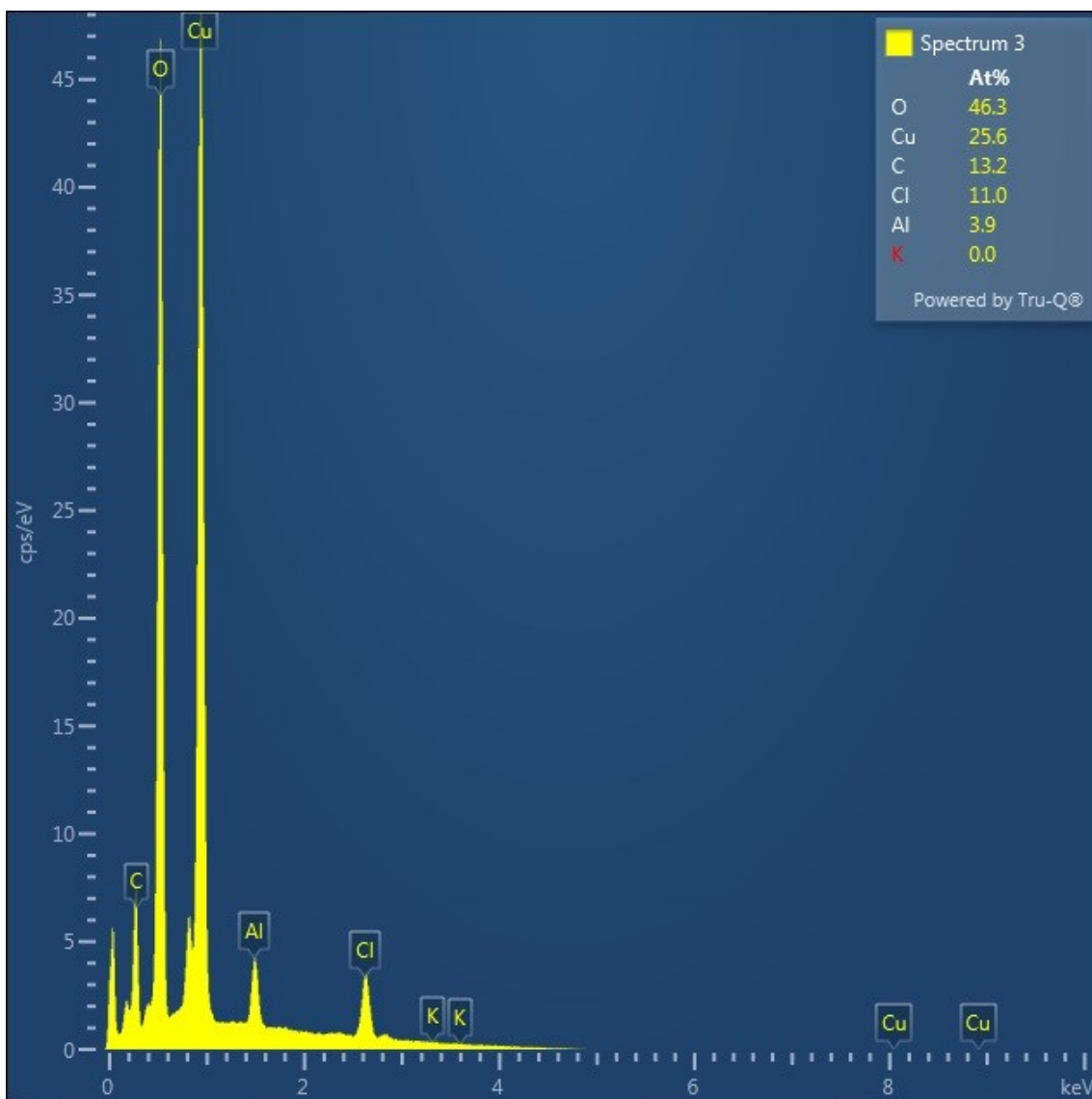


Figure 38: Spectrum 3 from Figure 30

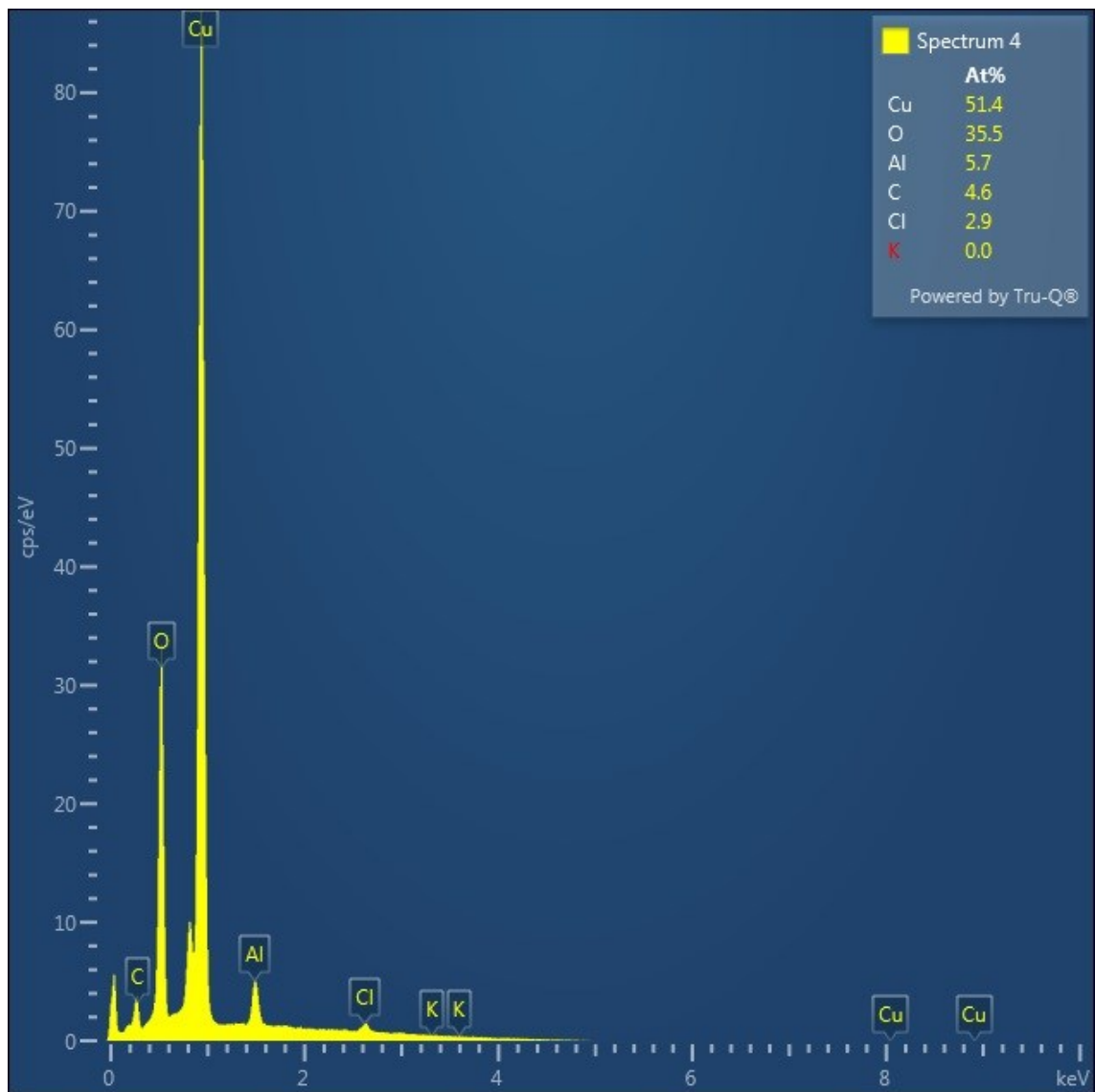


Figure 39: Spectrum 4 from Figure 30

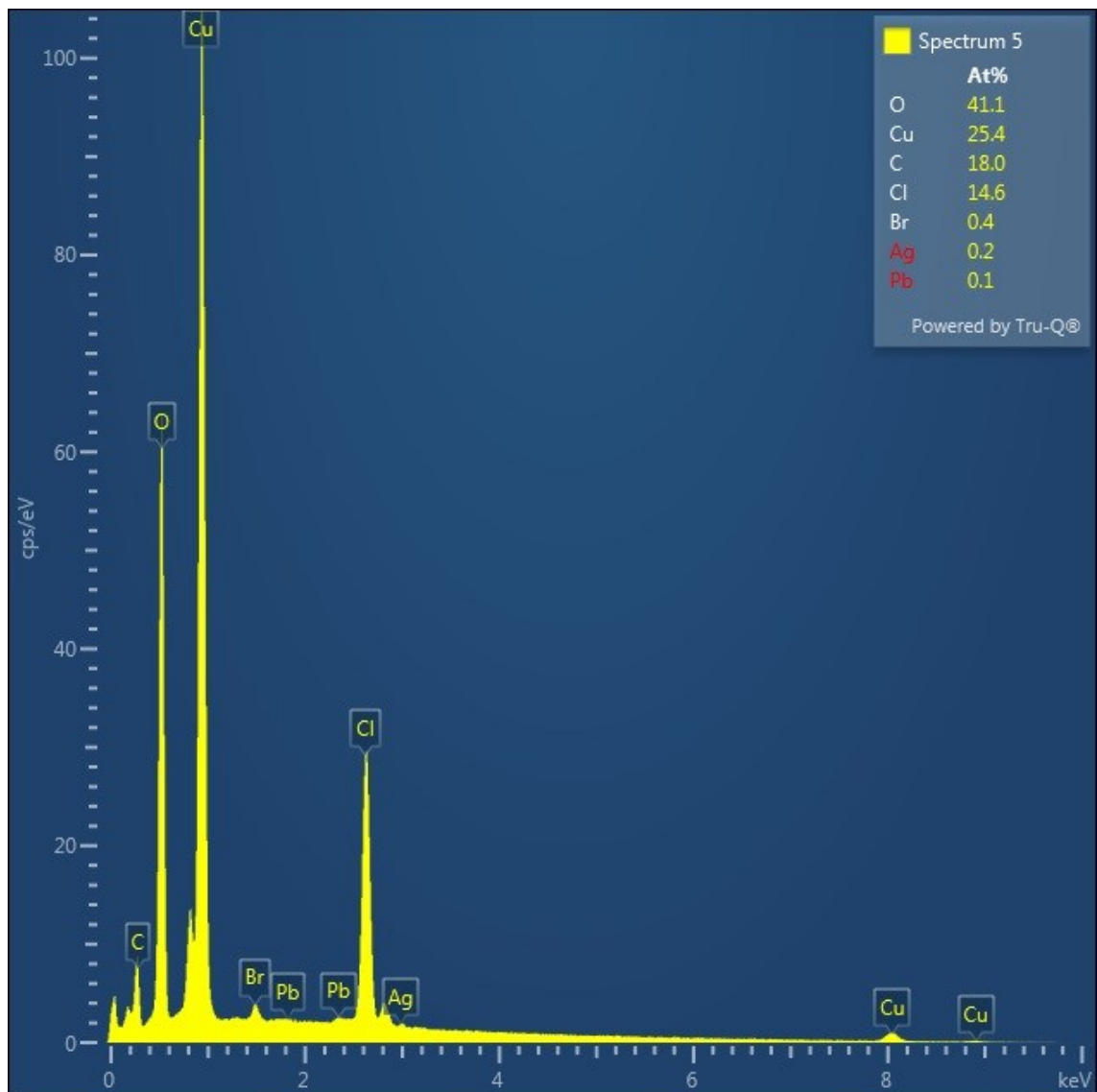


Figure 40: Spectrum 5 from Figure 31

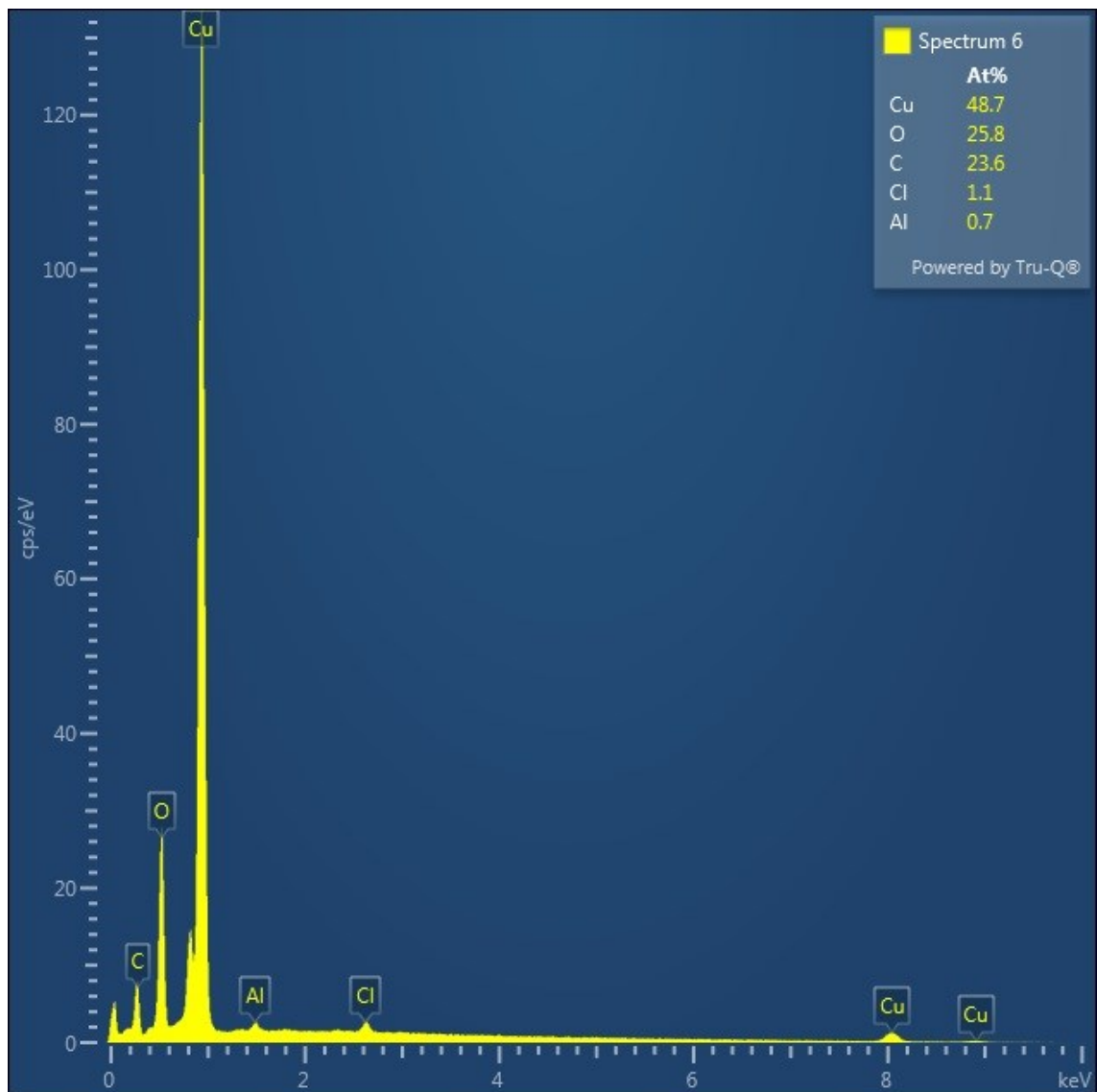


