Aleksi Pienimäki

# Desalination of iron

A comparison of fresh, wet finds and dry, storaged ones.

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Tässä opinnäytetyössä verrataan arkeologisen raudan suolanpoistoprosesseja kuivilla, hapettumaan päässeillä löydöillä, sekä kosteina kaivauksilta suolanpoistoon säilytetyillä löydöillä. Projektissa käytettiin Hangastenmäen linnavuorelta (mj-numero 1000023482) vuosina 2013 ja 2014 nostettua 26 metallinilmaisinlöytöä, sekä syksyllä 2015 arkeologisilla kaivauksilla löydettyä 46 metalliesinettä. Suolanpoisto suoritettiin molemmille esine-erille ns. alkalisulfiittimenetelmällä, jossa esineitä säilytetään 0,1 M $NaOH$ ja 0,05 M $Na_2SO_3$ –liuoksessa noin 50 asteen lämpötilassa kloridien poistamiseksi. Opinnäytetyöprojektin aikana käyttöliuokset vaihdettiin kahden-kolmen viikon välein, kunnes liuoksen kloridipitoisuus oli vähintään kolmen vaihdon yhteydessä ollut alle 10 ppm.

Suolanpoistoprosessien etenemistä seurattiin käyttöliuosten kloridipitoisuuksia mittaamalla. Mittaukset suoritettiin Merckin valmistamalla pikatestisarjalla (Aquamerck® 1.11106.0001) sekä ionikromatografianalyysilaitteistolla (Metrohm 761 Compact IC). Ionikromatografilaitteistossa päädyttiin käyttämään dialyysiyksikköä näytteille, joiden kloridikonsentraatio oli yli 20 ppm. Näin pyrittiin suojaamaan herkkää analyysilaitteistoa näytteiden sisältämiltä epäpuhtauksilta. Alle 20 ppm kloridipitoisuuden sisältävät näytteet analysoitiin ionikromatografilla suoraan.

Kuivuneiden ja kosteina säilytettyjen löytöjen käyttäytymisessä suolanpoistoprosessin aikana havaittiin selkeä ero. Kuivuneista löydöistä ehdottomasti suurin osa klorideista poistui jo ensimmäisen kaksiviikkoisen käsittelyjakson aikana, kun taas kosteina kentältä suolapoistoon säilytetyistä löydöistä kloridit poistuivat huomattavasti hitaammin ja tasaisemmin. Koska projektin yhteydessä ei ollut mahdollisuutta mitata jäännöskloorin määrää esineissä tai tehdä rakenteellista analyysiä säilyneille löydöille, oli syytä erolle haettava teoriapohjalta. Todennäköisimmin ero selittyy kosteana säilytettyjen löytöjen korroosiokerrosten kiinteydellä – nämä muodostavat diffuusiolle kuivuneiden löytöjen halkeilleita korroosiokerroksia suuremman esteen.

Projektin yhteydessä käsiteltyjen 72 esineen konservointi suoritettiin loppuun saakka. Suolanpoiston jälkeen löydöt puhdistettiin mekaanisesti, ja suurin osa aineistosta suojattiin mikrokidevahalla. Käytännön osuus toteutettiin välillä lokakuu 2015 – huhtikuu 2016.

| Keywords | Archaeology, iron, desalination, chloride |
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Helsinki
**Metropolia**
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# 1    Introduction

This thesis covers conservation treatment of two batches of metal objects from a single archaeological site in Finland with emphasis on their desalination processes. In 2013 a metal detectorist group discovered a number of objects from a hilltop called Hangastenmäki in Janakkala, Tavastia Proper. Most of the finds were nails, in addition to one horseshoe and some objects that remained unidentified at the time of discovery. At this stage the importance of the find was not fully understood, but when the group returned to the site in 2014 more objects started to turn out, this time mostly weaponry and horse apparel. Later the same year the site was inspected by archaeologists and was found to be a previously unknown hillfort. The hillfort was listed as an archaeological site protected by the Finnish law, with the name Hangastenmäki, (reg. no. 1000023482). The discovery was quite unusual and called for further attention, which it got in the autumn of 2015 when a small scale excavation was launched at Hangastenmäki. The three week excavation yielded a number of finds, including several iron objects.

Twenty six of the objects recovered by metal detectorists had been claimed by the National Board of Antiquities of Finland and had remained untouched in storage ever since. Combined with the objects from the 2015 excavation they formed a conservationwise interesting group of objects where stored, dry iron and freshly excavated, moist objects were available from the same site. This allowed an old desalination related hypothesis – that oxidised, dry iron objects would react differently to a desalination treatment compared to fresh, moist objects that have had little time to react with oxygen – to be tested.

It was decided that care would be taken to keep the excavated iron moist and cool all the way from the ground to the conservation lab, where they and the metal detector finds would be subjected to similar alkaline desalination treatments. The treatments would be thoroughly documented with the ion chromatography equipment of the Helsinki Metropolia University of Applied Sciences providing accurate means to bring out any differences in the chloride extraction rate between the different batches of objects.

Since the beginning of professional archaeological research in the Northern Europe, iron has been regarded as one of the most problematic find materials. In the largely acidic and moist environment of the north, iron corrosion takes a pretty aggressive form, often

consuming ancient artefacts altogether in the soil before they can be excavated and brought to the conservator's workstation. Even when the objects reach a reasonable balance with their burial environment and manage to survive to our days, they will face a great risk upon being taken out of this environment. Being exposed to the conditions above ground – moisture, oxygen and fluctuating temperatures – they often begin a re-newed degradation process that has proven to be very stubborn and difficult to stop.

This is all the more disturbing as iron has been an extremely useful material in the past and vast amounts of archaeological material consist of objects made of it. These objects along with the structures revealed upon excavation will form the core material of archae-ological research. Whilst the destruction of stationary structures can most often not be avoided on an archaeological excavation, the portable objects are usually recovered and stored for further investigation and research. Letting this material get destroyed wold be a huge waste of resources and an irreversible loss. The heritage institutions can also be seen to have a special responsibility over the object's survival as it is their very excava-tions that often have exposed the objects to the environment and caused their rapid destruction process.

During the last fifteen years the archaeological conservation field has shown signs of increasing interest on alkaline desalination methods of archaeological iron objects. As will be described in the following chapters, surveys made in this period have shown that attempts to control corrosion of antique iron objects by climate control have been largely expensive and ineffective, leaving desalination – the removal of chlorides that are re-sponsible for the aggressive post excavation corrosion – as the most viable course of treatment despite the risks it poses to the objects. Alkaline desalination methods have been proven to reach good results and increase the survivability of the objects signifi-cantly, but they have their shortcomings. Perhaps the most obvious of these is the fact that research on alkaline desalination is still ongoing despite more than forty years of active use at the time of writing. It seems that the closer look conservation science takes at the phenomenon, the more complex it looks.

The chemistry behind alkaline desalination is varied and cannot be easily summarised. Judging by the research done on the subject as well as the practical experiences re-ported by conservators doing the treatment, it is obvious that alkaline methods cause changes in the object, and not all of these changes are desired. The risks involved range from minimal and aesthetical to disintegration and total loss of cultural and informational

value. As the chemistry behind the phenomenon is not entirely understood a conservator takes a risk whenever he or she decides to use the method on very heterogeneous archaeological material. This, and a general lack of resources and information, has led many conservators to avoid desalination altogether (Rimmer, Wang & Watkinson 2012, p. 30; Schmutzler 2006, pp. 12-13 of 15).

However, damages caused by the lack of action are just as much the responsibility of the conservator as are damages caused by action, even if they feel less personal. Research has shown that a vast amount of archaeological iron will face destruction if left untreated and thus actively corroding iron cannot be left to wait in the hopes of discovering a risk-free treatment method in the future. The acute corrosion problem needs to be addressed immediately.

The practical part of this thesis was carried out at the Conservation Laboratory of the National Museum as the objects are also a part of their collection, apart from chloride analysis that was carried out at the Helsinki Metropolia University of Applied Sciences. The work was carried out between October 2015 and April 2016.

## 2 History of iron desalination methods

### 2.1 Pre 1970's

The early 19th century was a period of rapid establishment and growth of museum institutions and the whole cultural heritage field in general. This led to a rise in the number of museums and objects in their collections, as well as a new interest in old relics and archaeological sites. New and more professional ways of treatment, storage and cataloguing were developed and adopted. However, it was not until closer to the end of the century that conservation science started to emerge as a field of its own, conservation of antiquities being the responsibility of artisans familiar with the materials being treated up until the late 1800's (Sease 1996, p. 158).

This also means that systematic treatment records are often not available from the pre-1880's period, and the applied methods have to be deduced from indirect sources, such as letters between academicians or receipts for artisans' services (Madsen & Andersen 2013). Thankfully the records in Scandinavia and Germany belong to the earliest and most comprehensive in the world, with early pioneers such as Christian Jürgensen Thomsen, Axel Krefting and Friedrich Rathgen who had a profound effect on the establishment and development of the entire field of archaeological conservation. (Jakobsen 1988).

### 2.1.1 Consolidation with oils and resins

The earliest records show that rapid post excavation corrosion was a known phenomenon for the earliest generations of scholars and conservators, too, and many different approaches were employed to stop this from happening. The earliest applied methods included boiling the objects in various mixtures of oils and varnishes. This was probably an intuitive solution to the problem of objects falling apart as a result of corrosion, as it was hoped that the oil or varnish would impregnate the corrosion layers, bind them together and form a protective coating against the atmosphere. Employed mediums included linseed oil, copal varnish and even isinglass and rubber. Even though many of the early treated objects have survived to this day, it was not a secure way to treat iron, and the results often were aesthetically displeasing. (Hansen 2001; Scott & Eggert 2009, pp. 131-132).

### 2.1.2 Soaking

By the late 19th century chloride had also been discovered to be the main reason for the rapid degradation of iron, and since then its removal or inactivation has been the main focus of stabilization treatments. Probably the first one to acknowledge the central role of chlorides in the corrosion of archaeological iron was a German engineer, Edward Krause, whose publication was also the first one to introduce washing or soaking the objects in water specifically as a desalination treatment (Krause 1882). His method included soaking the objects in consecutive baths of hot and cold distilled water until no more chlorides would be detected in the washing liquid. He argued that since chloride ions need to be free in order to be able to contribute to the corrosion processes, any remaining insoluble chloride compounds would be harmless. Very quickly it was discovered that this is not the case, but still, Krause's method would be the first one in a very long list of various soaking methods employed on iron to wash out the harmful chloride salts.

### 2.1.3 Heat treatment

Iron was also heat treated to stabilize it. This method dates back to at least 1860's and documentation of the method survive at least in Denmark (reviewed by Tove Jakobsen in 1984, 1987a, 1987b & 1988) and in Eastern Prussia (Blell 1883). The process included heating the object up to a temperature of circa 800 °C for varying lengths of time, after which they would be soaked in diluted sulphuric acid. On modern standards the process sounds extreme, and led to a practically total stripping of corrosion products. Whilst this method often led to the stabilization of the object (Gilberg & Vivian 2001) the importance of corrosion layers as a crucial informative part of the object would later be realized (Bertholon 2001) and the method was discarded.

However, another form of heat treatment was developed in Denmark, where the red hot objects would be soaked in a solution of potassium carbonate. The next step would be soaking the objects in water to remove chlorides and other hygroscopic salts, after which the object was ready for mechanical treatment. This method would be applied until 1980's, especially for finds from cremation burials, as there the inevitable alterations caused by this method to the microstructure of objects already annealed in the pyre were seen as acceptable (Christensen 1967).

2.1.4   Electrochemical methods

Another late 19<sup>th</sup> century phenomenon was the adaptation of electrochemistry to the field of conservation. The first and most significant of the early adaptations comes from a Norwegian engineer, Axel Krefting, who published his method for cleaning of archaeological iron in 1892. The method was based on electrochemical reduction, where bare metal was revealed by filing on several places in the object to be treated, and then these spots were connected to a zinc wrapping. When placed into a caustic soda bath the object and the zinc would form a cell where the zinc would act as an anode and the object as a cathode, resulting in reduction of the corrosion layers. The method was gentler than acid or heat based stripping of corrosion layers, but still unpredictable, and would occasionally lead to disintegration of some finds. It still marks the beginning of electrochemical conservation treatments that are still in use in various forms, especially in marine conservation. As an interesting side note, Krefting's method was in use in the National Museum of Helsinki in 1887, before the publication of his method, as he had authorised conservator Hjalmar Appelgren-Kivalo to use it when Appelgren was visiting Norway on a study trip in 1887 (Appelgren 1896; Reijonen 2010, p.120)

One interesting phase of water based desalination was the implementation of ionophoresis to force the chlorides out of the objects. This was achieved by placing the object to be desalinated into a distilled water bath between two stainless steel plates that would work as the cathode and the anode. The idea of this treatment was that ions within the object, including chloride, would be attracted to their appropriate electrodes. The solution would ideally be changed at least every 24 hours, more frequently if the amount of chlorides was high. Low heating was used to fasten the process. (Wihr 1975). Another version of the same procedure, carried out in England, is described by Keene and Orton (1985). Here a solution of 5% sodium benzoate is used as an electrolyte instead of water, probably to make the solution more conductive and further improve the removal rate of chlorides.

## 2.2    1970's to 2000's

### 2.2.1    Further water based methods

Water based soaking has continued in various forms to this day. Employed methods include heated baths, boiling, water with corrosion as well as vapour phase inhibitors (e.g. Keene & Orton 1985, pp. 137-138), and soxhlet extraction (Scott & Seley 1987). The strong side of water based treatments is that they are in general gentle to the objects, at least if boiling is excluded, and can be used on fragile finds and composite objects. The problem is that they have been relatively ineffective in stabilizing objects.

### 2.2.2    Plasma treatment

An interesting 20th century development has been the plasma reduction treatment (Daniels, Holland & Pascoe 1979), that has shown some success in increasing stability of corroding iron, especially when combined with other methods of chloride removal. It is still in use today, even though nowadays it is used as a lightened version of previous treatments, to increase porosity before alkaline desalination treatment (Schmidt-Ott & Boissonnas 2002; Schmidt-Ott 2004).

### 2.2.3    Alkaline soaking methods

Several alkaline desalination treatments were developed during the latter half of the 1900's, including solutions of lithium hydroxide (Bresle 1974a) and sodium sesquicarbonate (Oddy & Hughes 1970), but results are often non-satisfactory and the corrosion problem remains largely unsolved (Hjelm-Hansen et al. 1992; Watkinson 1982).

Desalination treatments take a new turn as North and Pearson publish their alkaline sulphite desalination method in 1975 (North & Pearson 1975a). This publication would have a huge impact on the whole desalination field, as it introduced a detailed description of a relatively low-cost and simple, yet effective desalination treatment that involved soaking the objects in 0,5M $NaOH$ and $Na_sSO_3$ solution in a temperature of 60 °C, along with a theoretic background of how the method works. At this point they argued that the release of chlorides would be based on a relatively simple equilibrium reaction where

$FeOCl$ would turn into $FeOOH$, and the aim of the treatment would be to create conditions that favour the latter chemical compound, through heat and a high $OH^-$ ion content.

North & Pearson had also found out that at times spalling and cracking of the corrosion layers took place when iron objects were placed into desalination baths, and this they attributed to the formation of voluminous hydrated haematite, $Fe_2O_3$ x n $H_2O$. Where exactly this compound was formed they could not say, but to keep it from forming they wanted to create a more reducing atmosphere to the solution. This was achieved with the addition of sulphite ion, $SO_3^{2-}$, that would oxidise to, $SO_4^{2-}$ eliminating oxygen from the solution and leading to the formation of magnetite, $Fe_3O_4$, instead of haematite. The drawback of this is that the treatment has to be carried out in a sealed container to block out any further oxygen. Magnetite is a lot more compact that hydrated haematite, so less cracking and spalling would take place, and this compound seemed to have a further benefit of being far less likely to reabsorb chlorides back into the corrosion layers like hydrated haematite would do in concentrations greater than 500 ppm, according to North and Pearson.

However, already within a couple of years North and Pearson themselves report the alkaline sulphite treatment failing to stabilize some of the treated objects, putting the blame on the highly heterogeneous nature of the find material. They argued that thick graphitized corrosion layers found on marine cast iron were acting as a diffusion barrier, slowing down the rate at which chlorides could be extracted to the washing solution. They tested their hypothesis further, providing solid theoretical basis for their argument and simulating it with a test batch of graphitized archaeological samples. They also tested several of the various reagents available at the time, coming to the conclusion that the form of basic ion in the solution was even more important than the pH. Hydroxyl ion, $OH^-$, being small and mobile and thus able to penetrate into the microscopic pores and cracks within the crust on marine iron objects, was superior to the carbonate ion ($CO_3^{2-}$) that was also used to stabilize iron back then. They tested efficiencies of $LiOH$ in methanol and pure acetone as desalinating agents, but found out $NaOH$-water combination to be clearly the most effective one. (North & Pearson 1978b).

With their two articles North and Pearson had secured a very firm start for the alkaline sulphite treatment. Although originally developed mainly for cast iron from marine sites, it was soon employed on wrought iron objects from terrestrial sites, too (Rinuy &

Schweizer 1981; Rinuy 1979). However, it did not take long for things to get more complicated than they had originally proposed. Contrary to what they stated on their original article from 1975, some artefacts were reported to become fragile during treatment (Bryce 1979; McCawley 1984), when they were supposed to become more solid and robust thanks to reduction to magnetite. Also, the chemical formulas originally suggested by North and Pearson would be quite soon questioned, and parts of the theory have later been proven to be likely wrong – for example the presence of $FeOCl$ in archaeological objects was never confirmed (Gilberg & Seeley 1981; Kergourlay et al. 2010).

After the promising start in the late 1970's, it seemed in the late 1980's that active desalination methods were once again facing unresolvable problems. North & Pearson (1975a) had suggested that the formation of hydrated haematite would be the factor behind delamination and cracking reported on some objects in alkaline desalination baths, but further changes were reported to take place on objects facing the reducing conditions of alkaline sulphite treatments (Keene 1994, pp. 260-261; Selwyn & Argyropoulos 2005; Selwyn & Logan 1993). Considering the expenses in resources and time that the laborious desalination treatments would require it is no surprise that some conservators would question the whole point of desalination treatments.

Even with its drawbacks, the alkaline sulphite method, as well as a simpler soaking method using a sodium hydroxide solution without the sulphite part, have usually been the most reliable means to achieve good results in desalination (Al-Zahrani 1999; Costain & Logan 1985; Keene 1994; North & Pearson 1978b; Rimmer, Wang & Watkinson 2012; Selwyn & Logan 1993; Watkinson 1982, 1996). Even though North and Pearson were overly optimistic in their views of the effectiveness and safety of their method, alkaline desalination treatments have stayed in use to this very day and research around them continues.

Especially the German speaking world has distinguished itself in further tweaking the method, with conservators such as Susanne Greiff and Detlef Bach (2000) Catherine Schmidt-Ott and Niklaus Oswald (2006), Britta Schmutzler and Nicole Ebinger-Rist (2008) or Anne Rinuy (1979) and Francois Schweizer (Rinuy & Schweizer 1982b) providing the conservation field with their insights into the method as well as invaluable practical instructions on how to practically carry out the treatment in a meaningful and efficient way.

In Finland publications on desalination methods, and archaeological conservation in general, have been scarce. A thesis by Pia Klaavu from 1997 is one of the most comprehensive reviews of the mass conservation methods that were available for the Finnish speaking audience it the late 1990's, but naturally it doesn't include research that has been carried out in the 2000's. The alkaline sulphite method has been in use in Finland at the Turku Museum Centre (former Provincial Museum of Turku) since 2002, and few method descriptions, comments and experiences about the treatment have been published (Ehanti 2003; Saarinen & Hirvilammi 2008). At the time of writing, a collaboration of conservation professionals to critically review the current treatment methods in the light of the very influential research of the past few decades would be timely in Finland.

## 2.3    Contemporary research and future perspectives

Contemporary desalination research is marked by an ever increasing accuracy, which has inevitably led to an ever increasing complexity. New insights into corrosion chemistry and the treatments trying to topple these stubborn corrosion cycles are often achieved with modern, high-tech analysis equipment. These are little more than useless and expensive toys without a group of very skilled operators who know where the results of their analysis are based on, and what exactly the results can tell us. Very quickly the amount of information is too vast for a single researcher to handle and the interpretation of the meaning of the results will require collaboration of several professionals from different fields.

A very large and heterogeneous find material combined with the relatively low resourcing of the cultural heritage field are a tricky combination for a conservation scientist. Research has been spread over several different institutions all over the world, all too often involving only a few finds and few people over a very limited amount of time. This makes general conclusions, long-term follow-ups to determine treatment success rates and comparison between different researches difficult. Further improving the method would require long term research projects, preferably with international collaboration or at least a tight collaboration between conservators and corrosion scientists. The most usable results in the field of active desalination methods since the late 1990's have been achieved in institutions or research projects where these conditions have been met.

### 2.3.1 Canadian Conservation Institute (CCI)

At the CCI the publications of Dr. Lyndsie Selwyn and Dr. Vasilike Argyropoulos have made a strong contribution to the general development of desalination studies (Selwyn & Logan 1993; Selwyn & Argyropoulos 2005, 2006; Selwyn, McKinnon & Argyropoulos 2001). In addition to producing new research of their own, they have distinguished themselves as critical gatherers of current research that is extremely beneficial to a student in the subject as well as conservation professionals tackling with desalination problems (Selwyn, Sirois & Argyropoulos 1999; Selwyn 2004).

An archaeological Basque whaling site at Red Bay, Newfoundland, excavated from the late 1970's onwards, has produced a plethora of conservation publications for a single site. The strengths of research around Red Bay are that the iron material from the site is vast, and it was excavated in a planned and orderly manner, conservation starting already in the field. (Logan 1984; Selwyn & Logan 1993). The excavation produced a large amount of unstable iron which would be treated using different methods (McCawley 1984). This has allowed conservators to monitor their success or failure on a large group of objects, over a long period of time (Costain & Logan 1985; Costain 2000; Selwyn & Logan 1993). What is striking in the case of Red Bay is the clear effectiveness of alkaline desalination and storage methods over a relatively ineffective hot wash treatment.

### 2.3.2 Cardiff University

In Great Britain the Cardiff University has a long history of producing seminal research, and the work of Dr Stephen Turgoose (1982a, 1982b, 1985a, 1985b, 1993) has been continued by Professor David Watkinson. In addition to the research of Professor Watkinson (1982, 1983, 1996, 2010), several influential PhD theses have been delivered in Cardiff, including those of Dr Abdulnasser Al-Zahrani (1999), Dr Mark R.T. Lewis (2009) and Dr Melanie Rimmer (2010), as well as numerous jointly published articles (Rimmer & Wang 2010; Rimmer & Watkinson 2011; Rimmer, Wang & Watkinson 2012; Watkinson & Al-Zahrani 2008; Watkinson & Lewis 2005a, 2005b; Watkinson & Rimmer 2013).

The strength of Cardiff research tradition is its quantitative long term approach, where the aim is to treat large enough batches of objects to enable conclusions on such a large and heterogeneous research subject as archaeological iron. The three year EPSRC (Evidence-based Condition-Monitoring Strategy for Preservation of Heritage Iron) project, undertaken in 2007-2010 as a partnership project between Cardiff University and the

University of Manchester School of Materials as well as a Collaborative Doctoral Award of the Arts and Humanities Research Council (AHRC) have provided a solid foundation for the argument that even though alkaline desalination methods have their shortcomings, they pose a considerably lower risk fort the objects than unaddressed chloride contamination would do (Rimmer 2010; Rimmer & Wang 2010; Rimmer, Wang & Watkinson 2012; Watkinson & Rimmer 2013).

### 2.3.3    ODéFA project

Another interesting research collaboration took place in France where a collaboration between conservation-restoration workshops and scientists was set to further develop desalination processes and chemistry behind them. The two year program was called ODéFA (Optimisation de la Déchloruration des objets Ferreux Archéologiques). The program was initiated in 2007 (Réguer et al. 2007a) and final results were published in 2012 (Guilminot et al. 2012). In between results from various analyses were published, too (Guilminot et al 2008, 2012; Kergourlay et al. 2010, 2011; Réguer et al. 2007a, 2007c, 2007d, 2009; Rémazeilles et al. 2009, 2010). Originally it was intended to be a study concerning both marine and terrestrial iron, but unfortunately the 76 iron nails chosen for the study appeared to contain too little chloride to be of use in the study (Réguer et al. 2007a). Still, their structure, as well as the structure of the marine iron samples, could be examined with extreme detail with a combination of micro X-ray diffraction, micro-Raman spectroscopy and micro-X-ray absorption spectroscopy. Even with a very limited amount of samples (13 marine ingots Saintes-Maries-de-la-Mer site) the results are a very interesting in-depth window to what actually happens during a desalination process, and what factors the conservator should consider when choosing the right treatment. The most important findings of the ODéFA project include further confirming the role of $\beta - Fe_2(OH)_3Cl$ as a major chloride containing compound in fresh archaeological iron, as well as stressing the importance of proper handling of iron before the actual desalination treatment.

### 2.3.4    Subcritical treatment and the Warren Lasch Conservation Center (WLCC)

A new, very interesting development has been the deployment of subcritical fluid treatment on archaeological iron. The method involves heating alkaline treatment solution, usually 0,5 wt% $NaOH$, into 180 °C in circa 40-50 bar pressure. Under these parameters water is on a subcritical level, and its transport properties as a solvent are somewhere between a liquid $H_2O$ and a dense gas. Viscosity, density and surface tension are all

reduced, enhancing the water's ability to penetrate corrosion layers. This speeds up the penetration of washing liquid into the surface of the metal, as well as the diffusion based exchange of $Cl^-$ and $OH^-$ ions, shortening treatment times considerably. (Näsänen et al. 2012) It also seems to facilitate transformation of unstable and problematic chloride containing iron corrosion products into stable ones (Drews et al. 2012), resulting in very stable and virtually chloride free objects.

A lot of the research and experimenting has revolved around objects recovered from the U.S. civil war era submarine H.L. Hunley. Hunley was raised from the bottom in the year 2000. Since then it has been housed at a laboratory especially designed for it at the WLCC. As can be expected, raising an entire submarine has been an enormous under-taking with many serious conservation problems, chloride driven corrosion of the iron parts not the least one amongst them. (Näsänen et al. 2012).

Reduction processes taking place within the corrosion layers of the object during sub-critical treatment once again rise the question whether it is truly safe to use for fragile artefacts with loose flakes and delaminated corrosion layers, but at the time of writing no severe s have been reported even though some very badly corroded artefacts have been treated (González-Pereyra et al. 2013). No delamination or total fracturing of objects, as has been witnessed occasionally on objects in typical alkaline desalination treatments, has so far been reported under subcritical treatment.

In the light of the research done in the past ten years, subcritical fluid treatment sounds extremely promising. Probably the biggest setback of the method is the high initial cost, as the equipment required is expensive. However, if positive results keep coming up the method could have a lot of potential in the future. In case the equipment proves to be sturdy and relatively inexpensive to keep up, high initial expenses could be compensated for in the long run as treatment times are dramatically reduced and results become more consistently positive. (Gonzaléz et al. 2013, pp. 461-463)

Even with ten years behind it, subcritical fluid can still be considered a newcomer amongst the available desalination treatments. Long-term stabilization results are still needed, as well as more research on a wider number of treated objects to get a more thorough picture of how total the real level of desalination is, and what limitations the treatment has when it comes to composites, objects with surface treatments, inlays,

pseudomorphs etc. The time will tell if it proves to be the "holy grail" of desalination that it appears to be in the light of current research.

## 3 Iron corrosion in soil and in atmosphere and its connection to desalination chemistry

Iron corrosion processes are inevitably linked with the treatments that are aimed to stop them. Without a thorough understanding of what exactly happens in a corroding iron artefact there can be little hope of success when trying to bring these processes to halt. This fact has been acknowledged for over a hundred years - as long as there has been a scientific approach to conservation studies (Gilberg & Vivian 2001) - and it is a powerful testimony for the complexity of iron corrosion that the research is still ongoing. Because of the overwhelming amount of information and studies around iron corrosion in soil, the following chapter will concentrate on studies that have been most influential for desalination treatments, namely research centred on the chloride driven corrosion processes.

### 3.1.1 Basic reactions in iron corrosion

Iron corrosion in soil can be seen an electrochemical reaction, where iron surface works as the anode, producing ferrous ions, $Fe^{2+}$, that can further oxidise to ferric ions, $Fe^{3+}$. This oxidation process creates an excess of electrons that have to be passed on to maintain equilibrium. In the case of iron corrosion the final recipient of these electrons is oxygen that reduces on cathodic sites, or then the extra electrons can be consumed by hydrogen evolution, though the latter reaction is argued to have a minor role in the corrosion of archaeological iron. Both cathodic and anodic reactions take place in an electrolyte which in the case of buried objects is ground water. Once formed, the ferrous ions usually undergo a series of secondary reactions that vary greatly depending on the circumstances. In low pH and high oxygen contents iron objects can undergo a total mineralization, but usually a thick layer of complex iron corrosion products will precipitate on top of the iron surface, leading to the passivation of the iron surface. As a result the corrosion rate can be dramatically slowed down, allowing the survival of objects even over several millennia. (Selwyn, Sirois & Argyropoulos 1999).

### 3.1.2 Typical composition of a buried iron artefact

The parameters affecting iron oxidation in soil form an extremely complex system where all components are interlinked. Thus, up to this, day no total understanding of the whole corrosion complex has been formed, but in 2004 and 2005 (Neff et al.) a study of some 40 terrestrial iron artefacts was made to characterize their corrosion layers, and this characterization has proved to be very useful on most archaeological objects, even if the exact mechanisms of their formation is still under debate.

The studied objects exhibited a clear layered construction, where the surviving metallic core was surrounded by a layer of dense, dark corrosion products. This layer was named the Dense Product Layer (DPL) according to its characteristics, and if any details of the original shape or surface details of the object survive, they are usually retained in this layer. The DPL was found to consist of elongated strips of magnetite ($Fe_3O_4$) and maghemite ($Fe_2O_3$) held in a matrix of goethite ($\alpha - FeOOH$), all relatively stable compounds.

On top of the DPL a more voluminous layer of soil particles and minerals held together by iron oxidation products, the result of ferrous ions migrating through the DPL and precipitating in the soil, can be found. This layer is called the Altered Layer (AL) or Transformed Medium (TM) to stress its nature as a combination of matter tied together as a result of the corrosion process.

### 3.1.3 Chloride driven corrosion

The history of corrosion research is long, and several generations of scientists have already tried to shed more light on the various chemical reactions taking place in a buried iron artefact, and the many factors affecting them. Modern understanding of corrosion processes taking place in archaeological iron often trace back to the late 1970's and 1980's and many influential works from this period, such as studies by Turgoose (1982a, 1982b, 1985a, 1985b, 1993), Watkinson (1983), Knight (1982) and Argo (1981) are having a profound effect on conservation this very day.

They investigated the form and role of chlorides in the corrosion cycle of both marine and buried iron archaeological artefacts, revealing that they are drawn to the corroding iron objects by the weak positive charge created by the positive $Fe$-ions releasing from the corroding iron core. The chloride ions are not chemically bound to the object until it is dried and exposed to oxygen, and thus would diffuse back to the environment once

the iron core is completely mineralized and no further positive micro charge exists on the iron surface.

Turgoose (1985b, 1993) argued that the build-up of iron corrosion products on the iron surface will lead to a separation of cathodic and anodic sites, the conjunction of metal and first layer of corrosion products forming the anodic surface, whilst cathodic reaction would take place at the outermost conducting surface. This would strengthen the potential gradient drawing the chlorides to the iron surface.

Chloride also forms a soluble salt with iron, promoting its corrosion in the acidic environment close to the surface. Because this salt is soluble, iron will remain in ferrous form in the solution and is free to oxidise further and precipitate, often as oxyhydroxides through complex intermediate stages. Chlorides, on the other hand, don't precipitate and are free react with further iron atoms, creating a cycle where metallic iron is continually turned into ions and further into oxidation products. In soil this process is limited by the scarce supply of oxygen, but once out of the ground, oxygen levels rise dramatically and the corrosion cycle speeds up accordingly.

Because of their role as a counter ion in the corrosion cell, the chloride ions would not be free to leave the corrosion cycle as long as it is active. This explained why simple soaking techniques had often failed to dechlorinate objects in the past (Selwyn & Logan 1993; Watkinson 1996), as the hot water treatments would often simply hasten the corrosion process in the core, binding the chloride ions to the surface even more tightly. In the worst case, soaking in water could prompt chlorides from passive, stable positions in the corrosion crust to migrate to the vulnerable metallic iron surface, making them less stable (Keene 1987a).

Upon drying chlorides would precipitate. Where they are present in high concentrations ferrous chloride, $FeCl_2$, would form. This compound is highly hygroscopic and can deliquescence in an RH greater than 55 %, creating very acidic droplets rich in $Cl^-$ and ferrous ions. (Turgoose 1985a). This phenomenon is known as the "weeping iron". $FeCl$ is also not a very stable compound, and it is known to easily oxidise further into oxyhydroxides, especially α-oxyhydroxide and β-oxyhydroxide, depending on the chloride contents. These compounds are very voluminous compared to metallic iron and cause stress in the corrosion layers, which often leads to cracking and spalling. They also have an ability to bind further chlorides onto the surface, and the chloride infestation persists.

### 3.1.4   The role of β-oxyhydroxide, β-FeOOH

Another post 1970's revelation was the central role of iron β-oxyhydroxide (β-FeOOH), also called akaganéite, in the structure and corrosion processes of chloride infested iron. Synthetic akaganéite was first recognised in 1935 (Weiser & Milligan) and recorded for the first time on archaeological iron in 1977 (Zucchi, Morigi & Bertolasi). Akaganéite is an iron corrosion product that forms on archaeological object after the excavation, once chloride-containing corrosion layers dry and are subjected to oxidation. Researchwise it was associated with chloride infested iron at a very early stage, but its exact role was debated for a long time, and this debate is partly still on going.

It was discovered that chloride (or fluoride, but this is very seldom the case in archaeological objects) was necessary to hold up the crystal lattice of akaganéite, so its formation was a certain sign that chloride was present in the object. However, to play a part in the corrosion cycle of an iron object, chloride has to be available as a free ion, so, chlorides that would remain bound into the crystal lattice of akaganéite, posed no threat to the object.

Still, akaganéite would pose a possible threat to the objects for at least two reasons. First, it has a significantly lower density and thus a greater molar volume (Selwyn, Sirois & Argyropoulos 1999, pp. 220-221) than a lot of the other corrosion products encountered in archaeological iron, especially those within the DPL. This means than when it is formed, and it is often formed right down by the surface of the metallic core of the object where a major part of the chlorides are situated, too, it causes cracking, spalling and delamination of the corrosion layers. As details of the original surface, as well as pseudomorphs, details of surface treatments or surviving original organic materials are usually found within these corrosion layers, in case they have survived in the first place (Cronyn 1990, pp.182-188), having them flake of uncontrollably can lead to a disastrous loss of the object's value as an archaeological artefact.

Another reason for concern in connection with akaganéite is the fact that it is known to be unstable (Rimmer 2010 pp. 46-48; Thickett & Odlyha 2013). Research has indicated that it has a tendency to slowly transform into other, more stable corrosion products that would no longer incorporate chlorides in their crystal lattice, leading to the release of the

chlorides originally trapped within the lattice of the transforming akaganéite. These chlorides would then be free to contribute to the corrosion cycle of the remaining iron core, causing renewed active corrosion. Thus, akaganéite was seen as an unstable "chloride reserve" that would cause instability in the objects in the long run. In addition to this, chlorides trapped at the surface of akaganéite crystal lattice seem to pose a serious threat to iron, because untreated akaganéite in itself has been proven to cause aggressive corrosion of iron (Watkinson & Lewis 2005), but this effect could be dramatically reduced by washing, which could indicate that surface-bound chlorides can be exchanged to $OH^-$ ions (Réguer et al. 2009).

Akaganéite is a difficult substance also because even though it is unstable, it is very stubborn, and would resist reduction or phase transformation to other compounds in both alkaline desalination baths as well as in electrolytic reduction treatments. When transformation to other compounds was recorded - by heating for instance - the method would often be considered too drastic for fragile archaeological finds (Ståhl et al. 2003). Also, even though reduction has been achieved in laboratory conditions, there is no guarantee that it would happen in the complex corrosion layers of actual archaeological objects.

### 3.1.5   The role of β-oxychloride, β-Fe$_2$(OH)$_3$Cl

Long-term storage of nuclear waste was debated in France in the early 2000's. Planned nuclear waste containers contained steel parts, and it had to be assured that they would survive in the ground for several millennia. This evoked an interest in the corrosion processes observed in archaeological iron and a very powerful combination of microscopy–energy-dispersive X-ray (SEM–EDX) analysis, X-ray micro-diffraction under synchrotron radiation (µXRD) and micro-Raman spectroscopy (Neff et al. 2004).