Figure 41: Spectrum 6 from Figure 31

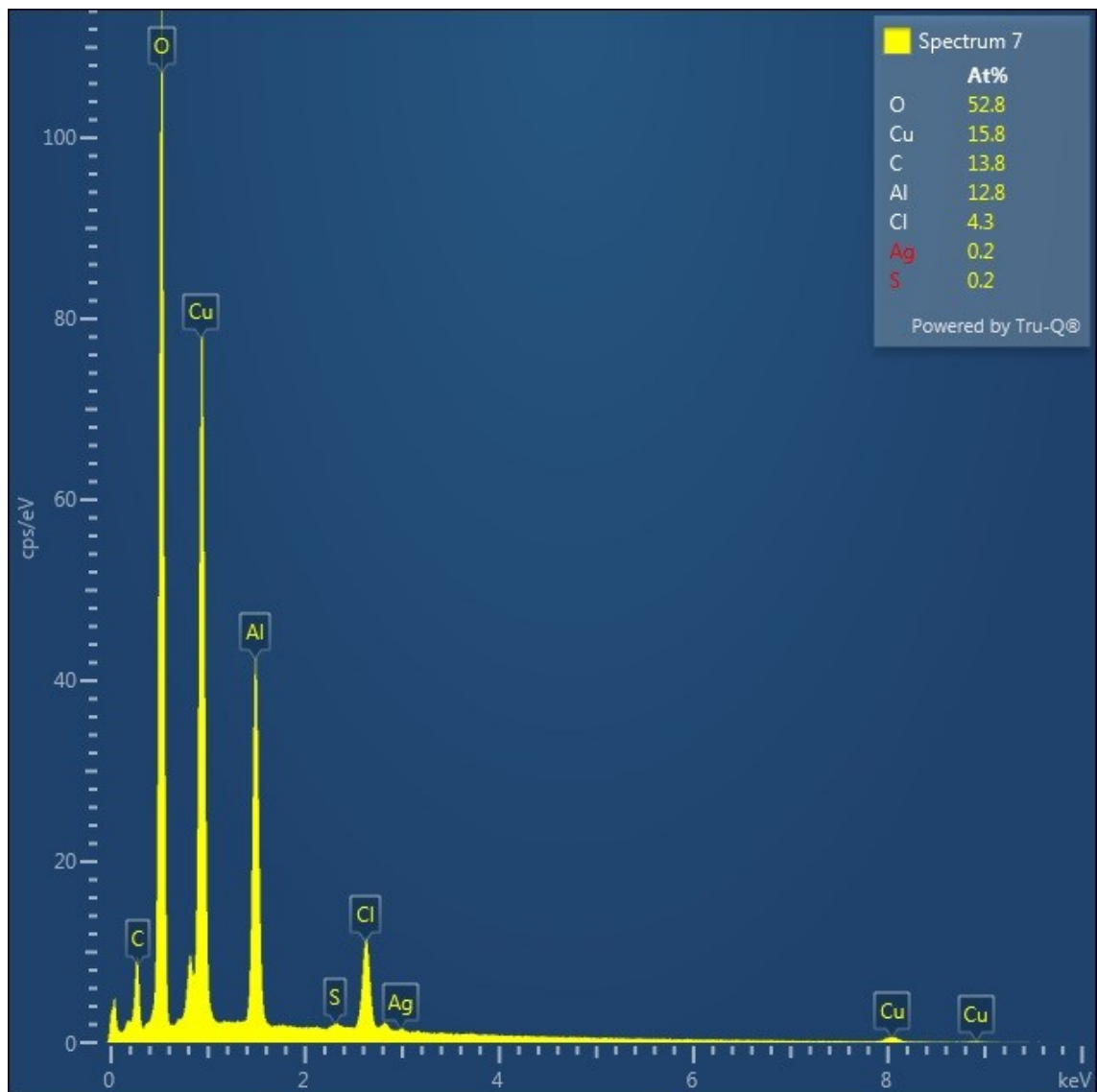


Figure 42: Spectrum 7 from Figure 31

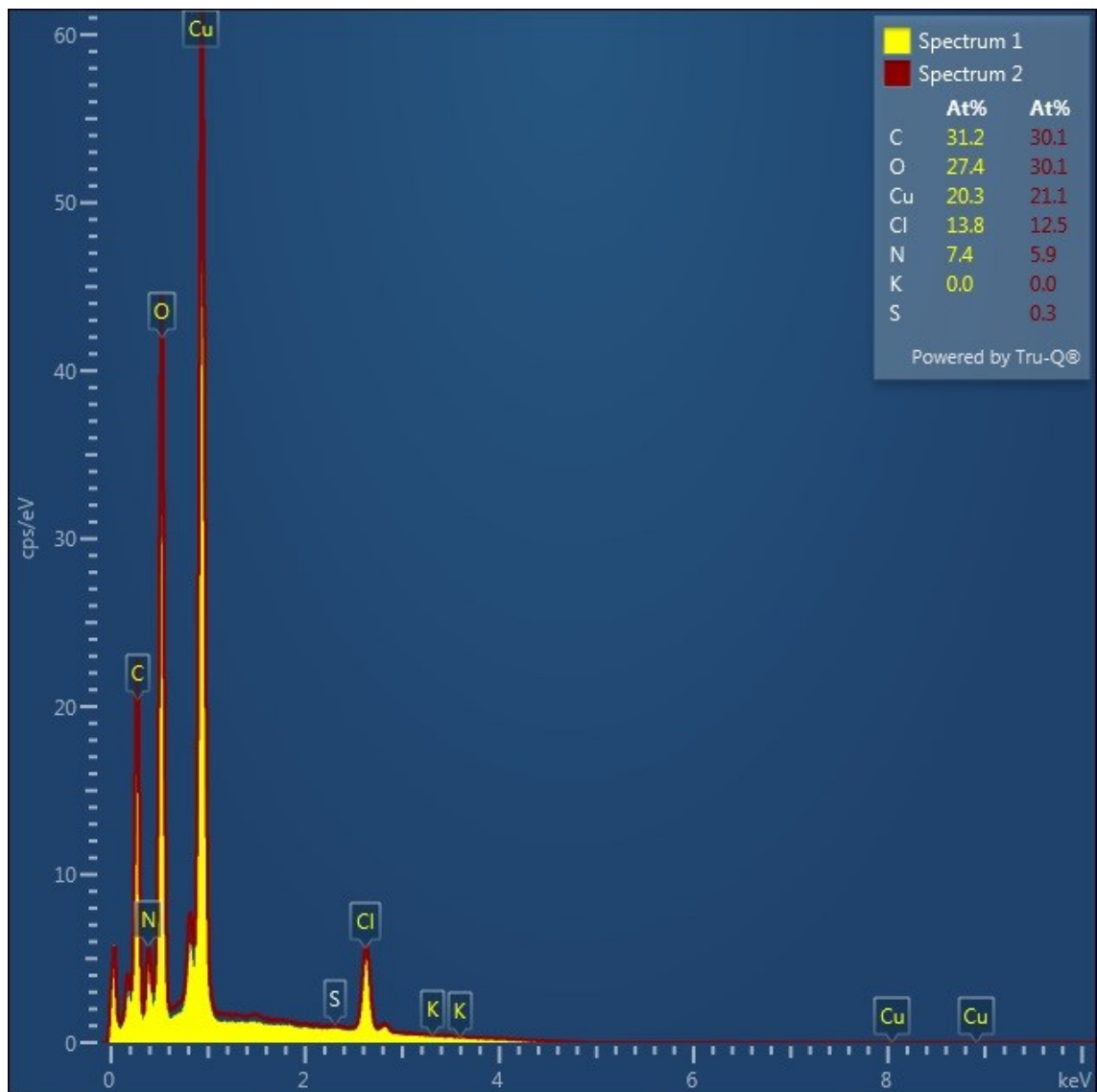


Figure 43: Spectrum 1 from Figure 32



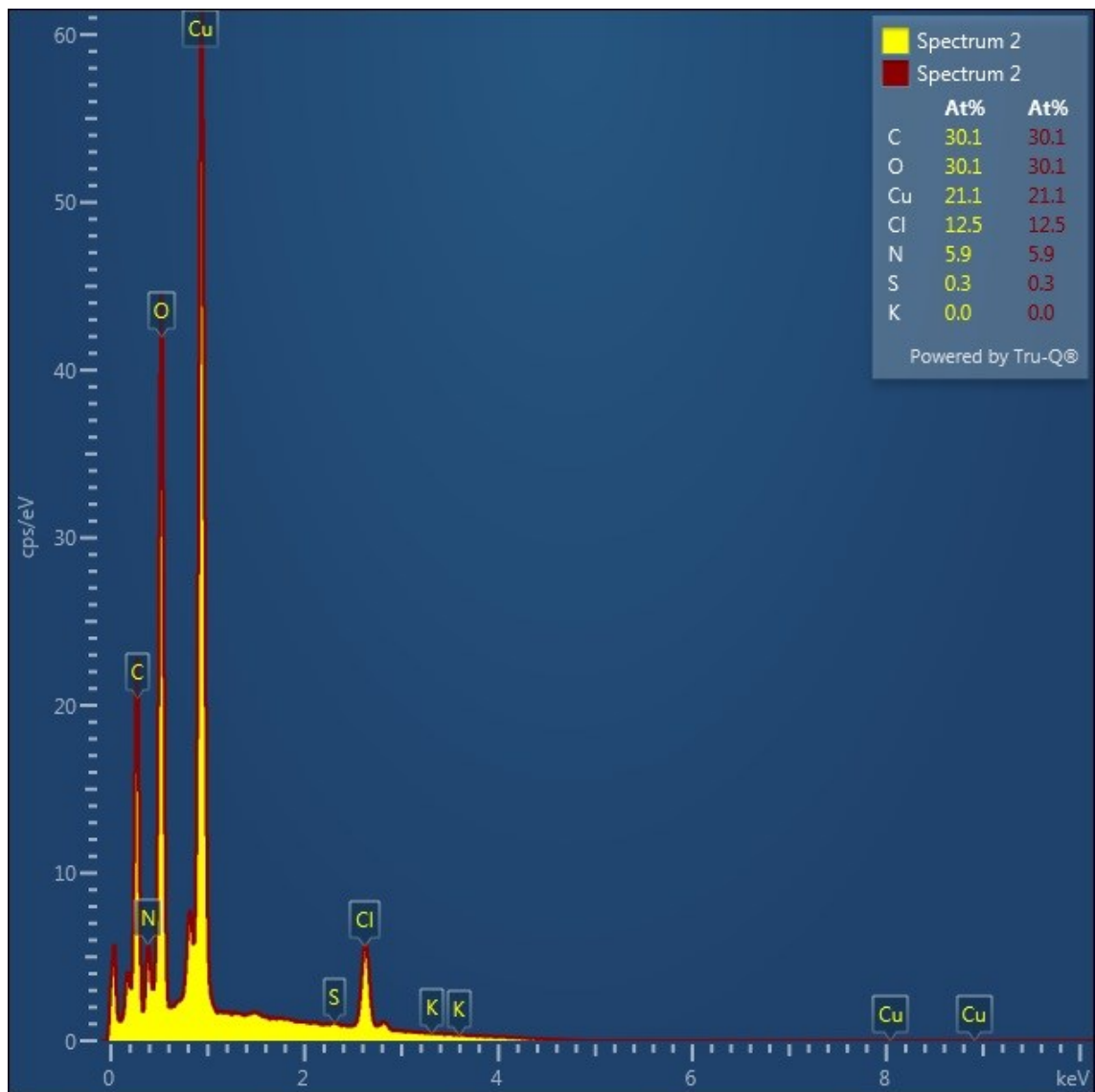


Figure 44: Spectrum 2 from Figure 32

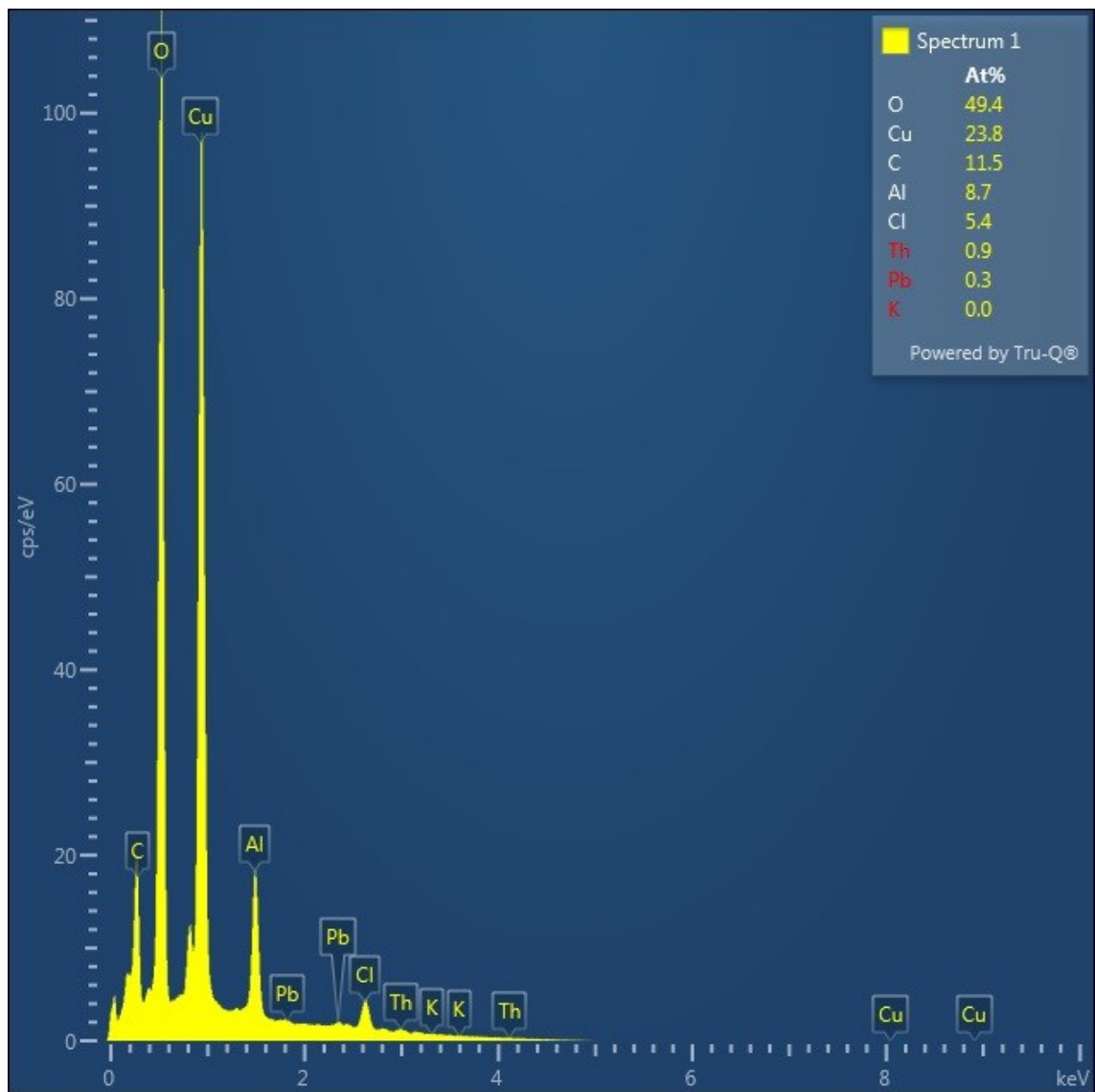


Figure 45: Spectrum 1 from Figure 34

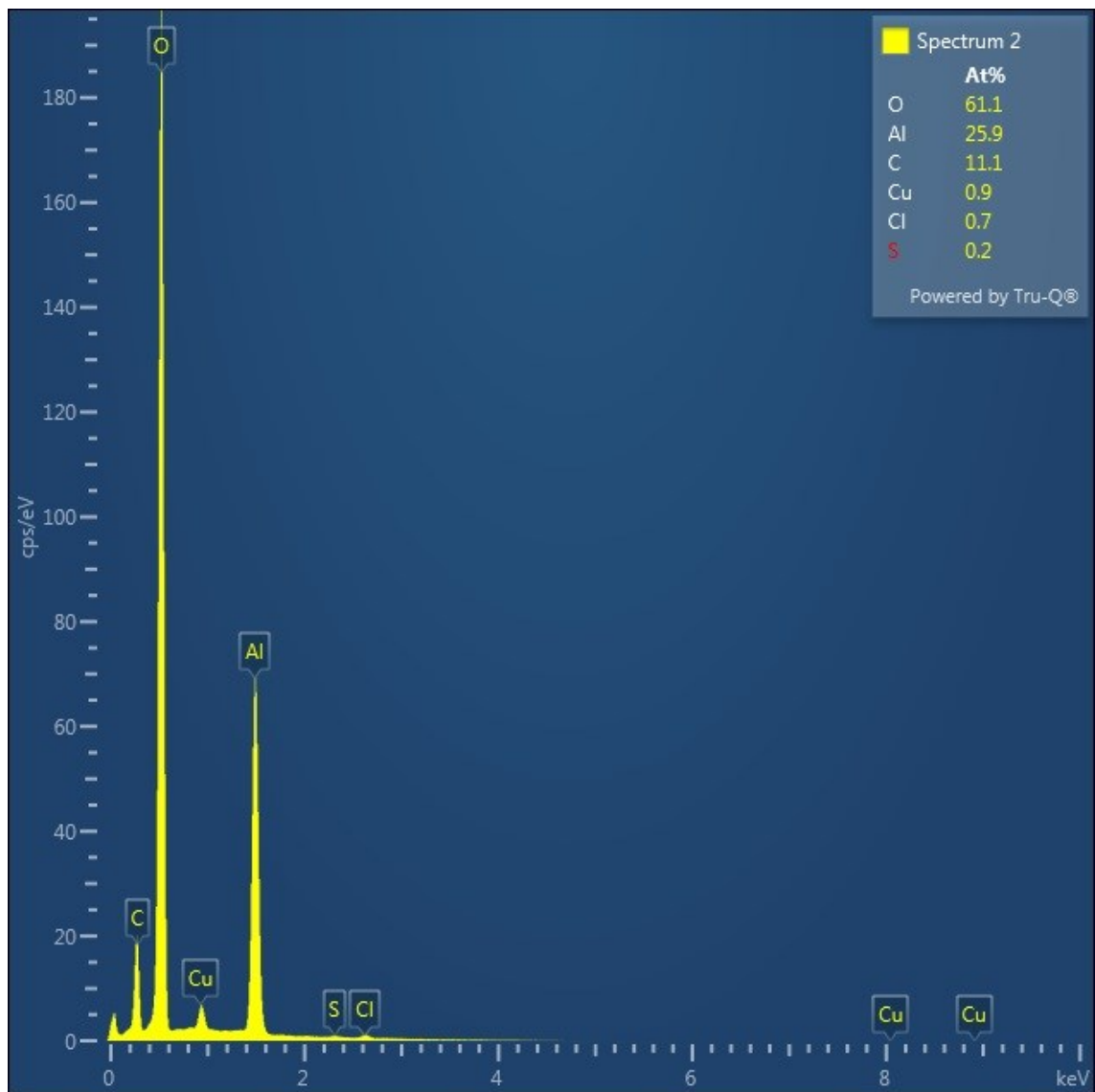


Figure 46: Spectrum 2 from Figure 34

## Report of the Länsitonttu finds (in finnish)

### Kohteen löytöhistoria

Länsitontun ploomulöytö tuli Museoviraston tietoon ensimmäisen kerran vuonna 1977, kun Aulis Lerkka nosti kaksi Länsitonttu-nimisen luodon läheltä löytämänsä ploomuraha, ja toimitti ne Kansallismuseon Rahakammioon. Lerkka kertoi löytäneensä ploomut luodon lounaispuolelta, missä ne olivat olleet noin 12 metrin syvyydessä louhikkoisella kalliopohjalla noin 10 metrin päässä toisistaan. Enempää rahoja Lerkka ei useista sukelluksista huolimatta ollut löytänyt. Nostetuista ploomuista toinen lunastettiin Lerkalta Kansallismuseon kokoelmiin alkuvuodesta 1978, toinen ploomu jätettiin lunastamatta huonokuntoisuuden vuoksi, ja se jäi Lerkan haltuun.<sup>1</sup> Rahakammion silloinen intendentti Pekka Sarvas määritteli lunastetun kappaleen 1700-luvun alun ruotsalaiseksi kahden taalerin ploomurahaksi.<sup>2</sup>