This allowed very accurate detection of corrosion products to be carried out and lead to the discovery of a new corrosion product that contained chlorides on a significant scale: β-oxychloride, β-Fe$_2$(OH)$_3$Cl (Neff et al. 2005). It has not been reported on finds that have had ample time to oxidise, which is no surprise as it is known to be unstable in oxidised environments. However, in the anoxic, chloride rich environment that prevails within the pores and cracks of buried archaeological iron, the conditions seem to favour its formation. Soon β-oxychloride would be recognized on marine archaeological material, too (Réguer et al. 2007d), and results of the ODéFA project suggest that it has a crucial role in desalination processes, discussed in detail in chapter 9.1.

## 4    Background of the Hangastenmäki conservation project

### 4.1    The site

Hangastenmäki is located in Hakoinen, in the municipality of Janakkala in Tavastia Proper, Finland, on the southwestern bank or river Räikälä, some 800 m southwest from Janakkala church. Some 120 metres above the sea level and some 25 metres above the surrounding terrain, the hill stands out in the landscape. Hangastenmäki is approximately 230m x 170m and it is elongated on a NW-SE –orientation, roughly parallel to the river Räikälä. The slopes of the hill are largely open outcrops, but on the top a thin layer of soil largely covers the bedrock. The north-eastern, north-western and south-western slopes of the hill are very steep, practically impassable, whilst the south-eastern slope is less steep and can be climbed up. (Rantanen & Tiilikkala 2016b, *in press*)
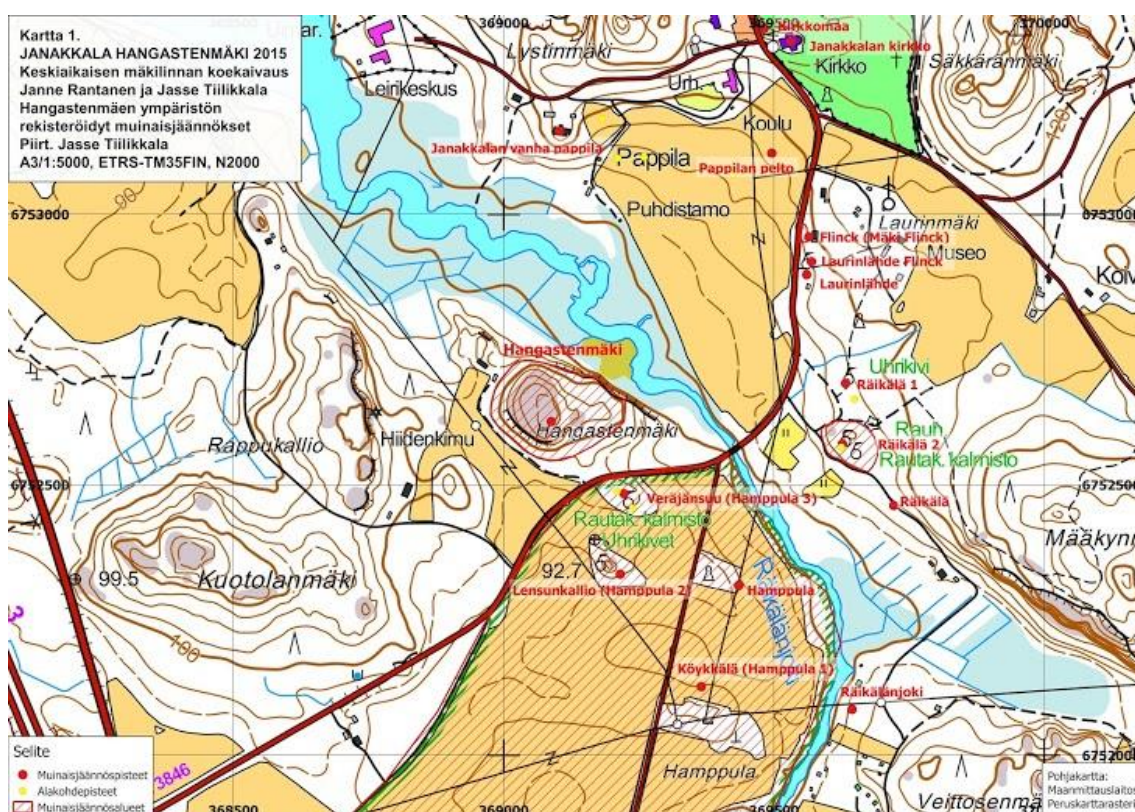


Figure 1. A map of the Hangastenmäki and its surroundings. Protected archaeological sites marked with red. Map by Jasse Tiilikkala (2015).

About one kilometre south from Hangastenmäki is situated one of the best known hillforts in Finland, Hakoinen (National Bureau of Antiquities (NBA) reg. no. 165010040). Next to the Hakoinen hillfort is situated Hakoinen manor that traces its history back to the middle ages and possibly even to the Iron Age. Janakkala church, the Church of St. Lawrence, was built by the early 1500's, (Hiekkanen 2014, pp. 304-307). Together Hakoinen hillfort,

manor and the church of St. Lawrence form a conjunction of power that speaks for the importance of the place during mediaeval and prehistoric times, and the landscape around Janakkala hillfort is littered with archaeological sites from the iron age, including several cemeteries (e.g. Veräjänsuu (Hamppula 3) NBA reg. no. 165010039), and cairn and sacrificial stone complexes cairns (e.g. Räikälä 1, NBA reg. no. 165010033, Köykkälä (Hamppula 1) NBA reg. no. 165010037) (Rantanen & Tiilikkala 2016b).

### 4.1.1 Discovery of the hillfort in 2014

It is strange that a hillfort managed to evade detection for so long on such an archaeologically active area in Tavastia Proper, but a possible explanation to this was presented by Rantanen & Tiilikkala (2016a) when they reviewed the research history around the site. An unfortunate misinterpretation by Berit Boström from mid-1900's stating that the stone settings at the top were formed when space for a potato field was cleared at the top of the hill in early 1900's (Boström 1942, p. 48) was probably never properly challenged, but would live on in consecutive archaeological inventories. It is possible, too, that even with the relatively clear and visible fortifications on the Hangastenmäki, the idea of a new hillfort, only a kilometre away from the one of the best known hillforts in Finland in an area that has seen much archaeological activity, was too much for many and the threshold to announce the site was high.

The interpretation had to be re-evaluated when a member of a metal detectorist group called Kanta-Hämeen menneisyyden etsijät (Seekers of the past of Tavastia Proper), Reijo Hyvönen, visited the site with his detector on 3 August 2013. On the first visit only relatively commonplace items were recovered: 9 nails, an iron shoe reinforcement, and two objects that would not be identified at the time of recovery. Later, on 22 April 2014 another member of the group, Mikko Mäkelä, visited the site, and this time more interesting objects, including a spearhead (KM 39994:1), started to come up. After these discoveries the group made another excursion to the site on 23 April 2014, this time with more people, and recovered several iron objects from the mediaeval period and the late Iron Age: horseshoes and horseshoe nails, spurs and spur fragments, bodkin arrowheads, knives, a sword pommel and a collection of less recognizable fragments. At this point the group announced their findings and the site was inspected by archaeologists in collaboration with the metal detectorist group. (Tiilikkala & Rantanen 2014). They also handed over their metal finds to the NBA.

## 4.1.2 Excavation plan

By Finnish standards the discovery of a new hillfort was significant and called for further attention. The archaeologists who were present at the inspection of the site, MA Janne Rantanen and BA Jasse Tiilikkala, applied for a grant along with their professor, JP Taavitsainen, for a small-scale research excavation in Hangastenmäki. This was granted, and thus the excavation plan was set in motion.

At this stage the Author began to collaborate with the research group. Hangastenmäki was an interesting site from a conservation point of view, because it had yielded several metal detector finds during autumn 2013 and spring 2014. These had been delivered to the NBA, catalogued and stored as found, without any further measures. This meant that they had had plenty of time to dry and oxidise at the NBA magazines, whilst the upcoming excavation was extremely likely to produce more finds. These could be recovered fresh from the ground, and this would allow an old hypothesis – that fresh, non-oxidised finds would release their chlorides more readily and completely than old, oxidised ones. (Gilberg & Seeley 1982a; Selwyn, Sirois & Argyropoulos 1999). It was decided that the Author would participate in the excavation and recover metal finds first hand to make sure that they arrive into the laboratory in the desired condition.

## 4.2 Frame and research questions of the thesis

The excavation permission had to be applied from the National Bureau of Antiquities (NBA) and the rules stated that all finds would be turned over to the collections of the National Museum of Finland (NBA decision MV/100/05.04.01.02/2015). Thus it was decided that the best most reasonable place for their conservation was the Conservation Laboratory of the said museum, and a permission was sought to do the conservation of the find material using the facilities of the Conservation Laboratory. This was granted (NBA Decision MV/100/05.04.01.02/2015) It was decided that the thesis would concentrate on the following questions:

1. Is there a difference in the behaviour during desalination of old, oxidised finds compared to new, fresh finds? If, then what might explain these differences?
2. What kind of desalination method would be, in the light of the current research, the most reasonable one for the types of finds made in Hangastenmäki?

3. How easily could the chosen method be implemented with the equipment and reagents available at the Conservation laboratory of the National Museum of Finland in the future?

Conservation department was planning to move in to a new facilities and the moving provided a good opportunity to re-evaluate different methods at the department. One important area of critical evaluation and development was desalination of iron, which largely depended on aqueous boiling. As expectable, the results of this method were inconsistent and a new method had been in the planning for some time already. This thesis gave one more opportunity to consider the different options available and test them out in practice before bringing any method out on a larger scale.

4.3  Excavation

The excavation on Hangastgenmäki took place on 5.-19 October 2015. The first week, 5.-9 October was used surveying, mapping and clearing the place from foliage. This week produced two unintentional finds, however, a horseshoe nail (KM 40551:81) very close to the surface on 6 October 2015 and an iron fragment (KM 40551:28) on 9 October 2015. The Author did not participate in the excavation yet this week, but instructions were given to keep the finds moist by packing it into a resealable, low-density polyethylene bags (Minigrip®) with an adequate amount of soil, and storing them refrigerated. It was made sure beforehand that the fridge in the lodging place would not contain a freezer box that could lower the RH inside.

For the next two weeks author participated in the excavation in a mixed field conservator / field assistant role. Author's responsibility covered the metallic find material and decisions related to the excavation were at the responsibility of Rantanen and Tiilikkala. A member of the metal detectorist group, Reijo Hyvönen, volunteered on the excavation, and worked on site part time. He was invaluable with his metal detector, as he could point out the positions of most objects beforehand, allowing their safe and controlled recovery.

The aim of the excavation was to reveal and identify possible structures on the hillfort, but leave them intact. A test trench, originally 1 m x 10 m in size was opened close to the southern edge of the top of the hillfort, where a possible large stone setting was recognized under the topsoil. This trench, called test trench 1 (Koeoja 1) was expanded

during the first week and in the end it covered an area of ca. 28 square meters. The soil on the trench was black, highly organic and often stained with soot. The area was excavated to a depth of c. 5-10 cm. At this depth, either a firm layer or a stone setting was met, and excavating was stopped. This trench yielded 8 pieces of metal finds, KM 40551:1-8, all of them iron. Most of them could be recognized already in the field, except fragmentary KM 40551:6, and in general the material seemed to have survived relatively well. The corrosion layers were compact and not too thick, and no signs of flaking, cracking or spalling were visible.

During the excavation, a pair of trees recently felled by the wind were investigated at the north-eastern side of the hill. The roots had raised a considerable bulk of soil with them, as is typical for full-grown spruce trees. The now vertical lump of soil was discovered to be black with soot and full of fragmentary iron finds and pieces of slag. The excavation was re-prioritised here, because it was clear that in a couple of years erosion would turn the soil into a disarranged heap of dirt, whilst now it was still in perfect order, only that the layers were vertical instead of horizontal.

It started to seem likely that the two trees had ripped up remains of an ancient smithy with them. This was further confirmed by hammerscale that was discovered in abundance at the site with a magnet. Altogether the smithy provided 36 metal objects or fragments of objects. These included some very interesting recognizable objects, too, including a sizeable bodkin arrowhead (KM 40551:52). Here two copper metal objects were recovered as well, a small buckle (KM 40551:51) and a bent piece of copper metal sheet (KM 40551:44). The soil on site was black and thick with soot, but mineralized and not very rich in organic material. The iron was noted to be in considerably worse condition than it was on test trench 1, with clearly visible deep cracks and thick and swollen corrosion layers. This raised some concerns as well as some questions. Possibly the fact that these finds were recovered from the roots of two fallen trees was the explanation to their condition, as soil between the roots had had ample time to dry, or perhaps it was in the sandy soil that would make a more oxygenated conditions for the artefacts in the first place. Whatever the reason, their bad condition had to be taken into account when choosing a desalination method.

Towards the end of the excavation a further test trench, test trench 2 (Koeoja 2), was opened through the base of a probable fortification on the western side of the hill. This trench yielded two more iron finds, a relatively slim bodkin arrowhead (KM 40551:21),

recovered in-situ from topsoil, tip towards the ground, and a horseshoe nail fragment, (KM 40551:2). The condition of these two finds resembled the condition of those from test trench 1.

All the metal finds received the same treatment in the field: they were photographed in situ if discovered from a vertical plane and packed with adequate amount of soil into resalable low-density polyethylene bags (Minigrip®). Most of the finds from the smithy, however, were not, so they were not photographed in the field. Most of the bags were further moistened with a tap water spray to make sure that the finds would remain moist until desalination could be commenced. In the lodging they were packed into a bigger plastic container that was stored in the fridge to minimize evaporation and to slow down corrosion processes.

It was known that further moistening was a threat for the objects because extra water would act as a catalyst for corrosion. This was considered a reasonable trade-off, however, because drying out of the objects before desalination was seen as a greater risk, especially since it was clear that they would be treated reasonably soon. The amount of water in the bags was also kept at a level where the soil was well moist, but no so wet that the water would be running inside the bag.

There was no way to monitor the conditions at the fridge in the lodging for the duration of the excavation. As stated before, it was specifically checked for a freeze-box, because water depositing on the surfaces of the freeze-box could lower the RH in the fridge, and neither the polyethylene bags nor the plastic container box, even though it had a lid, could be trusted to be airtight. The condition of the finds was regularly checked, and water was added if the soil in the bag felt like it could be about to dry.

An exception to this pattern was made on three iron finds that were detected as slag on site (KM 40551:73-75). These were allowed to dry and would accompany the rest of the finds at a later stage in conservation.

A further 1m x 1m test pit was opened close to a spot where a sword pommel (KM 39993:1) had been found by Hyvönen, but this test pit produced no finds or archaeological features. A third test trench, (koeoja 3) was also opened during the excavation, but this produced no metal finds that would have required conservation. All metal finds were recovered by the end of Thursday 22 October 2015 – altogether 46 metal finds, three of

which were recorded as slag at this point. The 43 finds correctly recognized as metal finds were taken to the cold storage facilities at the magazines of the National Museum of Finland on the final day of the excavation, Friday 23 October.2015. A detailed excavation report is provided by Rantanen and Tiilikkala (Rantanen & Tiilikkala 2016b).

## 5    Documentation before treatment

### 5.1    Photography

The examination of the finds started with photography on 25-26 October 2016. The objects from the 2015 excavation were photographed in the condition they were when found. Only the most bulky soil particles were gently brushed off their surfaces to reveal the shape of the objects. The finds were photographed wet, and the glare on the surfaces caused some slight problems. A symmetrical lighting setup was used, which brought out the silhouettes of the objects quite nicely but caused the pictures to look somewhat flat. This was partly compensated by the wet glare on their surfaces that gave at least some impression of their form.

Figure 2. Before conservation –pictures studio setup, symmetrical lighting.

The metal detector finds were photographed on 29 October 2015 in the condition they were stored, without any preliminary cleaning. Several of the finds had loose flakes in their storage containers, and a decision was made not to photograph these with the finds, as mostly they were fallen out pieces of the Altered Medium and contained no parts of the original surface.

The pictures were taken in a raw format with a Canon EOS 5D Mark III and later edited in Adobe Photoshop CC. White balance was set with the help of a grey target and automated lens corrections were carried out. The pictures were sharpened and the histogram was adjusted to enhance contrast and bring out further details.

5.2   X-ray investigation

Especially, as alkaline desalination treatment was planned, it was crucial to carry out an X-ray investigation of the material before proceeding any further. The material was X-rayed with the digital X-ray unit of the National Museum:

Eresco MF4 portable X-ray generator
CRx Vision, Computed Radiography scanner

Rhythm RT, version 6.0.47.0, reading program
Rhythm Review, version 5.1 (Spa12) (0.93), viewing program

X-ray investigation of the metal detector finds took place on 27 October 2015 and 3 November 2015. Finds from the excavation were X-rayed on 5 November 2015, except for KM40551:73-75 that were recognized as iron post excavation, and had not yet arrived to the conservation lab. They would be X-rayed on 5 February 2016. The images were post-processed with a Flash-filter found on Rhythm Review viewing program. This greatly enhanced the clarity of the pictures, bringing out details that otherwise would have been difficult or impossible to spot. Both the original unaltered and the Flash-filtered pictures were saved. X-rays of the finds can be found on appendix 9.

In addition to the structure and technical details, an eye was kept at all features that would affect desalination: materials, state of corrosion and general integrity of the finds. It was revealed that even though most of the material had an iron core left, corrosion had advanced pretty far in many objects, especially on those acquired on the 2015 excavation. Solder was also revealed from a barrel padlock bolt, KM 39993:3. A spot was cleaned down to the metal surface to recognize the type of the solder, and based on its yellowish orange colour it was identified as brazing.

The biggest revelations of the X-ray investigations were precious metal decorations on objects KM 39993:1 and KM 39994:1 (appendix 9, pp. 1, 4). The finds, identified as a Petersen T1-type pommel (Petersen 1919, pp. 150-153) and a K-type spearhead (ibid pp. 31-33) respectively, were metal detector finds recovered on a plateau on the south-eastern slope (KM 39993:1) and close to the south-eastern edge of the hilltop (KM 39994:1) (Tiilikkala & Rantanen 2014, p. 8).

A twisted and straight precious metal wire could clearly be seen on the objects. This type of decoration where precious metal wire, usually silver or copper alloys, is inlayed into a chiselled iron surface, was typical for the late Iron Age (Moilanen 2015, pp. 275-277). Only straight wire of very homogenous width could be seen on the pommel KM 39993:1 whilst a pattern of alternating rhombic decoration of straight and twisted wire was observed on the socket of KM 39994:1.

## 6   Conservation plan

### 6.1   Desalination treatment

With photography, X-ray investigation and sensory investigation of the material, enough information was gathered for a conservation plan. Special consideration was given for the desalination method since the state of the finds and their materials play a crucial role when choosing the most suitable treatment.