Vuosia myöhemmin, 11.7.2005 urheilusukeltaja Kari Mäkinieniemi toi Kansallismuseoon kaksi Länsitontulta 13-14 metrin syvyydestä löytämänsä syöpynyttä kupariploomua. Löytöpaikalla oli Mäkinienien mukaan myös kolikkorahoja.<sup>3</sup> Kyseiset ploomut ajoittuvat Tuukka Talvion mukaan 1670-luvulle. Mäkinienien tekemän löydön jälkeen, 11.9.2005 kävi meriarkeologian yksikön työmestari Pekka Paanasalo Mäkinienien kanssa etsimässä löytöpaikkaa, mutta tuloksetta.<sup>4</sup> Paikan etsintöjä jatkettiin vielä seuraavanakin vuonna: 11.5.2006 alueella sukelsivat apulaistutkija Rami Kokko, Pekka Paanasalo ja Topi Sellman, mutta ploomujen sijaintipaikkaa ei vielä tuolloinkaan löytynyt.<sup>5</sup> Tämän jälkeen Immi Wallin ryhtyi tekemään alueella etsintöjä. Hän kartoitti aluetta viistokaikuluotaimen avulla

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<sup>1</sup> Talvio 2009b.

<sup>2</sup> Sarvas 1977.

<sup>3</sup> Talvio 2005.

<sup>4</sup> Mäkinieniemi 2005.

<sup>5</sup> Paanasalo 2009.

löytämättä kuitenkaan hylyn jäänteitä. Lisäksi hän kuvasi ROV:lla isokokoisten kiven lohcareiden vierustoja, jollaiseksi löytöpaikkaa oli kuvailtu. Plootujen sijaintipaikka löytyi lopulta pienemmistä kivistä, sorarinteestä ja kalliosta muodostuvalla alueella luodon pohjoispuolelta. ROV:n kuvasta oli erotettavissa noin 15 kpl plooturahoja. Wallin toi kuvaamansa ROV-nauhan meriarkeologian yksikköön katsottavaksi 16.6.2009. Nauhan katsomisen jälkeen päädyttiin löytöalueen dokumentoimiseen ja näkyvissä olevien esineiden nostamiseen seuraavista syistä:

- Alue on erittäin suosittu sukelluskohde, joten löytökokonaisuus on vaarassa hajota ankkurointien tai sukeltajien muun toiminnan vuoksi. Yksi ROV-nauhalla näkyvistä plootuista vaikuttaa jo siirretyltä.
- Museovirasto on kiinnostunut ottamaan/lunastamaan kyseiset irtolöydöiksi toistaiseksi luokiteltavat esineet, konservoimaan ne ja ottamaan ne kokoelmiinsa.
- Löytöpaikan alueelta ei toistaiseksi tunneta hylkyä, mutta on täysin mahdollista, että löytöpaikan lähistöllä sijaitsisi hylyn jäänteet.

On mahdollista, että alueella on useampiakin rahakeskittymiä. Länsitontun läheisyydestä on löydetty myös nk. partamiehenkannu (id. 2187) alle kahden kilometrin päästä plootujen löytöpaikasta.<sup>6</sup> Löytöpaikkaa lähimpänä oleva muinaisjäännökseksi vedenalaislöytöjen rekisteriin merkitty kohde on Sokea Tonttu (id. 1299). Kyseessä on hylky jota ei etsinnöistä huolimatta ole löydetty.

### **Kenttätyöt kohteella**

Plootujen ja kolikkorahojen nosto toteutettiin maanantaina 22.6.2009. Tutkialuksena käytettiin Immi Wallinin Yoldia -nimistä venettä. Kenttätyöhön

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<sup>6</sup> Tulonen 2009.

osallistuivat meriarkeologian yksiköstä tutkijat Sallamaria Tikkanen, Essi Tulonen, Johanna Mäkinen ja Eero Ehanti joka oli paikalla konservaattorin ominaisuudessa, sekä työmestari Pekka Paanasalo. Lisäksi mukana oli Kansallismuseon Rahakammion johtaja Tuukka Talvio, kaksi löytämäänsä plootua vuonna 2005 Rahakammioon toimittanut sukeltaja Kari Mäkineniemi, tukialuksen omistaja Immi Wallin poikansa Villen kanssa, joka toimi aluksen kansimiehenä.

Työt kohteella aloitettiin etsimällä plootujen sijaintipaikka ROV:n avulla, pilottina toimi Immi Wallin. Plootut löytyivätkin miltei saman tien, kun ROV oli ohjattu pohjaan. ROV jätettiin pohjalle plootujen viereen, jotta sukeltajat löytäisivät paikan vaivattomasti kaapelia seuraamalla. Näkyvyys kohteella oli hyvä. Sukellustyön hoitivat Essi Tulonen ja Johanna Mäkinen, sekä Pekka Paanasalo ja Kari Mäkineniemi. Ensimmäisellä sukelluksella kohde kuvattiin videokameralla eri suunnista. Tämän lisäksi ROV kuvasi kohdetta ja sukeltajien työskentelyä koko sukelluksen ajan. Videokameralla kuvattiin löytökeskittymän ympäristöä löytöalueen laajuuden selvittämiseksi. Suurin osa löytökokonaisuudesta – kaksi ”nippua” plooturahoja joiden ympärillä oli jäänteitä kangaspussista tai –säkistä, huomattava määrä kolikkorahoja, sekä suurehkon puisen laatikon jäänteet - sijaitsi noin puoli metriä korkean kivenlohkareen juurella. Tästä paikasta noin kahden metrin päässä oli erillinen plootu kalliota vasten, sekä jonkin verran kolikkorahoja, joista osa oli syöpynyt plootuun kiinni. Kari Mäkinien muistikuvan mukaan erillään oleva plootu oli ollut samassa kohdassa muiden plootujen kanssa silloin, kun hän löysi kohteen. Näiden lisäksi ei löytöpaikan ympäristössä ollut näkyvillä sen enempää plootuja kuin kolikoitakaan, lukuun ottamatta yhtä yksinäistä kolikkoa, joka myöhemmällä sukelluksella löytyi osittain pohjasoraan hautautuneena noin 1,5 metrin etäisyydeltä suuremmasta löytökeskittymästä.