Especially problematic were the objects of a very fragmentary nature and those containing more than one type of metal. These included the decorated objects KM 39993:1 and KM 39994:1 where all changes of the precious metal surfaces, including discoloration, were undesired. The task of finding a suitable desalination method was not easy as the literary sources are very silent and vague when it comes to composite objects, or objects with copper alloys.

There are several different desalination methods available, all with their pros and cons. Within the scope of this thesis the different options had to be narrowed down to those available at the Conservation Laboratory of the National Museum, and thus the options for ionophoresis or soxhlet extraction were ruled out, even though especially the latter one has been used for fragile finds up to these days (Logan et al. 2010 p. 130; Scott & Seeley 1987). A desiccated storage was also ruled out, as the RH required by chloride infested iron (under 12% according to a recent study by Watkinson & Lewis (2005b)) cannot be maintained at the storage facilities available at the National Board of Antiquities. The remaining realistic options were alkaline sulphite, sodium hydroxide, and aqueous boiling, the standard desalination method still in use at the National Museum.

Aqueous boiling has the advantage of being suitable for a large variety of materials. It is also a relatively short, even if also a relatively laborious treatment. In 1982 Watkinson

was working on a presumption that aqueous boiling would be more effective at removing chlorides than the either lithium or sodium hydroxide solutions. In the light of the subsequent research this claim is erroneous, as aqueous boiling, especially if used alone, has one of the lowest success rates of all desalination methods (Costain & Logan 1985; Keene & Orton 1985; Selwyn & Logan 1993; Wakinson 1996). It has also been reported to be a relatively dangerous process as objects have a tendency to get damaged because of the repeated changes in temperature as water in the container is changed, and gas generation (North &Pearson 1978b; Keene & Orton 1985)

Alkaline methods have a long history behind them and in most studies they have been found to be the most steadily successful treatment option for chloride contaminated iron (Al-Zahrani 1999; Costain & Logan 1985; Keene 1994; North & Pearson 1978; Rimmer, Wang & Watkinson 2012; Selwyn & Logan 1993; Watkinson 1982, 1996). However, the results are inconsistent and stabilization cannot be guaranteed, but then again this is the case with any desalination method. A bigger problem with alkaline treatments is that they are not considered entirely safe, as the alkaline environment has a tendency to damage especially organic materials associated with the finds, as well as cause changes in non-ferrous metals.

Unfortunately, detailed information of the risks related to alkaline desalination methods are hard to come by and often the warnings are anecdotal. Breaking up of objects with little remaining metallic core or damages to their corrosion layers have been reported, (Ehanti 2003; Keene 1994, pp. 260-261; Koh & Skogstad 2015; Selwyn & Logan 1993, p. 805; Selwyn & Argyropoulos 2005) but probably the most comprehensive study on risks associated with alkaline methods has been carried out by Melanie Rimmer (2010, pp. 157-166).

The study by Rimmer clearly brings out the fact that, even though there is a lot of data indicating that changes do take place in the structure of the corrosion layers in alkaline environments, the exact nature of these changes are not understood. She also concluded that major changes in the objects are rare, and it can be argued that consequences of not treating the objects are likely to be far more severe, often leading to a total disintegration, than carrying out the desalination treatment even if the objects suffer some damages in the process.

The objects that are in the worst condition at the beginning of the desalination process are at the greatest risk (Wang et al. 2008, p. 72). Very fragmented material is in any case very difficult to work with and no good solution is available. Often a major part of the damages occur post excavation as the objects are allowed to dry and then they are exposed to a fluctuating atmosphere, resulting in the precipitation of voluminous corrosion products in the iron-DPL interface (Selwyn, Sirois & Argyropoulos 1999, pp. 220-221; Watkinson 2010, p. 400).

This also means that dry storage, which is often presented as a safer, "passive" option to active desalination methods (Cronyn 1990, pp 196-200; Knight 1997) also causes changes in the objects, like cracks and fractures in the corrosion layers, even if this effect is less pronounced in desiccated environments than in storage areas with fluctuating RH. These changes could be considered damages, too, as stated also by Cronyn (ibid). This point is even more pressing as desiccated storage seems to be giving very poor results in treatment efficiency compared to desalination (Keene 1994). As stated above, it has also been found that chloride infested iron can be unstable in an RH higher that 12 % (Watkinson & Lewis 2005b) and keeping up to such rigorous condition requirements for any extended time is very labour and energy intensive.

In the light of this research it started to seem likely that carrying out the alkaline desalination of most of the material, even if it was in a highly corroded state, would pose a smaller risk in the long run than aqueous boiling or desiccated storage. However, the question of silver and copper metal alloys remained and unfortunately the sources were even more scattered and contradictory in regard to copper alloys than they were to possible damage on fragile finds.

The scarce sources are very unanimous when it comes to silver alloys, stating that they should survive the alkaline desalination treatment unharmed (Keene 1996 p. 262; Rinuy & Schweizer 1982a, p. 45; Schmidt-Ott & Oswald 2006, p. 128). The sources also state that copper alloys have survived the treatment without damage, or with only superficial changes. Keene (ibid) mentions that a thin black layer of patina can form on copper, but this can be easily removed during the following conservation procedures. There are a couple of sources stating that all non-ferrous materials should be excluded from alkaline treatments, but they are associated with mass treatment of iron directly after excavation, and they are instructing conservators to use caution and inspect their material carefully before commencing with treatment rather than specifically warning about changes taking

place on copper alloys during treatment (Bryce 1979, p. 20; Keene 1987a, p. 40). For this reason their value here are limited.

The only sources specifically mentioning damage on copper alloys are papers by Schmidt-Ott and Oswald (2006 p. 128) and Bach and Greiff (2000 p. 328) where changes occurring on copper are discussed in detail. They reported colour changes on copper alloys and its corrosion products and even copper precipitating on other metals. Bach & Greiff stress that tin and especially zinc get chemically attacked in an alkaline treatment solution, zinc also when it is present in copper alloys, though this effect is unlikely to be very strong. Still, especially in the case of decorated objects from Hangastenmäki, this would be undesirable.

Because sources were so inconclusive when it comes to reactions of copper in alkaline desalination treatments Vegard Vike, an archaeological objects conservator at the Museum of Cultural History in Oslo was contacted. In a personal e-mail (11 November 2015) he commented that objects with metallic copper alloys usually survive alkaline desalination with minor changes. Vike mentioned the formation of a thin black patina on copper surfaces, but this layer would be easily removed with air abrasives, as also stated by Keene (1996, p. 262).

As also stated by Bach and Greiff (2000, p. 328) above, of more concern would be brass surfaces that could change colour from bright yellow typical of brass into reddish brown typical of pure copper. This was likely due to de-zincing of the surface in an alkaline environment, but based on his practical experience and a small scale experimentation, Vike stated that the de-zinced layer would be likely to be only film thin, and the natural brass colour could be brought back with a gentle use of air abrasives.

Another cause of concern would be areas where very little metallic copper survives, because copper corrosion products seem to be more vulnerable to changes in an alkaline environment than metallic copper. Thus discoloration and damage would be more likely to take place on areas of very thin and thoroughly corroded copper surfaces, or on thicker copper parts with lots of porous corrosion products, as also stated by Schmidt-Ott and Oswald (2006, p. 128).

Once all outcomes were thoroughly considered it was decided to use alkaline desalination methods for all of the material that would be chosen for desalination, including the

decorated finds. It was reasoned that this course of action would pose less of a risk for the objects than using more unreliable aqueous boiling, or leaving them untreated, especially as signs of chloride infestation could be seen on a lot of the material and breakage had already begun on many metal detector finds, including the decorated objects (KM 39994:1 and especially KM 39993:1). Also, monitoring of the objects would not be possible after the treatment within the scope of the conservation project, so it would be safer to implement a method with a high success rate from the beginning.

The decision to use alkaline desalination was also influenced by the fact that the finds from 2015 excavation had been stored wet, and even though many of them were in a relatively fragmented state, their corrosion layers were still stable and they were structurally relatively sound. It was unlikely that lots of corrosion products would have precipitated within the layers, so they were likely to survive the treatment better than finds of a similar condition that would have been allowed to dry after the excavation.

## 6.2    Aerated or deaerated alkaline treatment

Practically two alkaline desalination methods were available for the conservation project at hand: the alkaline sulphite treatment or soaking in a dilute sodium hydroxide solution. The alkaline sulphite treatment differs from a simple soaking in dilute sodium hydroxide by the addition of sulphite ions into the solution. Sulphite ion, $SO_3^{2-}$ that was originally introduced to make the conditions in the solution more reducing (North & Pearson 1975a, p. 4) but later studies have questioned its role as a reducing agent and stressed its role as an oxygen scavenger (Turgoose 1982, p. 100). Al-Zahrani (1999) demonstrated that deaerated solutions of sodium hydroxide are more effective in removing chlorides from archaeological iron objects than similar aerated solutions, probably because the lack of oxygen will stop corrosion on the iron surface and release Cl⁻ ions form their counter role in the corrosion cycle. Even though Al-Zahrani's astonishingly high chloride extraction rates could not be later replicated, further studies have confirmed deaerated sodium hydroxide's effectiveness as a desalinating agent (Schmutzler & Eggert 2011; Rimmer, Wang & Watkinson 2012, Watkinson & Al-Zahrani 2008). Even though it seems that the role of the sulphite ion is simply to remove oxygen from the treatment solution, its exact role is still unknown. It is possible that it is playing a part in some reducing reactions in iron objects, at least on fresh marine finds that are not allowed to dry (Gilberg & Seeley 1982a).

Electrochemical measurements of iron finds in sodium hydroxide solutions have demonstrated that the finds undergo rapid changes at the very beginning of the treatment. Although the exact nature of these changes are not clear, it is likely that they are oxidation-reduction reactions taking place in the corrosion layers of the objects, involving metal, magnetite and $Fe^{2+}$ compounds. (Hjelm-Hansen et al. 1992, 1993). If the reducing effects of alkaline treatment methods can be attributed to the hydroxyl ion, rather that the sulphite ion, then the alkaline sulphite treatment might actually be gentler to the objects because the sulphite ion negates the effect of the ongoing corrosion that has been demonstrated on aerated sodium hydroxide solutions, especially if chlorides are present (Watkinson 1982).

In the light of the research it seemed that desalination with sodium hydroxide deaerated with nitrogen would combine the good qualities of alkaline treatments, as it would exclude the somewhat troublesome $SO_3^{2-}$ and the $SO_4^{2-}$ ions from the solution. This would create a potentially safer environment for the objects under treatment and also make chloride content determinations from the desalination solution easier, because sulphite ions have a tendency to interfere in the process. In most cases they have to be oxidised to sulphate before any accurate measurements can be made (e.g. Selwyn 2001, p. 1; Wang et al. 2008, pp. 68-69). It would also make disposal of the treatment solution easier, as large amounts of sulphites should not be allowed into the sewage.

This option was examined further, especially since the Conservation Laboratory already possessed a vacuum oven with a pre-set ability to create a deoxygenated atmosphere with an inert gas, such as nitrogen. Ensuring an oxygen free atmosphere would have required a slight nitrogen overpressure in the vacuum oven and a weak flow of nitrogen through the system. This would have demanded nitrogen exiting the system to be safely ventilated out of the room, because even though nitrogen in itself is not dangerous, in large quantities it can replace oxygen in air quite easily and become life threatening. There was no time to do a thorough risk-assessment for this treatment so it was abandoned for the time being, but in the future it could be fruitful to reconsider it at the Conservation Laboratory when more time is available.

Assessing the suitability of oxygenated or deaerated alkaline solution was somewhat inconclusive. The sources are conflicting when it comes to aggressiveness of the treatment solutions, some claiming that corrosion continues in an aerated sodium hydroxide solution, or that corrosion products could precipitate into the pores of the object and form

a diffusion barrier. On the other hand preparation, chloride content measurement and disposal of alkaline sulphite solution is more complicated than same procedures carried out for a sodium hydroxide solution. Both methods are giving very promising results, aerated sodium hydroxide even slightly besting alkaline sulphite in a post-treatment stability comparison carried out by Keene (1994).

In the end alkaline sulphite was chosen for this project, because there is very little data to back up the claim that it would be more aggressive to iron finds or other metals, while its chloride extraction rate has steadily been at the top of treatment comparisons. Also, the method has a long history and several surveys of objects treated with various methods have shown that iron that has been treated with alkaline sulphite has a very high survival rate.

A toned down version of the treatment, introduced by Schmidt-Ott and Oswald (2006) was chosen because according to the study it has the same effect as stronger treatments, but is safer for the environment and conservators and makes treatment of the waste solution easier. The chosen method is otherwise similar to that introduced by North & Pearson (1975a) but involves the use of a 0,1 M $\mathrm{NaOH}$ (4g/l) and 0,05 M $\mathrm{Na_2SO_3}$ (6,3 g/l) solution – respectively one fifth and one tenth of the proposed original strengths. Also, no barium hydroxide treatment would be carried out as this would introduce another chemical to the object, and the possible residual chemicals from an alkaline sulphite treatment itself are anyway found to be relatively safe (Rimmer & Watkinson 2011).

## 7   Conservation

### 7.1   Preparing the material for desalination

Practically all of the iron material was chosen for desalination. A buckle, KM 39994:8, was initially omitted because it seemed to be in a very corroded and fragmentary shape. An iron fragment, KM 45551:70 was also omitted from the desalination treatment because according to the X-ray inspection (appendix 9, p. 10) it does not possess an iron core, and would thus be stable without treatment (Watkinson 1983).

The metal detector finds were put into treatment as they were, without preliminary cleaning, except for the pommel KM 39993:1 that was covered by a particularly thick layer of dry soil. This was carefully picked off with a scalped and a bamboo stick, as it would

have formed an unnecessarily thick diffusion barrier, introduced lots of material to the treatment solution, and in any case fallen off within the first couple of baths. Also, the grooves connecting the holes to each other were preliminarily cleaned, paying extra attention around the surviving piece of silver wire cord in the groove. Once the wire was visible it was consolidated with a 20% Paraloid B-72 in acetone. Extra care was taken to expose as little of the silver surface as possible, as exposed precious metal surfaces have a tendency to get stained or discoloured in desalination solutions and adhering corrosion seems to protect them from this effect (Klaavu pers. comm.; Vike ers. comm. 11 November 2015). After the procedure the pommel was photographed.

The insides of the sockets of the arrowheads (KM 39993:2, KM 39995:2-5, KM 40551:21, KM 40551:52) were examined under a microscope to detect any remains of shafts, as these could be at a risk in an alkaline desalination treatment. None were found.

All of the objects were weighted before commencing with the treatment. It should be noted that weights of the metal detector finds (KM 39993-39996) are not comparable with the weights of the 2015 excavation finds (KM 40551) as the excavated material was weighted wet and the metal detector finds were weighted dry.

Once weighted, the material was divided into 3 groups that would be desalinated individually: 2015 excavation finds in one batch, decorated metal detector finds (KM 39993:1 and KM 39994:1) in another, and the rest of the metal detector finds in the last batch. Amounts of desalination solution were calculated for each batch so that the object's weight to solution volume ratio would fall between the range 1:6 and 1:9, as suggested by Watkinson (1982 p. 31). Objects from the 2015 excavation were gently washed before the treatment to remove loose soil. This procedure was carried out to get rid of the moist layer of soil adhering to the objects, as this would have introduced a lot of extraneous material to the desalination solution. For details of the treatment batches see appendix 4.

All of the objects were placed on low density polyethylene bags (Minigrip®) and the bags were perforated. Plastic identification tags were created with a Dymo® marking device, and these would accompany the finds in the perforated bags during the treatment. When everything was expected to be ready it was discovered that the amount of sodium sulphite at the Conservation Laboratory was not enough for the first batch of objects, the 2015 excavation finds. As the material had already undergone light washing and the

bags the finds had previously been stored in were already discarded, it was decided that the best course of action would be to leave the objects into tap water overnight until more reagent would be available.

## 7.2    Desalination treatment

Desalination was carried out in an elevated temperature of 50°C. It has been argued that since chloride removal is supposedly diffusion based then heating the desalination solution should significantly reduce treatment times (North & Pearson 1978a), though this point has been questioned by later practical experiments  that have led to good extraction result within reasonable periods of time in room temperature (Al-Zahrani 1999; Watkinson 1996). Still, since heating could be easily arranged and desalination had to be carried out within a reasonable timeframe it was decided to use elevated temperature, especially as it was unlikely to be detrimental for the objects treated in a virtually oxygen free environment. Studies also suggest that whilst elevated temperature might not affect the total amount of chlorides extracted, it probably does speed up the process (Rimmer, Wang & Watkinson 2012).



Figure 3. Batch 1 uder desalination treatment.

Desalination solutions were prepared into stainless steel containers (GN-series intended for foodstuffs) with silicone insulated lids. On the lids c. 5 mm holes intended for pressure equalization could be found, but since the containers would only reach only slightly elevated temperature and alkaline sulphite method requires an airtight environment to work, the holes were blocked with duct tape. Two sizes of containers were used: 6 and 8 litres. Bathes 1 and 3 were prepared on 6 litre containers whilst the largest batch, batch 2, was prepared on an 8 litre container.

The amount of oxygen in the treatment solutions could not be monitored and thus it could not be guaranteed that the containers were truly airtight. In addition containers of

batches 1 and 3 were only half-full, when it is recommended that at least three fourths of the containers should be filled with alkaline sulphite solution to ensure an oxygen free environment (North & Pearson 1975a). This was a result of trying to keep the object/solution ratio close to the desired 1:6, though, as a critical hindsight, it seems likely that any excess oxygen in the solution will have a more drastic effect on the treatment than a difference in the ratio, as long as it stays above 1:4 (Watkinson 1982; Al-Zahrani 1999).

The treatment solutions were changed approximately every two to three weeks and their chloride contents were measured using two different methods: a chloride quick test kit produced by Merck was used to get a basic idea of the amount of chlorides in the solution, and later the solutions would be analysed using a Metrohm 761 Compact Ion Chromatograph (IC). Descriptions of the methods are provided in chapters 8.2.1 and 8.2.2, and results of the determinations are discussed in chapter 9.

In general the objects survived the treatment well. Especially objects from the 2015 excavation suffered mostly minimal damages, if any, with very little dust-like black corrosion occasionally building up inside the plastic bags the objects were stored in for the duration of the treatment. Some of the metal detector finds lost pieces that extended into the DPL. The observation that finds in a bad condition seem to suffer bigger damages during the treatment held true in the metal detector group of objects, objects with an exfoliated surface structure such as horse shoe KM 39995:6 (X-ray: appendix 9 p. 7; pictures: appendix 8 p. 14) or, to a lesser extent, one of the spurs, KM 39994:2 (X-ray: appendix 9 p. 7; pictures: appendix 8, p. 10). From these objects pieces of the surface tended to flake off during treatment, and in both cases not all pieces could be fitted back later.

It was interesting that no such damages were observed in the objects from the 2015 excavation, even when they were heavily corroded, such as in the case of iron fragment KM 40551:6 (X-ray: appendix 9, p. 8; pictures: appendix 8, p. 17), nail KM 40551:54 (X-ray: appendix 9, p. 9; pictures: appendix 8, p. 19), or iron object KM 40551:58 (X-ray: appendix 9, p. 9; pictures: appendix 8 p. 20). Also several iron objects with very little iron core were treated, such as fragment KM 40551:67 (X-ray: appendix 9, p. 10; pictures: appendix 8, p. 21).

All of the above mentioned objects survived desalination treatment unharmed or with only superficial damages, even though beforehand it raised some concerns whether their condition would allow alkaline desalination at all. Even though the sample size is too

small to draw any conclusions from it, and any accurate measurement of damage is difficult because what constitutes as "damage" is highly subjective, the observation that finds that entered the treatment wet seemed to survive it better is worth paying attention to. All in all damages were very limited in the metal detector finds as well as in the excavated finds, which seems to be well in line with the observations of Rimmer (2010 pp.157-166).

Both silver and copper metal objects survived the alkaline sulphite treatment without obvious damages or discolorations. All of the objects containing copper metals, KM 40551:39, KM 39993:1, KM 39994:1, KM 39993:3, had their copper surfaces covered in tightly adhering dark corrosion layer after conservation. Copper on KM 40551:39 was revealed as a surprise during mechanical cleaning, as it was not recognized at the X-ray image (appendix 9, p. 9). All of the copper alloy surfaces had a warm brown colour typical of alloys with a high copper content, but it is difficult to say whether any of the copper alloy surfaces are composed of bright yellow brass discoloured by alkaline desalination treatment, as has been reported to happen (Vike, V 2015, pers. comm., 11 November; Bach & Greiff 2000, p. 328).

Interestingly a white metal surface was revealed from a spur KM 39993:5 during mechanical cleaning. This surface had also evaded detection from the X-ray (appendix 9, p. 2) and was first tested by Pia Klaavu, a conservator at the Conservation Laboratory, for silver with a 4N $H_2SO_4 + CrO_3$ spot test on 25.2.2016. When this was negative it was decided to carry out an XRF analysis with the equipment of the NBA, and Oxford Instruments X-MET 7500. The test was carried out with on 5.4.2016 and tin (4,73 %) and lead (1,24 %) were detected (appendix 7). This indicates that the coating is soft solder, which is not unusual on mediaeval spurs (Jope 1956). If this coating had been recognised before treatment an alternative method of desalination would have been sought, because tin is known to be chemically attacked by alkaline desalination treatments (Bach & Greiff 2000, p. 328). It is very interesting to note that the soft solder surface survived. It is possible that it was partly protected by the overlying corrosion layer.

Risks associated with alkaline treatments seem to be relatively low, and even if very serious damages can occasionally occur on very fragmentary of highly corroded material, at least in the context of mass conservation this does not seem like a too bad trade-off for an improvement in the expected lifespan of the material as a whole.

All desalination treatments were initiated on 18 November 2015 and finished after varying periods of time. All treatments were terminated when at least two baths had taken place after the chloride content of the solution had fallen beneath 10 ppm. This happened at different moments in time for the treatments, first one to get ready being batch 3 on 25 January 2016 after four baths, batch 2 following on 3 February 2016 after five baths. The last ones to get ready were the excavated objects in batch 1: their treatment was terminated on 2 March 2016 after seven baths. Detailed information about the lengths of individual baths and their chloride contents are provided in appendices 3 and 4.

After the treatment objects were washed in 50°C in deionized water to remove residual chemicals, changing the water twice a day, until the pH fell to a natural level. Details of the washing process are provided in appendix 3. Once washing was complete the objects were dried in an oven at 110°C at least overnight. Once the objects were dry all procedures directly related to their desalination were finished.

## 7.3 Mechanical cleaning

### 7.3.1 Consloidation

A considerable portion of the material was in a fragmented state and it was unlikely that it would survive mechanical cleaning unharmed without consolidation. For this purpose a 20% w/v solution of Paraloid B-72 (ethyl-methacrylate copolymer (Museum of Fine Arts Boston (MFA) 2015)) in acetone was prepared. Paraloid B-72 has the advantage that it can be removed with solvents, at least in theory. In practice it is probably very difficult, if not impossible, to totally remove all consolidant residues from the deep fissures and pores of the archaeological objects.

Consolidation was carried out by first seeping pure acetone through into the cracks and fissures on the objects with a syringe to promote the spread of the resin, and then the cracks were saturated with B-72. Because full hardness would be achieved in 24 hours this work was ideally done a day before cleaning took place. This treatment would bind together the delaminated surfaces and greatly increase the handling characteristics of the objects, allowing objects with fragile and delaminated surfaces, such as KM 40551:55, KM 40551:58 and KM 40551:59 to be cleaned to the same extent as the more solid proportion of the material.

This method of consolidation has a couple of drawbacks. First, the resin will also consolidate dirt onto the objects, and in these areas cleaning becomes more laborious. The best approach to remove this resin-dirt mixture was to first remove the bulk of it with a scalpel and then clean the surface with a sandblaster. If there were very wide cracks in the objects B-72 would consolidate all dirt in the crack in place, and this dirt-resin mixture would obviously be visible to the naked eye. This was a minor aesthetical issue, however, and all in all the results were very pleasing.

Another problem associated with the use of Paraloid was that it is thermoplastic and will soften if treatment involving heat, such as waxing in the case of this project, will take place. This was not found to be a problem if the object was simply consolidated when it was still whole, as the softened Paraloid and probably the surface tension of the molten wax would be enough to keep it together through the waxing process. At times, especially if the objects were left into the hot oven before they would be immersed into the wax, small amounts of molten B-72 would run out of the cracks and cover patches of the objects surface. This, too, was a minor aesthetic issue, though, as the wax coating would anyway fade the differences in glossiness. Of more concern were parts that had actually been glued in place with Paraloid, because they would almost invariably become loose during waxing, even the small ones with a very good fit.

Because of the poor performance of B-72 as a glue during waxing, another product, UHU hart (polyvinyl acetate, (MFA 2006)), was chosen. Often the two adhesives were used in combination: UHU hart for parts that have come loose during treatment, and B-72 when consolidation was necessary. UHU hart was also used to glue back in place parts that had come off during the waxing process. Even though it was possible to attach parts after the waxing it was less than ideal, as the waxed surfaces were likely to result into a pretty unreliable joint.

A resin in the joints of a porous object will also form a diffusion barrier, should the objects require retreatment in the future. It is probable that the resin will soften and dissolve during treatment, at least partially, and at least in alkaline treatment solutions. It might also be possible for the chloride ions to diffuse through the resin layer, but to what extent this might happen cannot be said without a thorough investigation. In any case, having this extra material in the objects is undesired when it comes to retreatability, and soaking out the resin could be considered if the desalination procedure needs to be repeated at some point.

On an aging test carried out at the CCI (Down et al. 1996) it was found out that pH of Paraloid B-72 had a tendency to drop over time. This effect was achieved only when exposed to light though, which is not the case for archaeological iron carefully packed and stored in a magazine. If the pH-drop could be expected over time then having an acidic substance deep within the corrosion layers of iron would be potentially dangerous. However, since no such changes were recorded in B-72 in a dark environment the risk of lowered the pH was assessed to be very low in the case of Hangastenmäki finds. Acrylic resins have been used as a coating for archaeological iron too. Then the risk posed by light exposure should be taken more seriously, and the use of a more stable Paraloid B-44 has been employed by Schmidt-Ott and Oswald (2006).

### 7.3.2    Cleaning of unadorned iron

Mechanical cleaning was mostly carried out with a Sandmaster FG-1 Restauro fine sand-blasting unit. A stereomicroscope was attached to the blasting cabinet to allow for more precision and control over the cleaning process. Solid glass beads were used as an abrasive medium. Corundum (aluminium oxide) was also tried on some metal detector finds without historical value originating from outside of the project, but whilst it was discovered to be very effective, it was decided that it has too aggressive an effect on the surface, making it pitted and dull – especially if a well preserved original surface was present. Thus it was discarded, but it would be very useful when removing thick concretions from objects.

The thin and long nozzle of the FG-1 combined with a microscope and glass beads allowed very precise work to be carried out, but at the expense of efficiency. Large and thick corrosion surfaces on some of the bulkier objects, such as horse shoes, were very time consuming to clean and another unit with a shorter nozzle and a more spread abrasive stream, as well as a more aggressive abrasive medium, would have been handy to have in addition to the "high precision" unit. A bit counterintuitively the accuracy brought by the microscope allowed for a more thorough and aggressive blasting as locating the DPL-TM interface was easier when the extent of microscopic soil particles could be more easily monitored whilst cleaning. Microscopic soil particles are some of the most recognizable indicators (also called "external markers") that the material being removed is still above the original surface (Blackshaw 1982, p. 21; Neff et al. 2005, p. 521). But even

with such aides locating the "original surface" will partly rely on the interpretation of the conservator.

The condition of the finds from Hangastenmäki varied greatly. A large portion of the surfaces of some objects from Hangastenmäki had the original surface so well preserved that it was practically composed of metallic iron with a film thin blackish patina, the smooth surface disrupted by corrosion pits. Examples include knives KM 39993:7 (appendix 8, p. 7) and KM 39995:7, (appendix 8, p. 15), and a horse shoe nail, KM 39994:5, (appendix 8, p. 11). At the other end of the spectrum were many of the finds from the 2015 dig with thick DPL layers underneath their distorted original surfaces (examples of this group of objects include nail KM 40551:61 (appendix 8, p. 20), and KM 40551:58, appendix 8, p. 20). The condition of the surfaces varied a lot even within the same object, as can be seen on the above referenced KM 40551:58, where a small batch of well-preserved original surface can be seen at the base of the curve, even when the rest of the surfaces are badly distorted.

During mechanical cleaning many technical details were uncovered form the objects. The extent of brazing at the padlock bolt KM 39993:3 was uncovered (appendix 8, p. 5) and a thin layer of copper metal was discovered from KM 40551:39 – possibly brazing too. Also, a longitudal line was spotted on large knife KM 39995:1 (appendix 8, p. 13), possibly indicating a weld, especially when combined with a discontinuation in structure seen at the same spot at the X-ray (appendix 9, p. 6). Cut surfaces were revealed on an iron ingot, KM 39994:7, indicating that a hardy was probably used to cut the red hot piece almost through from an iron bar, and then bent loose. An impression of a bluntish edged tool can be seen a bit from the other end of the ingot: probably this is caused by the same tool that was used to cut the piece (appendix 8, p. 12). Also, several deformed pieces of iron were revealed to have a surface and a shape by cleaning, even if they could not be recognized as anything more than fragments.

Some of the finds from the smithy site at Hangastenmäki were also revealed to have their surfaces covered in slag, especially KM 40551:28 where some of the slag had a green glass-like colour and consistency. It is also possible that objects KM 40551:57 and KM 40551:64 could be just suspiciously formed pieces of slag, though especially KM 40551:64 seems to contain some iron based on the X-ray (appendix 9, p. 10).

### 7.3.3 Cleaning the decorated objects, KM 39993:1 and KM 39994:1

A different approach had to be taken with the objects with precious metal decorations. Here it was decided to avoid abrasion as far as possible to avoid alterations on the probably metallic silver and copper metal surfaces. The blade of the spearhead KM 39994:1 and the insides of the pommel KM 39993:1 were exceptions, and they were cleaned with the sandblaster prior to the rest of the mechanical cleaning. This way the decorated surfaces would be safe under corrosion layers when air abrasion took place. Also, when mechanical cleaning of the decorated surfaces was commenced they were consolidated with 20% w/v Paraloid B-72 in acetone wherever the decoration was found to be unstable.

To speed up this process two airscribes, HW-Tools HW-323 and HW-80 were used. Being small enough to be used under a microscope, and running very steadily with minimal vibrations they worked nicely, speeding up the process of removing the outer corrosion layers, but struggled to remove corrosion at the transition zone from TM to DPL. Thick black corrosion products had seeped out from between the precious metal threads, forming a very tough layer that no longer was brittle enough to be broken by the airscribe stylus. Instead the stylus would forge and polish the corrosion layer, and it was obvious that a satisfactory result could not be achieved without the use of abrasives.



Figure 4. Airscribes, HW-80 and HW-323, used in the project

On the socket of the spearhead at least six scratches or notches, less than a millimetre wide and slightly under a centimetre long, were observed. These scratches or notches were at a relatively sharp angle compared to the socket, and filled with very hard black corrosion products. Also both parallel and perpendicular groups of lines were observed on the silver surfaces of both of the two objects. These are likely original polishing tool marks left by artisan or artisans who inlaid the surfaces.
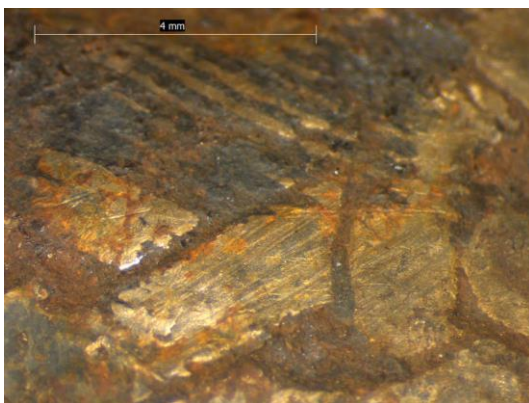
Figure 6. KM 39993:1 surface before sand-blasting
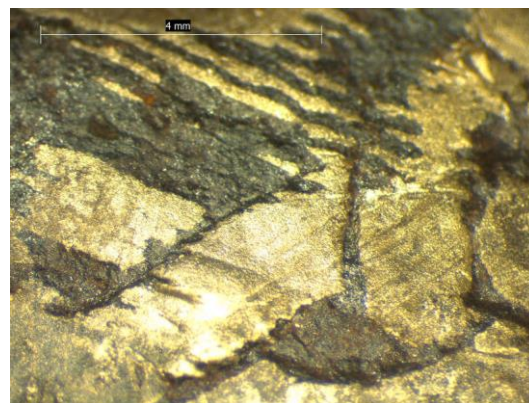


Figure 5. KM 39993:1 surface after sandblasting

A very light sandblasting with glass beads was conducted on the decorated surfaces of both objects. The cleaning was kept to a necessary minimum to ensure that the surfaces would be damaged as little as possible. Still, unfortunately, a lot of the fine detail of the probable tool marks were lost (figures 5 & 6). For the plain eye the result was very satisfactory, but loss of microscopic surface details was not desired. However, the longitudal scratches on the spear socket could be made a lot clearer. For future reference it would be interesting to explore the possibilities of a very careful chemical cleaning method, should a similar situation be faced again. Despite the loss of some finer details the sandblasting was a trade-off worth making, since the objects became significantly clearer, their decorations a lot easier to read.

### 7.3.4   Copper alloy objects

Two copper alloy objects were recovered on excavation: a buckle KM 40551:51, and a plate fragment, KM 40551:44. Both were cleaned with manual tools only, scalpel, brush and glass fibre brush being used on KM 40551:51 and only brush on KM 40551:44. Dark residue covered a lot of the surfaces of KM 40551:44 and this was not possible to remove without removing the outermost corrosion layer from the object, so it was left in place. It was not touched also because there is a possibility that it might originate from the plate's period of use, and thus be of archaeological importance.

No impregnation or coatings were used on the copper alloy objects, as both seemed very stable. Naturally this means that care must be taken when handling the objects in the future.

7.4    Coating

A majority of the objects were coated with a microcrystalline wax, Cosmoloid H80. Copper alloy objects, KM 40551:44 and KM 40551:51 were not coated, and neither was thoroughly corroded KM 40551:70 or the very slag-like KM 40551:57. The wax was impregnated into the objects in a vacuum oven at a temperature of ≤ 120°C, and at a pressure of around 5 kPa. Usually the objects were taken into oven to dry for a couple of hours at a normal atmospheric pressure but elevated temperature. Then they would be put into molten wax or, in case they were very fragile, on top of still solid wax and allowed to slowly be immersed as the wax melted.

Underpressure was introduced in increments, allowing the objects to adjust themselves to the new pressure, especially if they were very fragile or glued. When underpressure was introduced, air would start to escape from the cracks and pores in the objects and bubbling would ensue. If it was about to get too vigorous the process was halted before pressure was further lowered. It is worth noting that the majority of the air seemed to escape from the pores at pressures below 20 kPa. The objects were left to a pressure of c.a. 5 kPa for at least 6 hours, often overnight.

Once the impregnation treatment was ready, air was slowly introduced into the vacuum oven. The objects would be taken out of the wax and placed on top of blotting paper in ≤ 120°C to remove any excessive wax. When a satisfactory result was achieved the objects were taken out of the oven and allowed to cool down in room temperature.

Organic coatings offer only a limited protection from the elements because of their moisture and oxygen permeability (Scott & Eggert 2009, pp. 146-147; de la Rie 1992). They offer the benefits of greater physical integrity of the treated objects, as well as some protection from stains resulting from improper handling, as well as a pleasing glossy surface texture. Possibly they help to buffer fluctuations in RH too, and manage to hold objects with active corrosion problems together for a bit longer.

However, microcrystalline wax has its drawbacks. It has a tendency to accumulate into grooves, edges and cracks on the objects, making the surface structure appear softer than it actually is and even blocking some finer details altogether (e.g. Moilanen 2015, p. 275). All surface analysis methods could also be disturbed by the wax layer, though this matter should be thoroughly investigated before anything can be concluded.

The treatment is also irreversible, even though it has been found that wax can be removed at least from the surface of the objects (Johnson 1984), but one would be very sceptic about the possibility to completely remove wax from the pores and fissures of archaeological iron. Also, the solvents used in the operation are not healthy and the process described by Johnson is laborious and can be implemented on a very limited amount of objects at a time.

No treatment can ascertain the stability of archaeological iron as there is always a degree of variation in the amount of chlorides remaining in the objects (Schmutzler & Eggert 2011; Watkinson 2010). Thus iron should still be seen as an unstable material that needs constant monitoring and care (Cronyn 1990, pp. 201-202). It is not uncommon for objects to become unstable over time and thus retreatability is a major concern. Also, iron stabilization research is still ongoing and it is possible that new and better methods will become available in the future. Thus it should be questioned whether the benefits offered by microcrystalline wax are worth introducing an irreversible coat of foreign material to the objects.