Löytöalueen dokumentointia seurasi löytöjen nosto. Tukialuksesta laskettiin köysien varassa pohjaan kaksi nostokoria, joihin sukeltajat siirsivät plootut. Kun korit olivat nostovalmiit, antoivat sukeltajat vieressä työskentelyä kuvanneelle

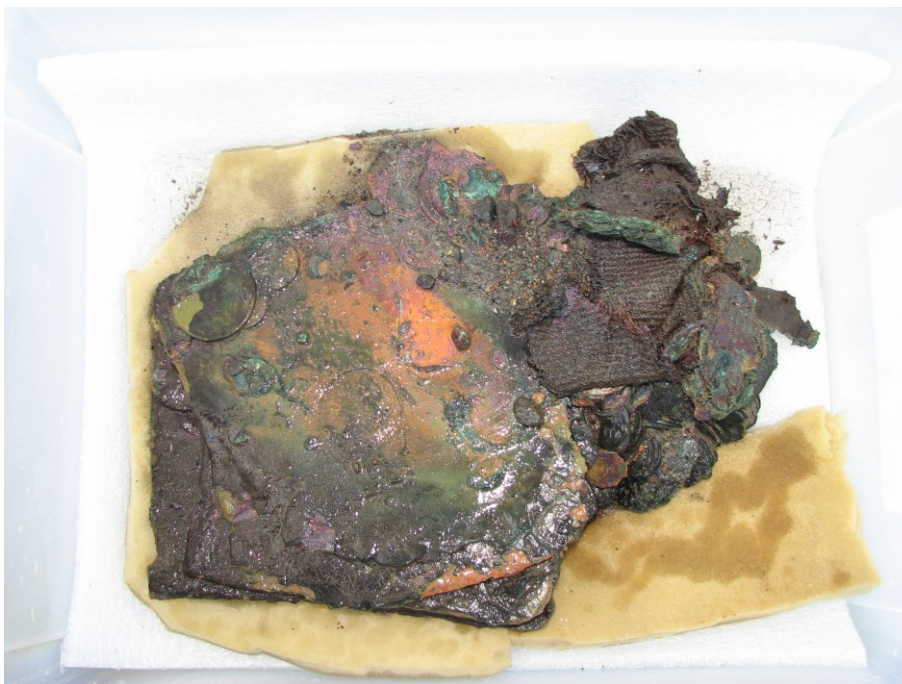
ROV:lle merkin korien nostamiseksi. Tämän jälkeen korit nostettiin pintaan tukialuksesta käsin. Kolikkorahat kerättiin pienempään ”karkkilaatikkoon”, jonka sukeltajat toivat mukanaan pintaan. Puisen laatikon (mahdollisen kirstun) ympäriltä ja vierestä siirrettiin pohjasedimenttiä sen verran, että pystyttiin hahmottamaan esineen koko, mutta sen enempää tähän löytöön ei koskettu. Puulaatikon jäännökset koostuvat luultavasti laatikon pohjasta ja sen vieressä olevasta kanasta tai sen osasta. ”Kirstun” jäänteiden esiin kaivaminen ja nosto toteutetaan myöhemmin erillisenä, suunniteltuna työnä. Löytöjen nostot tehtiin kahden sukelluksen aikana, ja näistä sukelluksista jälkimmäisellä tutkittiin myös pohjaa löytöalueen ympäriltä muutaman metrin säteeltä. Tutkitulla alueella ei kuitenkaan yllä mainittua erillistä kolikkoa lukuun ottamatta ollut näkyvissä löytöjä.

Kun näkyvissä olleet löydöt oli saatu nostettua, löytöpaikka dokumentoitiin vielä kertaalleen videoimalla. Nostamatta jätetyt puulaatikon jäännökset peiteltiin soralla siltä osin, kun niitä oli kaivettu esiin. ROV kuvasi ja nauhoitti sukeltajien työskentelyä jokaisen sukelluksen aikana.

Noston jälkeen löydöistä huolehti Eero Ehanti, joka pakkasi löydöt kuljetuksen ajaksi. Tuukka Talvio, katsottuaan juuri merestä nostettuja rahoja, totesi niiden olevan ajoitukseltaan yhdenmukaiset Kari Mäkinien aiemmin nostamien ploitujen kanssa<sup>7</sup>. Löydöt kuljetettiin Hylkysaareen konservointilaboratorioon.

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<sup>7</sup> Talvio 2009a.



Kuva: MA200908:9. Juuri merestä nostettu löytö, jossa on toisiinsa kiinnittyneinä kupariplootuja, kolikkorahoja sekä tekstiiliä.

### **Jatkotoimenpiteet**

Tämän tekstin kirjoittamishetkellä plooturahat ja kolikot odottavat laboratoriossa konservointityön alkamista. Vielä on epäselvää, sijoitetaanko löytö kokonaisuudessaan Rahakammion kokoelmaan vai Suomen merimuseon kokoelmaan, vai jaetaanko se kenties näiden kahden kokoelman kesken. Löytöpaikalle toistaiseksi jätetty puukirstun jäännös aiotaan nostaa ja konservoida, mutta tämän esineen nosto vaatii suunnittelua sekä erilaista kalustoa, kuin mitä rahalöydön nostamiseen käytettiin. Tällä hetkellä ei myöskään ole tietoa siitä, onko löytöpaikalla vielä lisää tavaraa pohjasedimenttiin hautautuneena. Rahalöydön noston yhteydessä pohjasedimenttiä ei kaivettu lukuun ottamatta "kirstun" jäännöksen päältä ja vierestä siirrettyä vähäistä määrää soraa. Mahdollisten hautautuneiden



esineiden löytäminen edellyttää kajoavaa tutkimusta, joka tulee toteuttaa asianmukaisin kaivausmenetelmin.