## 8 Packing and documentation after conservation and

### 8.1 Photography

The objects were photographed after conservation. Some of the material – the K-type spearhead, KM 39994:1, T1-type pommel, KM 39993:1, and the large knife, KM 39995:1, were photographed using the same symmetrical lighting as was used in the before conservation –pictures. To make the precious metal decorations on the spearhead and the pommel clear and easy to read, it was important to bring out the colour differences in these objects in a neutral manner.



Figure 7. After conservation –pictures studio setup, asymmetrical lighting.

The results with the knife were less satisfactory, though, as the colour of the object was largely uniform satin black and the most important information was in its form and surface texture. In symmetrical lighting these were hard to see, because the uniform light made the pictures look flat. To bring out surface detail a different lighting was necessary. A new studio setup was built, using a single flash with a soft box that was used as an indirect light source. This made it a lot easier to read the form and surface of the objects from the pictures. The rest of the material was photographed with this asymmetrical setup, including the detail and assemblage pictures.

## 8.2   Packing

Packing is a crucial part of the conservation process of any archaeological object as mishandling poses a serious threat for this fragile material. The objects were packed into acid-free cardboard boxes with a layer of Tyvek® fabric (high density polyethylene (MFA 2016)) at the bottom to provide some cushioning for the objects and keep any possible loose parts from disappearing into the folds of the cardboard box. Then the objects were immobilized with a layer of paper and a recognition note was put on top of the packing. Transparent plastic lids were used on the smaller boxes to keep the notes from falling out. Recognition numbers would later be applied directly onto the objects by archaeologists reviewing the material.

This manner of packing has its shortcomings. A big drawback is that it is not possible to see the contents of the box unless the object is unpacked. Repeated packing and unpacking of the objects causes unnecessary stress and especially objects with fragile protruding parts are at a risk. Still, immobilizing the objects with a piece of paper was preferred to keeping them loose inside the cardboard boxes.

## 9 Chloride analysis

### 9.1 Background information on chloride measurement

Following the chloride content of the solutions is an essential part of any desalination process. Chloride content has to be measured in order to get an idea of the magnitude of chloride infestation in the objects, as well as determine whether the treatment should be continued or considered ready and terminated.

Chloride measurement from neutral solutions is a relatively straightforward task, but getting accurate readings from a sulphite infested, highly alkaline and impure treatment solution is a very different matter. High pH of the treatment solution and the high concentration of sulphite ions will disturb most analytical equipment, and thus the samples usually need to be pre-treated to get accurate readings (Costain 1985; Selwyn 2001; Schmidt-Ott & Oswald 2006; Wang et al. 2008). Usually this includes oxidation of sulphites to sulphates as well as neutralization of the solution.

One of the earliest methods to indicate chlorides in treatment solutions was to add a few drops of a dilute solution of silver nitrate to the treatment solution. This would cause white silver chloride to precipitate into the solution according to the reaction $Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$. This was a qualitative test, however, indicating only whether the wash solution contained chloride at a concentration of circa 5 ppm or above. (Semczak 1977).

To get a quantitative analysis and more control over the desalination process an ion selective electrode was soon introduces (ibid; Costain 1985; Wang et al. 2008) as well as potentiometric titration (Selwyn 2001). An ion selective electrode turns the activity of a specific ion, in this case chloride, into an electric potential, which can be measured against a reference electrode that will maintain a constant potential, allowing changes at the measurement electrode to be followed reliably. The electrode is made chloride specific with the use of an ion specific membrane that will, to a certain extent, neutralize the effect of other ions in a solution.

Chloride measurement with an ion specific electrode has been found to be one of the most accurate and usable methods for standard measurements of solutions in mass scale, but to work they will have to be calibrated with standard solutions that have a

chemical composition that resembles the composition of the treatment solution as closely as possible. Samples will also usually have to be pre-treated to fit the electrode, and accurate readings will require use of chemicals and some effort. A detailed description of the use of an ion selective electrode has been provided by Wang, Dove, Shearman and Smirinou (2008).

Another method for quantitative measurement of chlorides is the use of potentiometric titration. This method is based on the reaction of silver nitrate with chlorides, as described above. In the reaction silver and chloride react with each other at a ratio of 1:1. Thus, when silver nitrate is introduced into a solution containing chlorides, the moment free silver is found in the solution it is known all chloride has been consumed and precipitated as solid silver chloride. This is called the end point of the titration. When the amount of silver nitrate consumed in the reaction is known, the original chloride content of the solution can be calculated. (Selwyn 2001).

An indicator, such as potassium chromate (Wihr 1975, p. 190) can be used to determine the end point of a silver nitrate titration method, but more accurate readings are achieved through the use of a silver specific electrode that works according to the same principle as the chloride selective one, just for a different type of ion. An automated titrator can also be utilised to speed up the process and make it less labour intensive (Jarva & Haavisto 2011). A detailed description of how to perform a potentiometric titration has been provided by Selwyn (2001) although the accuracy of this method has been questioned in later research (Wang et al. 2008).

All in all getting accurate chloride readings from an alkaline treatment solution seems to be a surprisingly difficult task, with even methods that are normally considered precise failing the task. The reason seems to be the high ion content of the solution and probably wild variation between the different treatment batches. Condition and content of archaeological objects provide a degree of variation and uncertainty. Since they often enter the solution dirty it has been shown that a wide range of other compounds besides chloride will dissolve into the treatment solution over the weeks (Selwyn & Argyropoulos 2005, pp. 91-92). These probably differ strongly according to local soil conditions and composition of the objects.

The problem with chloride determinations from alkaline treatment solutions is thus probably largely similar as are those associated with predicting the outcomes of desalination

treatments: variation of objects and solutions is so great that even if the measurement protocol is the same every time, the solutions will invariably differ from the standards. A lot of the problems could be overcome by simply omitting the sulphite ion from the treatment solution, however, as has been done using solutions deoxygenated with nitrogen (Al-Zahrani 1999; Rimmer, Wang & Watkinson 2012; Watkinson & Al-Zahrani 2008) or by using subcritical fluids (e.g. Drews et al. 2013; Gonzáles-Pereyra et al. 2013; Näsänen et al. 2013) or even plain dilute sodium hydroxide, as that too has given some very promising results (Keene 1994). This would make pre-treatment of the samples a lot easier.

## 9.2    Chloride measurements at the Hangastenmäki project

With each change of treatment solution a sample of ca. 2 dl was taken from the alkaline sulphite desalination baths. The samples were tightly capped and stored refrigerated to slow down any potential chemical reactions and minimize chances of anything evaporating out of the solution.

Two methods were used to determine chloride contents of the treatment solutions. A quick test produced by Merck was used to get a rough idea about the amount of chloride ions in the solution. This method was applied because it is relatively fast and easy, but still accurate enough to monitor treatment progression The quick test kit had its limits though, especially when the chloride content of the solution started to fall below 20 ppm. Even if the accuracy in these low levels was enough to allow the end point of the treatment to be determined, it was not enough to accurately bring out quantitative differences between the different treatment batches. For this purpose Ion Chromatography (IC) was used.

### 9.2.1    Aquamerck® quick test kit 1.11106.0001

The Merck chloride quick test kit used in the project, Aquamerck® 1.11106.0001, is basically a titration kit where indication is based on the reaction of mercury(II) nitrate against a 1,5-diphenylcarbazone indicator. The titration procedure included oxidising any sulphites from the 5 ml samples with a drop of 33 % $H_2O_2$ and neutralizing the samples with nitric acid. Once neutral or close to neutral, two drops of 1,5-diphenylcarbazone indicator solution was added. At this point the sample would turn blue if close to neutral, or red if still slightly alkaline. Sample pH would be further adjusted with a couple of drops of $HNO_3$

as the test requires the sample to be acidic. When correct pH was achieved the sample would turn bright yellow.

Once the sample was pre-treated as described above the titration could commence. A syringe delivered with the test kit would be filled with mercury(II) nitrate solution that would be added dropwise into the sample that is constantly mixed by a magnetic stirrer. Once the end point was reached the sample would turn bright violet-blue, indicating that all chlorides have been consumed. The chloride content (ppm) of the sample could now be read directly from a scale at the side of the syringe.

In theory the accuracy of the test kit would allow concentrations as low as 2 ppm to be measured, but since the reagent solution has to be added dropwise it was practically impossible to measure chloride contents more accurately than at ca. 10 ppm intervals. Also, end point was open to interpretation, because the colour change was gradual and happened at a range of ca. 10-15 ppm. Concentrations lower than 10 ppm were thus very difficult to measure, but the accuracy was enough to follow the development of the treatment and decide the end point.

The use of the Aquamerck® quick test kit has been previously covered by Schmidt-Ott and Oswald (2006, pp. 128-129) but their instructions concerned measurements made form a 0,5M $NaOH$, 0,5 M $Na_2SO_3$ solution – respectively five and ten times stronger concentrations than have been used in this project. Thus especially the amount of sodium peroxide was heavily downgraded from the 0,4 ml suggested in the source. Also the use of tetra-sodium diphosphate to eliminate any free iron ions in the solution was omitted because it was found very unlikely that deoxygenated basic solution would contain iron ions in concentrations that would have disturbed the measurement to any significant extent.

It should be noted that all waste solutions produces by the Aquamerck® quick test contain mercury and must be handled and disposed of appropriately. Also the test has to be carried out with adequate safety measures.

9.2.2   Ion Chromatography (IC), Metrohm 761 Compact IC

Even though the quick test kit provided accurate enough information to carry out the desalination treatments it was decided to carry out ion exchange chromatography to bring out especially chloride concentrations lower than 10 ppm. Accurate analyses were necessary also to bring out differences between the desalination batches.

Ion exchange chromatograph is based on interaction of ions with two different phases – mobile and stationary – within the analysis equipment. The sample is injected into the liquid mobile phase called eluent that is then pumped through a column that contains the stationary phase, also called an adsorbent. Ions within the sample will interact with both phases, stationary phase holding them back and the mobile phase driving them forwards in the column. Depending on the individual characteristics of the ions they will interact with each phase at different strengths. Thus ions in the sample will become separated before they reach a detector, which in the case of the equipment used here was a conductivity meter. The separation ensures that the ions will reach the detector after different time periods called retention times. Ions and their concentrations should be such that no overlap will occur between them, but each type of ion will enter the detector one at a time, with enough of a pause in between.

Ion Chromatography has been used in chloride measurements for alkaline sulphite solutions by Schmidt-Ott and Oswald (2006), but rather unsuccessfully. The problem was that even though chloride and sulphite ions have clearly different retention times, the difference in their concentrations were so vast that sulphite ions would still interfere with the chloride measurement. It was still decided to try out the IC analysis in this projects as the sulphite concentration of the desalination solutions are only one tenth of the concentration used by Schmidt-Ott and Oswald (0,05 M compared to 0,5 M). This decision was backed up by the fact that IC has a very low detection limit and when it works properly it can deliver accurate results at the lower end of chloride contents that are problematic to measure accurately with methods based on titration.

Another application of the IC has been residual chloride determination (Wang 2007a; Wang et al. 2008). The method has been to grind down flakes that have come loose from the objects during treatment and soak them thoroughly in water, which was then analysed with the IC. As stated by Schmutzler and Eggert (2011, p .25) these results are of a limited use since water is not enough to dissolve bound chlorides. Chloride content has

also been shown to vary wildly within an archaeological objects corrosion layers (Koh & Skogstad 2015; Rimmer & Wang 2010; Réguer et al. 2007d,), and thus using results obtained from a small flake to represent the whole artefact will probably not produce very good results.

The IC analysis was carried out with the equipment of the Helsinki Metropolia University of Applied Sciences, Leiritie Campus in Myyrmäki, Finland:

Unit: Metrohm 761 Compact IC

Column: 6.1006.510, 100 x 4,0 mm column
Column packing: polyvinyl alcohol with quaternary ammonium groups, particle size 5 μm
Eluent: 3,2 mmol/L $Na_2CO_3$, 1,0 mmol/L $NaHCO_3$, std. flow 0,7 mL/min

Dialysis unit: Metrohm 754 Dialysis Unit

Analysis program: METROHM LTD Chromatography Control and Data Acquisition System, Version 2.3 SR6

By the time the IC analysis was carried out the quick test results of the solutions were already available and thus the IC device could be calibrated for a narrower and more accurate range. Altogether 16 desalination solution samples were analysed with the IC using two different analysis procedures. The first procedure was used for all samples where chloride content was below 20 ppm. In all three batches this incorporated all but the first couple of samples from the beginning of the treatment. These samples were all relatively clean, so cation exchange followed by a filtration through a nylon mesh were enough to remove all unwanted compounds out of them. This group was composed of 10 samples as listed in appendix 4.

The remaining six samples had chloride contents that were off the calibration chart and too contaminated to be simply filtered through a nylon mesh. Thus it was decided to use dialysis for these samples. Higher chloride contents also meant that calibration would have to be made for a different range, and the samples with the highest contents would still have to be diluted.

Samples that didn't go through dialysis were prepared as follows. Iron ions would have had a major impact on the measurements so 20 ml of each sample was injected through a Metrohm 6.1012.010 IC-H cation exchange cartridge that was renewed every fourth filtration with 10 ml of 2,5M $HNO_3$ and flushed with 10 ml of ultrapure water. The pH of the samples (around 13) was too high for the equipment that had a maximum pH on 12. To meet this requirement 0,5 ml of 1M $HNO_3$ was added to each filtered 20 ml sample. The resulting increase in volume has to be taken into account when the results are analysed.

The equipment was calibrated using five standard solutions prepared with sodium chloride into deionised water, 1 ppm, 5 ppm, 10 ppm, 15 ppm and 20 ppm respectively. All standard solutions were prepared from a 1000 ppm solution with one step dilution, except 1 ppm solution that required a secondary dilution from the 10 ppm solution and 75 ppm solution that had to be diluted from 150 ppm solution. The 75 ppm solution was diluted once more to produce a 37,5 ppm solution for the dialysis procedure. Standard solution quality suffers with every dilution step, and thus especially second and third dilution steps were carried out at larger solution ratios.

The samples were injected into the IC through a 45 µm nylon mesh to filter out any remaining solids. Both nitrate from the nitrile acid and sulphites and sulphates from the disodium sulphite caused spikes that were clearly outside the chloride calibration chart but they had clearly defined retention times without any noticeable lagging in the conductivity, which returned to the standard level typical of the eluent once the ions had passed the detector. Thus it was considered that they were probably not affecting the chloride measurement in any radical way, especially as the measurements were of the same magnitude as those obtained with the quick test kit. To be sure the column was flushed with ultrapure water between the samples.

Dialysed samples were prepared in a similar manner, but no pH adjustment was necessary and thus the results can be used as such because their volumes remained unchanged, except for the two diluted samples. Sample 1 of batch 2 was diluted 1:9 v/v and sample 1 from batch 3 was diluted 1:1 v/v, both to deionised water. A 37,5 ppm standard was prepared by diluting 75 ppm standard and 10 ppm, 15 ppm, 20 ppm, 30 ppm and 37,5 ppm standard solutions were chosen for calibration.

9.3    Analysis results

It was found that there is a considerable deviation in the results obtained with the quick titration kit and the IC. Especially the results that were obtained from dialysed samples differ significantly from those obtained with the quick titration kit, especially in the case of batch 1. Furthermore the rise in chloride content in the first three samples of this batch is counter-intuitive if the chloride removal is expected to be diffusion controlled as suggested by North and Pearson (1978b). A possible explanation to this phenomena is the greater integrity of the fresh finds, as proposed by Selwyn, McKinnon and Argyropoulos (2001), as will be discussed in more detail in chapter 9.1. The tendency for the chloride contents to rise subsequently for the first three baths of batch 1 is even more pronounced in the IC analyses than it is in the results obtained with the titration kit. When this sway is combined with the differences in the early stage samples taken from batches 1 and 3 a serious doubt has to be cast upon the results obtained with the dialysis method.

Ion chromatogram results obtained with the direct method seem to be more constant, showing a steady fall in the chloride contents with each analysed bath. Largely because of the inaccuracy of the quick test kit in concentrations lower than 10 ppm, there is an unfortunately short overlap with the results obtained with the IC and the quick test kit, and the results cannot be properly crosschecked. Judging by the couple of samples where a reasonable result was obtained with both methods they seem to be of a similar magnitude at least. At this overlap range of ca 10-20 ppm the IC seems to give results that are 1-2 ppm lower than those obtained with the quick test kit, and this deviation of around 10% is still acceptable.

Judging the reliability of the IC results at the lower end of chloride consecration scale is very problematic when there is no alternative that would allow crosschecking. Thus they will have to be taken for what they are within the scope of this project. Not knowing the exact amount of chlorides in the samples is not absolutely necessary either, because treatmentwise it can be considered enough to know that the content of the last desalination solution was well below 10 ppm. Also, since the research question here has been to evaluate differences in the behaviour of the dry objects compared to fresh, unoxidised ones, comparability of the results is more important than their absolute accuracy.

Because of the sway in the dialysis results, combination graphs were prepared where the dialysis results are omitted, in addition to separate the IC and quick test graphs. In

the combination graphs concentrations greater than 20 ppm are taken from the quick test results, as they could not be measured with the direct IC method. It is impossible to objectively estimate the relative accuracies of dialysed IC and quick test results, but the latter were favoured because of their consistency. Arguably these results combined with the IC results obtained with the direct method provide the best compromise when assessing the results.

Using two different analysis equipment proved to be more problematic than originally expected. Only limited crosscheck possibilities left a degree of uncertainty over the results at the lower end of the chloride concentrations. An ion selective electrode has been successfully used over a wide range of concentrations and using one as a third analysis tool would have allowed one more set of measurements to compare against. Ion selective electrodes have also been found to be amongst the most accurate and cost-effective tools in practical situations and they have been gaining favour since their introduction to the conservation field in the 1970's. Even with the electrode measurement is laborious, including careful sample and standard solution preparations (Wang et al. 2008). An accurate and simple chloride measurement tool would be a very welcome addition to the analysis tools available, though much of the problems are associated with the difficult nature of the treatment solution.

For details on standard solution preparation, calculations and results, see appendices 4-5.

## 10  Results and discussion

Even with the large deviation and uncertainty associated with the measurement methods, it is clear that the two object groups – fresh and oxidised finds – behaved very differently in desalination. Dry finds released a vast majority of their chlorides during the first two week bath, with batch 2 releasing 80% and batch 3 releasing 78% of the total amount of chlorides removed, as compared to the circa 21% released into the batch 1 during the first two weeks. These numbers are based on a combination of results obtained with the quick test kit and the IC.

It is also interesting to note that for the first three baths the amount of chlorides in washing solutions of batch 1 would rise roughly to the same level, peaking at the third bath and then starting a slow decline. It should be noted though that the third, most chloride rich

bath lasted for about three weeks, from 16 December 2015 to 7 January 2016. That's a week longer than the typical two weeks. In the case of the oxidised finds chloride levels peaked right in the beginning and fell to a fraction within a couple of baths. It is also worth paying attention to how the three week third bath removed only a relatively small amount of chlorides from baths 2 and 3.

It has been found that objects that have had the concentration of their last desalination bath below 5 ppm are fairly stable (Rimmer, Wang & Watkinson 2012, p. 39). All three treatment batches carried out in this project were below this limit when the treatment was terminated, though it would probably have been possible to still remove some chlorides from batch 1. Because objects were treated in masses the chloride measurements will represent the average for all objects in the bath, and it cannot be said with any certainty whether the treatment was over for each and every object. This would have required individual treatment baths for each object, which would have multiplied the amount of work and pushed the treatment of the Hangastenmäki finds far beyond the capacity of this project.

It has to be remembered that there are several variables associated with chloride content measurements and success of the method relies on many factors not all of which can be easily measured, as discussed in detail by Watkinson (2010). The most common and often the only measurement carried out during routine conservation is measurement of the content of dissolved chloride in the treatment solution. However, it doesn't tell any-thing about the amount or form of chlorides remaining in the objects after treatment, even though this information would be most important when considering the stability of the objects and success of the desalination treatment.

There is unfortunately no easy way to measure the amount of residual chloride. The most common way has been to completely digest the objects in nitric acid and measure the amount of chlorides in the resulting solution (Al-Zahrani 1999; Gonzáles et al. 2004; Rimmer, Wang & Watkinson 2012; Watkinson & Al-Zahrani 2008; Watkinson 1996). The problem of this determination is that it is destructive, leading to the complete dissolution of the objects. Obviously it cannot be used on objects with scientific and cultural historical value, and this has often led to relatively limited test batches in the past. Some serious sway has also been detected in the digestion results, and especially the astonishingly high chloride extraction rates reported by Al-Zahrani (ibid) have been questioned by later research (Rimmer, Wang & Watkinson 2012; Schmutzler & Eggert 2011; Scott & Eggert

2009 p. 141). It seems that if objects are digested in an open system then there is a significant risk of chlorides evaporating as hydrochloric acid. In subsequent research a closed system has been utilised. A non-destructive method, neutron activation analysis, has been used by Selwyn and Argyropoulos (2007) but this method is complex and expensive, and can only be used on relatively small objects.

No residual chlorides could be measured from the objects treated in this project. Because of the large differences in residual chloride amounts between objects reliable estimation would have required a large number of objects to be digested and naturally this would have been unacceptable. Even though the desalination treatment is very likely to increase the lifespan of the material it should still be regularly monitored for signs of renewed corrosion. Talking about desalination as a method to stabilise iron is misleading, since iron corrosion can be very stubborn and true stability cannot be guaranteed with any method, even with the very promising results of the subcritical method.

As argued by Rimmer, Wang and Watkinson (2012) and Watkinson also in an earlier paper (2010), the success of desalination methods should not be seen as an either-or situation where the treatment either succeeds or fails in stabilizing the object: it should rather be seen as a stability enhancing treatment that will buy more years for a very unstable group of objects. To say that a desalination treatment has failed just because an object is undergoing slight renewed corrosion can be misleading when inaction can lead to a spectacularly disastrous outcome.

10.1  Discussion on the differences between the treatments of dry and fresh finds

Even with the variation in analysis data it can be concluded that oxygenated finds reacted very differently compared to the fresh material from the 2015 excavation. Oxygenated finds released their chlorides very rapidly, whilst desalination rate of the fresh finds was a lot slower. Since the composition of the artefacts could only be examined on a macroscopic scale in this project the possible reason behind the different behaviour of the different find groups has to be interpreted against current research into the iron corrosion and desalination processes.

10.1.1 Variables affecting the treatment

According to recent understanding a successful desalination is achieved through a couple of steps. First the object has to be soaked into a solution with a high $OH^-$ ion content to ensure that hydroxyl ions will reach all areas where $Cl^-$ ions are situated. The second step is the replacement of chloride ions with hydroxyl ions, followed by the last step which is diffusion of the now free chloride ions into the treatment solution. (Gonzáles-Pereyra et al. 2013, p. 201).

According to Kergourlay and co-workers (2011, p. 2475) three different types of chlorides can be identified in archaeological objects: 1. located inside the pores and cracks as free chlorides, 2. trapped inside the structure of iron hydroxychlorides or 3. adsorbed at the surface of the grains of corrosion products. Free chlorides are the most mobile ones of the three, and can be readily diffused out of the object once they are dissolved and the potential gradient from ongoing corrosion at the metal surface is stopped. Surface adsorbed chlorides are also usually straightforward to remove, as in most cases they can be substituted with $OH^-$ ions (Réguer et al. 2009). The chlorides trapped inside the structure of hydroxychlorides presents the most difficult challenge for a dechlorination treatment, as depending on the compound chlorides are trapped in, they can be very difficult or impossible to safely oxidise or reduce into other compounds. As a result practically no simple soaking treatment is 100 % effective in removing chlorides (Rimmer, Wang & Watkinson 2012; Schmutzler & Eggert 2011).

According to research conducted by Hjelm-Hansen and co-workers (1992, 1993) the corrosion layers of an archaeological object undergo rapid chemical changes at the beginning of the treatment. A rapid electrochemical transformation was also recorded by Kergourlay and co-workers (2011 p. 2480) with synthetic beta ferrous hydroxychloride treated in sodium hydroxide. It seems that the chemical reactions taking place in an alkaline treatment bath are relatively fast compared to the long treatment times used. This would indicate that lots of the chlorides are trapped in meta-stabile corrosion products that are quickly turned into other compounds by the alkaline desalination solution, followed by a release of chlorides.

Effective desalination treatment requires that the treatment solution penetrates all cracks and pores of the artefacts and reaches the chlorides that have had hundreds if not thousands of years to penetrate into the complex corrosion layers. Thus the thickness and

porosity, or tortuosity of the object plays a crucial role in the desalination process (North & Pearson 1978b; Selwyn, McKinnon & Argyropoulos 2001; Selwyn 2004). The longer and narrower the path that an ion has to travel before it diffuses into the treatment solution is, the longer the treatment time can be expected to be.

10.1.2 Dechlorination treatment in the light of the theoretical background

The high chloride content of the treatment solution at first baths is probably a result of the dissolution of the so-called "free chlorides" – that is, chlorides trapped within the pores and crevices of the object – being released into the treatment solution (Réguer et al. 2007d, p. 65). In the case of wet finds these chlorides could survive in ionic form, $Cl^-_{aq}$ but if the objects have been allowed to dry the ions will precipitate, forming different compounds depending on the concentrations of elements within the corrosion layers. When chloride concentrations are high, such as in marine finds and in some terrestrial iron objects, excess chlorides can precipitate as ferrous chloride, $FeCl_2$ (Knight 1982). Ferrous chloride is highly hygroscopic and an important part of the so called "weeping iron" phenomenon where ferrous chloride deliquesces and forms very acidic liquid (Selwyn, Sirois & Argyropoulos 1999; Turgoose 1982b). It is also relatively unstable and in the presence of air can oxidise into goethite, lepidocrocite or akaganéite depending on the original ion concentrations (Rémazeilles & Refait 2006).

In aerated conditions and high enough $Cl^-$ concentrations iron β-oxyhydroxide, akaganéite, can form. It was first recognized in archaeological objects in 1977 (Zucchi et al.) and its central role in iron corrosion has since been recognized. Where access to oxygen is limited, as is the case in the original burial conditions in soil, beta ferrous hydroxychloride, $\beta - Fe_2(OH)_3Cl$, has been recognized as a major chloride containing compound (Neff et al. 2005). Beta ferrous hydroxychloride is known to be unstable and in aerated conditions it will relatively rapidly oxidise into akaganéite or γ-oxyhydroxide, lepidocrocite, depending on the chloride ion content (Réfait & Genin 1997). Thus it can only be found from relatively fresh archaeological samples that have not had much time to react with oxygen. Beta ferrous hydroxychloride is usually situated at the Metal-DPL interface and contains between 14-20 %mass chlorides whilst akaganéite can only absorb it in concentrations between 5-8 %mass (Réguer et al. 2005). It should be noted that even when Beta ferrous hydroxychloride is oxidised the released chlorides seem to remain within

the corrosion layers of an object (Neff et al. 2011, p. 1477). This is likely to lead to an increase in the amount of free chlorides at the vulnerable metal-DPL transition zone.

The relatively recently discovered distinction between akaganéite and beta ferrous hydroxychloride could have a paramount impact when the differences in desalination processes are assessed, because while only very limited results have been achieved when trying to dissolve chlorides from the former compound in an alkaline environment, the latter seems to be completely transformed into $Fe(OH)_2$ (Kergourlay et al. 2011). This transformation is followed by a release of chlorides, which are then free to diffuse out of the object. No such transformation was achieved with objects that had been stored in air for two years after excavation, as akaganéite could not be completely transformed by sodium hydroxide desalination treatment (Kergourlay et al. 2010).

Since recent research literature doesn't know a mechanism that would bind the chlorides tighter into the layers of fresh finds than oxidised ones the reason for the longer treatment time of batch 1 there is likely some other reason behind it. A likely cause is the greater integrity of the fresh finds, as drying the objects is connected with shrinkage, distortion and cracking of the corrosion layers on several publications (e.g. Conyn 1999, p. 196; Knight 1982; Kergourlay et al. 2010). If oxidised finds are more porous than ones finds then longer treatment times for the latter can be expected.

It has also been suggested that the free ferrous ions within the corrosion layers of fresh finds could precipitate within the pores of iron objects and clog them (North & Pearson 1975a; Turgoose 1993). Whilst some minor precipitation is possible and likely, no such clogging has been recorded on marine iron ingots treated in dilute sodium hydroxide at the ODéFA project (Guilminot et al. 2012). It could be expected that a relatively large marine iron object stored in seawater prior to being treated in aerated $NaOH$ solution would provide far more likely conditions for such clogging to take place, so it is unlikely that it has played a major role in this project. Also, it is argued by Turgoose (1985a) that the anoxic conditions of the alkaline sulphite bath would passivate the iron surface, making any further production of $Fe^{2+}$ ions and thus any large scale precipitation of hydrated ferric hydroxide or any other compound impossible.

Another difference in the treatments concerns the total amount of chloride removed from the objects. The results of the ODéFA projects, as well as current theory, would make one expect that more chlorides can be removed from fresh finds compared to oxidised

ones (Guliminot et al. 2012). In this project the largest total chloride amount, 1273 ppm, was extracted from the oxidised finds in batch 2, when the fresh finds produced some 2:3 of this amount, 828 ppm (appendix 4, p. 4). The difference is smaller in reality, as objects in batch 1 were weighted wet whilst objects in batch 2 were dry. It should be noted that these numbers are each average results received from a large number of probably very heterogeneous objects.

There were also clear differences between the objects entering baths 1 and 2, objects in batch 1 being significantly smaller and often of a very fragmentary nature while objects in batch 2 were clearly more robust with large surviving iron cores. The median mass of objects in batch 2 is over fourfold the median mass of objects in batch 1. This difference can be explained by their history: objects in batch 1 were made in an excavation where also small fragments are likely to be found and collected, whilst batch 2 objects were metal detector finds, and then objects with large surviving cores are more likely to be dug up. As chlorides are attracted to objects by the potential gradient of the corroding iron core it could be argued that objects with a large corroding metal surface will attract more chloride ions.

The picture becomes more complicated than that when the decorated objects of batch 3 are introduced to the comparison. These two massive finds, both around 200 grams, have the lowest amount of released chlorides of the three batches: 479 ppm. They had the shortest treatment time though, but with the chloride content of the final solution being only 1,5 ppm their treatment could be considered finished when it was terminated. With the very large deviation in the total extracted chloride content more emphasis should probably be given to the differences in treatment times and chloride release patterns, where the dry oxidised finds reacted to the treatment in a very similar way, clearly distinguishable from the slow chloride release of the fresh finds.

Unfortunately without any means to measure residual chlorides or the structure and composition of the finds after desalination it is impossible to come to a conclusion about the effectiveness of the treatments, as well as an explanation for the differences in the behaviour of the different batches of objects. In the future stability of the treated objects can indicate whether there is major amounts of harmful residual chlorides in the objects, especially in those from batches 1 and 3, or are the differences in the amounts of chlorides extracted explainable purely by the seemingly random heterogeneousness of the material.

## 11  Conclusions

Altogether 72 archaeological metal objects from the Hangastenmäki hillfort site were successfully treated during this project. Special attention was paid to the desalination process that was divided so that fresh, wet and un-oxidised finds, dry oxidised finds and finds with precious metal decorations would be treated separately. Clear differences in the behaviour between the dry oxidised finds and the wet un-oxidised ones emerged, un-oxidised finds releasing their chlorides far more slowly. Chosen desalination method was the so called alkaline sulphite method, published by North and Pearson (1975a), with lowered reagent concentrations (0,1 M $NaOH$, 0,05 M $Na_2SO_3$) suggested by Schmidt-Ott and Oswald (2006).

The total amount of chlorides for each batch of objects varied too much to allow any conclusions to be drawn. The small sample number of only three batches also sets limits for possible interpretations. Judging by the available theory it was concluded that the most likely reason for the different behaviour of the fresh and dry finds is the differences in the structure of the objects, the more integral structure of the fresh finds providing a stronger diffusion barrier for the chloride ions (Selwyn, McKinnon & Argyropoulos 2001).

Thorough interpretation of the efficiency of the treatment would require information about the residual chloride in the objects. This information could only have been obtained with destructive methods, which were not an option for this group of objects with cultural and scientific value. All three treatment batches had the chloride contents of their final treatment solutions below 5 ppm, which resulted in very promising survival rates in previous studies (Rimmer, Wang & Watkinson 2012). Monitoring the material in the future is still strongly recommended as stability can never be guaranteed (e.g. Wang 2007a).

It was concluded that the treatment was relatively easy to carry out with the equipment already available at the Conservation Laboratory of the National Museum of Finland, and thus alkaline sulphite treatment could be adopted with very small investments. For routine chloride content measurements either the Aquamerck® quick test kit 1.11106.0001 used in this project is recommended or, if possible, an ion selective electrode because of its success in published research literature (Wang et al. 2008). Because of the problems posed by the sulphite ions in chloride measurement phase and the waste solution

disposal it would be worth considering deaerated treatment solution as an option, especially since the Conservation Laboratory already has a vacuum oven with a pre-set possibility for this treatment.

Future research should include further treatment of dry and moist finds from similar find contexts to find out whether the different chloride extraction pattern seen during this project can be confirmed and explained. Preferably the desalination treatment should be carried out individually for each object and a possibility to carry out residual chloride analyses at a statistically significant scale would greatly enhance the scientific value of the research.

## 12 Acknowledgements

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## Objects list and conservation procedure timetable

| Object nr. | Object type | Photography before con-servation | X-ray investi-gation | Photography during con-servation | Consolidation | Mechanical cleaning | Photography after conservation | Packing | Total wor-king time |
|---|---|---|---|---|---|---|---|---|---|
| KM 39993:1 | Pommel, Pe-tersen t. T1 | 29.10.2015 | 28.10.2015 | 17.11. | Paraloid B-72 | 2.2.-24.2.2016 | 8.3.2016 | 7.4.2016 | |
| | | 0:15:00 | 2:20:00 | 1:00:00 | | 19:50:00 | 0:55:00 | 0:05:00 | 24:25:00 |
| KM 39993:2 | Bodkin ar-rowhead | 29.10.2015 | 3.11.2015 | 9.2.2016 | Paraloid B-72 | 25.2.2016 | 7.4./31.3.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | 0:05:00 | 0:35:00 | 0:10:00 | 0:05:00 | 1:32:30 |
| KM 39993:3 | Padlock bolt | 29.10.2015 | 3.11.2015 | 9.2.2016 | | 23.2.2016 | 1.4./31.3.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:45:00 | 0:07:30 | | 0:30:00 | 0:30:00 | 0:05:00 | 2:12:30 |
| KM 39993:4 | Spur frag-ment | 29.10.2015 | 3.11.2015 | 9.2.2016 | UHU hart | 2.3./25.2.2016 | 7.4./1.4.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | | 1:45:00 | 0:05:00 | 0:05:00 | 2:32:30 |
| KM 39993:5 | Spur frag-ment | 29.10.2015 | 3.11.2015 | 9.2.2016 | Paraloid B-72 | 25.2.2016 | 7.4./1.4.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | 0:05:00 | 1:10:00 | 0:20:00 | 0:05:00 | 2:17:30 |
| KM 39993:6 | Iron shoe reinforcement | 29.10.2015 | 3.11.2015 | 9.2.2016 | | 22.2.2016 | 31.3.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | | 0:25:00 | 0:10:00 | 0:05:00 | 1:17:30 |
| KM 39993:7 | Knife | 29.10.2015 | 3.11.2015 | 9.2.2016 | | 22.2.2016 | 1.4.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | | 0:55:00 | 0:05:00 | 0:05:00 | 1:42:30 |
| KM 39993:8 | Iron object | 29.10.2015 | 28.10.2015 | 9.2.2016 | | 25.2.2016 | 1.4.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:45:00 | 0:07:30 | | 0:20:00 | 0:05:00 | 0:05:00 | 1:37:30 |

| Object nr. | Object type | Photography before con-servation | X-ray investi-gation | Photography during con-servation | Consolidation | Mechanical cleaning | Photography after conservation | Packing | Total wor-king time |
|---|---|---|---|---|---|---|---|---|---|
| KM 39994:1 | Spearhead, Petersen t. K | 29.10.2015 | 28.10.2015 | 1.2./17.2. | Paraloid B-72 | 2.2.-17.2.2016 | 7.4./8.3.2016 | 7.4.2016 | |
| | | 0:15:00 | 3:45:00 | 0:30:00 | | 20:45:00 | 0:30:00 | 0:05:00 | 25:50:00 |
| KM 39994:2 | Spur | 29.10.2015 | 3.11.2015 | 9.2.2016 | Paraloid B-72 | 2.-3.3.2016 | 1.4.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | UHU hart | 1:35:00 | 0:20:00 | 0:05:00 | 2:37:30 |
| KM 39994:3 | Horseshoe fragments | 29.10.2015 | 3.11.2015 | 9.2.2016 | Paraloid B-72 | 17.-19.2.2016 | 1.4.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | UHU hart | 4:35:00 | 0:10:00 | 0:05:00 | 5:27:30 |
| KM 39994:4 | Horseshoe nail | 29.10.2015 | 3.11.2015 | 9.2.2016 | Paraloid B-72 | 22./25.2.2016 | 31.3.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | 0:10:00 | 0:35:00 | 0:10:00 | 0:05:00 | 1:37:30 |
| KM 39994:5 | Horseshoe nail | 29.10.2015 | 3.11.2015 | 9.2.2016 | | 16.2.2016 | 31.3.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | | 0:20:00 | 0:10:00 | 0:05:00 | 1:12:30 |
| KM 39994:6 | Knife | 29.10.2015 | 3.11.2015 | 9.2.2016 | Paraloid B-72 | 22.2.2016 | 31.3.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | | 0:55:00 | 0:10:00 | 0:05:00 | 1:47:30 |
| KM 39994:7 | Iron ingot | 29.10.2015 | 3.11.2015 | 9.2.2016 | Paraloid B-72 | 11./16.2.2016 | 31.3.2016 | 7.4.2016 | |
| | | 0:15:00 | 1:00:00 | 0:07:30 | UHU-hart | 2:50:00 | 0:10:00 | 0:05:00 | 4:27:30 |
| KM 39994:8 | Buckle | 29.10.2015 | 3.11.2015 | 9.2.2016 | Paraloid B-72 | 3.3.2016 | 7.4.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | 0:10:00 | 0:40:00 | 0:18:00 | 0:05:00 | 1:50:30 |

| Object nr. | Object type | Photography before conservation | X-ray investigation | Photography during conservation | Consolidation | Mechanical cleaning | Photography after conservation | Packing | Total working time |
|---|---|---|---|---|---|---|---|---|---|
| KM 39995:1 | Large knife | 29.10.2015 | 3.11.2015 | 9.2.2016 | | 19.-22.2.2016 | 7.4./8.3.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | | 3:15:00 | 0:15:00 | 0:05:00 | 4:12:30 |
| KM 39995:2 | Bodkin arrowhead | 29.10.2015 | 3.11.2015 | 9.2.2016 | Paraloid B-72 | 23.2.2016 | 7.4./31.3.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | 0:05:00 | 0:20:00 | 0:12:00 | 0:05:00 | 1:19:30 |
| KM 39995:3 | Bodkin arrowhead | 29.10.2015 | 3.11.2015 | 9.2.2016 | | 17.2.2016 | 7.4./31.3.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | | 0:20:00 | 0:12:00 | 0:05:00 | 1:14:30 |
| KM 39995:4 | Bodkin arrowhead | 29.10.2015 | 3.11.2015 | 9.2.2016 | Paraloid B-72 | 23.2.2016 | 7.4./31.3.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | 0:05:00 | 0:20:00 | 0:12:00 | 0:05:00 | 1:19:30 |
| KM 39995:5 | Bodkin arrowhead | 29.10.2015 | 3.11.2015 | 9.2.2016 | Paraloid B-72 | 23.2.2016 | 7.4./31.3.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | 0:05:00 | 0:20:00 | 0:12:00 | 0:05:00 | 1:19:30 |
| KM 39995:6 | Horseshoe | 29.10.2015 | 3.11.2015 | 9.2.2016 | Paraloid B-72 | 2.-4.3.2016 | 31.3.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | 0:10:00 | 6:30:00 | 0:12:00 | 0:05:00 | 7:34:30 |
| KM 39995:7 | Knife | 29.10.2015 | 3.11.2015 | 9.2.2016 | | 16.-17.2.2016 | 7.4./8.3./31.3.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | | 1:25:00 | 0:27:00 | 0:05:00 | 2:34:30 |
| KM 39995:8 | Iron shoe reinforcement | 29.10.2015 | 3.11.2015 | 9.2.2016 | | 11.2.2016 | 31.3.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | | 0:35:00 | 0:12:00 | 0:05:00 | 1:29:30 |
| KM 39995:9 | Cadleholder | 29.10.2015 | 3.11.2015 | 9.2.2016 | | 11.2.2016 | 8./31.3.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | | 0:35:00 | 0:27:00 | 0:05:00 | 1:44:30 |
| KM 39996:1 | Horseshoe fragment | 29.10.2015 | 3.11.2015 | 9.2.2016 | | 23.-25.2.2016 | 1.4.2016 | 7.4.2016 | |
| | | 0:15:00 | 0:15:00 | 0:07:30 | | 2:40:00 | 0:10:00 | 0:05:00 | 3:32:30 |

| Object nr. | Object type | Photography before con-servation | X-ray investi-gation | Photography during con-servation | Consolida-tion | Mechanical cleaning | Photography af-ter conservation | Packing | Total wor-king time |
|---|---|---|---|---|---|---|---|---|---|
| KM 40551:1 | Knife | 27.10.2015 | 11.5.2015 | | Paraloid B-72 | 7.3.2015 | 7.1./31.3.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:50:00 | 0:12:00 | 0:05:00 | 1:20:30 |
| MK 40551:2 | Horseshoe frag-ment | 27.10.2015 | 11.5.2015 | | Paraloid B-72 | 16.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:05:00 | 0:10:00 | 0:05:00 | 0:33:30 |
| KM 40551:3 | Rivet | 27.10.2015 | 11.5.2015 | | | 16.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:05:00 | 0:10:00 | 0:05:00 | 0:33:30 |
| KM 40551:4 | Rivet head | 27.10.2015 | 11.5.2015 | | | 16.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:10:00 | 0:10:00 | 0:05:00 | 0:38:30 |
| KM 40551:5 | Iron object | 27.10.2015 | 11.5.2015 | | | 16.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:05:00 | 0:10:00 | 0:05:00 | 0:33:30 |
| KM 40551:6 | Iron object | 27.10.2015 | 11.5.2015 | | | 16.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:10:00 | 0:10:00 | 0:05:00 | 0:38:30 |
| KM 40551:7 | Iron object | 27.10.2015 | 11.5.2015 | | | 14.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:15:00 | 0:10:00 | 0:05:00 | 0:43:30 |
| KM 40551:8 | Horseshoe nail | 27.10.2015 | 11.5.2015 | | | 14.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:10:00 | 0:10:00 | 0:05:00 | 0:38:30 |
| KM 40551:21 | Bodkin arrowhead | 27.10.2015 | 11.5.2015 | | Paraloid B-72 | 7.3.2016 | 7.4./31.3.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | UHU-hart | 1:00:00 | 0:12:00 | 0:05:00 | 1:30:30 |
| KM 40551:22 | Horseshoe nail fragment | 27.10.2015 | 11.5.2015 | | | 16.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:05:00 | 0:10:00 | 0:05:00 | 0:33:30 |

| Object nr. | Object type | Photography before con-servation | X-ray investi-gation | Photography during con-servation | Consolidation | Mechanical cleaning | Photography after conservation | Packing | Total wor-king time |
|---|---|---|---|---|---|---|---|---|---|
| KM 40551:27 | Iron objedct fragment | 26.10.2015 | 11.5.2015 | | | 14.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:10:00 | 0:10:00 | 0:05:00 | 0:38:30 |
| KM 40551:28 | Iron object fragment | 27.10.2015 | 11.5.2015 | | | 7./14.3.2016 | 31.3.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 2:05:00 | 0:12:00 | 0:05:00 | 2:35:30 |
| KM 40551:31 | Horseshoe nail | 27.10.2015 | 11.5.2015 | | | 14.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:15:00 | 0:10:00 | 0:05:00 | 0:43:30 |
| KM 40551:32 | Nail | 27.10.2015 | 11.5.2015 | | | 16.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:05:00 | 0:10:00 | 0:05:00 | 0:33:30 |
| KM 40551:33 | Iron object fragment | 26.10.2015 | 11.5.2015 | | | 16.3.2016 | 31.3.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:10:00 | 0:12:00 | 0:05:00 | 0:40:30 |
| KM 40551:34 | Iron object fragment | 26.10.2015 | 11.5.2015 | | | 16.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:05:00 | 0:10:00 | 0:05:00 | 0:33:30 |
| KM 40551:39 | Iron object fragment | 26.10.2015 | 11.5.2015 | | Paraloid B-72 | 16.3.2016 | 31.3.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | UHU-hart | 0:25:00 | 0:12:00 | 0:05:00 | 0:55:30 |
| KM 40551:40 | Nail | 26.10.2015 | 11.5.2015 | | UHU-hart | 14./16.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:20:00 | 0:10:00 | 0:05:00 | 0:48:30 |
| KM 40551:44 | Copper metal sheet frag-ment | 26.10.2015 | 11.5.2015 | | | 8.2.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:10:00 | 0:10:00 | 0:05:00 | 0:38:30 |
| KM 40551:47 | Iron object fragment | 26.10.2015 | 11.5.2015 | | | 16.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:15:00 | 0:10:00 | 0:05:00 | 0:43:30 |

| Object nr. | Object type | Photography before con-servation | X-ray investi-gation | Photography during con-servation | Consolidation | Mechanical cleaning | Photography after conservation | Packing | Total wor-king time |
|---|---|---|---|---|---|---|---|---|---|
| KM 40551:51 | Copper metal buckle | 26.10.2015 | 11.5.2015 | | | 8.2.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:20:00 | 0:10:00 | 0:05:00 | 0:48:30 |
| KM 40551:52 | Bodkin ar-rowhead | 27.10.2015 | 11.5.2015 | | Paraloid B-72 | 14.3.2016 | 7.4./31.3.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | UHU-hart | 1:45:00 | 0:12:00 | 0:05:00 | 2:15:30 |
| KM 40551:53 | Horseshoe nail | 27.10.2015 | 11.5.2015 | | | 7.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:20:00 | 0:10:00 | 0:05:00 | 0:48:30 |
| KM 40551:54 | Nail | 27.10.2015 | 11.5.2015 | | UHU-hart | 16.3.2016 | 31.3.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:20:00 | 0:12:00 | 0:05:00 | 0:50:30 |
| KM 40551:55 | | 27.10.2015 | 11.5.2015 | | Paraloid B-72 | 14.3.2016 | 31.3.2016 | 30.3.2016 | |
| | Iron object | 0:10:00 | 0:03:30 | | | 0:25:00 | 0:12:00 | 0:05:00 | 0:55:30 |
| KM 40551:56 | | 27.10.2015 | 11.5.2015 | | Paraloid B-72 | 14.3.2016 | 31.3.2016 | 30.3.2016 | |
| | Iron object | 0:10:00 | 0:03:30 | | | 0:20:00 | 0:12:00 | 0:05:00 | 0:50:30 |
| KM 40551:57 | Iron object, possibly slag | 27.10.2015 | 11.5.2015 | | | 16.3.2016 | 31.3.2016 | 7.4.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:05:00 | 0:12:00 | 0:05:00 | 0:35:30 |
| KM 40551:58 | Iron object fragment | 27.10.2015 | 11.5.2015 | | Paraloid B-72 | 14.3.2016 | 31.3.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:40:00 | 0:12:00 | 0:05:00 | 1:10:30 |
| KM 40551:59 | Iron object fragment | 26.10.2015 | 11.5.2015 | | Paraloid B-72 | 14.3.2016 | 31.3.2016 | 7.4.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:50:00 | 0:12:00 | 0:05:00 | 1:20:30 |
| KM 40551:60 | Iron object fragment | 26.10.2015 | 11.5.2015 | | | 14.3.2016 | 31.3.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 1:00:00 | 0:12:00 | 0:05:00 | 1:30:30 |

| Object nr. | Object type | Photography before con-servation | X-ray investi-gation | Photography during con-servation | Consolidation | Mechanical cleaning | Photography after conservation | Packing | Total wor-king time |
|---|---|---|---|---|---|---|---|---|---|
| KM 40551:61 | Nail | 26.10.2015 | 11.5.2015 | | Paraloid B-72 | 14.3.2016 | 31.3.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:20:00 | 0:12:00 | 0:05:00 | 0:50:30 |
| KM 40551:62 | Iron object fragment | 26.10.2015 | 11.5.2015 | | | 16.3.2016 | 31.3.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:20:00 | 0:12:00 | 0:05:00 | 0:50:30 |
| KM 40551:63 | Iron object fragment | 26.10.2015 | 11.5.2015 | | | 16.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:15:00 | 0:10:00 | 0:05:00 | 0:43:30 |
| KM 40551:64 | Iron object, possibly slag | 26.10.2015 | 11.5.2015 | | Paraloid B-72 | 16.3.2016 | 31.3.2016 | 7.4.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:10:00 | 0:12:00 | 0:05:00 | 0:40:30 |
| KM 40551:65 | Iron object fragment, drawn | 26.10.2015 | 11.5.2015 | | Paraloid B-72 | 14.3.2016 | 31.3.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:50:00 | 0:12:00 | 0:05:00 | 1:20:30 |
| KM 40551:66 | Iron ingot | 26.10.2015 | 11.5.2015 | | | 14.3.2016 | 31.3.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:30:00 | 0:12:00 | 0:05:00 | 1:00:30 |
| KM 40551:67 | Iron object fragment | 26.10.2015 | 11.5.2015 | | | 16.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:15:00 | 0:10:00 | 0:05:00 | 0:43:30 |
| KM 40551:68 | Iron object fragment | 26.10.2015 | 11.5.2015 | | Paraloid B-72 | 16.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:20:00 | 0:10:00 | 0:05:00 | 0:48:30 |
| KM 40551:69 | Iron object fragment | 26.10.2015 | 11.5.2015 | | Paraloid B-72 | 16.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:10:00 | 0:10:00 | 0:05:00 | 0:38:30 |
| KM 40551:70 | Iron object fragment | 26.10.2015 | 11.5.2015 | | Paraloid B-72 | 7.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:15:00 | 0:10:00 | 0:05:00 | 0:43:30 |

| Object nr. | Object type | Photography before con-servation | X-ray investi-gation | Photography during con-servation | Consolidation | Mechanical cleaning | Photography after conservation | Packing | Total wor-king time |
|---|---|---|---|---|---|---|---|---|---|
| KM 40551:71 | Iron object fragment | 26.10.2015 | 11.5.2015 | | | 16.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:20:00 | 0:10:00 | 0:05:00 | 0:48:30 |
| KM 40551:72 | Iron object fragment | 26.10.2015 | 11.5.2015 | | | 16.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10:00 | 0:03:30 | | | 0:05:00 | 0:10:00 | 0:05:00 | 0:33:30 |
| KM 40551:73 | Iron object fragment | 7.1.2016 | 5.2.2016 | | | 18.3.2016 | 7.4.2016 | 7.4.2016 | |
| | | 0:10:00 | 0:05:00 | | | 0:20:00 | 0:15:00 | 0:05:00 | 0:50:00 |
| KM 40551:74 | Iron object fragment | 7.1.2016 | 5.2.2016 | | | 18.3.2016 | 7.4.2016 | 7.4.2016 | |
| | | 0:10:00 | | | | 0:15:00 | 0:08:00 | 0:05:00 | 0:38:00 |
| KM 40551:75 | Iron object fragment | 7.1.2016 | 5.2.2016 | | | 18.3.2016 | 7.4.2016 | 7.4.2016 | |
| | | 0:10:00 | | | | 0:15:00 | 0:08:00 | 0:05:00 | 0:38:00 |
| KM 40551:81 | Horseshoe nail | 27.10.2015 | 11.5.2015 | | Paraloid B-72 | 16.3.2016 | 1.4.2016 | 30.3.2016 | |
| | | 0:10 | 0:03:30 | | | 0:25:00 | 0:10:00 | 0:05:00 | 0:53:30 |

# After conservation weights and dimensions

| Object nr. | weight (g) | dimensions (mm) |
|---|---|---|
| KM 39993:1 | 194,0 | 85 x 43 x 33 |
| KM 39993:2 | 11,3 | 71 x 8 |
| KM 39993:3 | 13,1 | 59 x 10 |
| KM 39993:4 | 38,7 | 130 x 29 |
| KM 39993:5 | 22,0 | 114 x 38 |
| KM 39993:6 | 28,9 | 47 x 53 x 7 |
| KM 39993:7 | 47,5 | 157 x 21 x 6 |
| KM 39993:8 | 67,7 | 93 x 16 |
| KM 39994:1 | 182,5 | 277 x 26 |
| KM 39994:2 | 34,2 | 147 x 65 |
| KM 39994:3 | 129,1 | 114 x 115 x 13 |
| KM 39994:4 | 5,9 | 21 x 16 |
| KM 39994:5 | 9,1 | 31 x 15 |
| KM 39994:6 | 23,1 | 120 x 16 x 5 |
| KM 39994:7 | 57,7 | 36 x 20 x 14 |
| KM 39994:8 | 6,7 | 39 x 25 x 11 |
| KM 39995:1 | 85,5 | 23 x 5 |
| KM 39995:2 | 11,3 | 71 x 8 |
| KM 39995:3 | 13,1 | 59 x 10 |
| KM 39995:4 | 13,2 | 59 x 10 |
| KM 39995:5 | 10,4 | 67 x 9 |
| KM 39995:6 | 96,6 | 103 x 108 x 6 |
| KM 39995:7 | 28,0 | 147 x 17 x 5 |
| KM 39995:8 | 15,0 | 13 x 45 x 3 |

| Object nr. | weight (g) | dimensions (mm) |
|---|---|---|
| KM 39995:9 | 15,6 | 57 |
| KM 39996:1 | 60,2 | 98 x 30 x 9 |
| KM 40551:1 | 16,0 | 116 x 7 x 6 |
| KM 40551:2 | 4,7 | 25 x 16 x 8 |
| KM 40551:3 | 1,1 | 9 |
| KM 40551:4 | 3,5 | 22 x 18 x 8 |
| KM 40551:5 | 1,3 | 15 x 13 |
| KM 40551:6 | 2,0 | 28 x 7 |
| KM 40551:7 | 8,9 | 18 x 15 x 10 |
| KM 40551:8 | 4,0 | 29 x 16 x 5 |
| KM 40551:21 | 11,1 | 66 x 11 |
| KM 40551:22 | 3,0 | 16 x 13 x 5 |
| KM 40551:27 | 5,6 | 31 x 11 x 7 |
| KM 40551:28 | 25,6 | 46 x 37 x 9 |
| KM 40551:31 | 3,5 | 27,5 x 13 x 4 |
| KM 40551:32 | 4,2 | 20 x 19 |
| KM 40551:33 | 11,3 | 38 x 17 x 7 |
| KM 40551:34 | 0,4 | 14 x 9 x 1 |
| KM 40551:39 | 4,6 | 47 x 9 |
| KM 40551:40 | 1,4 | 19 x 9 |
| KM 40551:44 | 0,5 | 19 x 13 x 5 |
| KM 40551:47 | 7,0 | 21 x 15 x 11 |
| KM 40551:51 | 2,2 | 21 x 15 x 2 |
| KM 40551:52 | 25,1 | 79 x 13 |

| Object nr. | weight (g) | dimensions (mm) |
|---|---|---|
| KM 40551:53 | 2,7 | 29 x 14 x 6 |
| KM 40551:54 | 4,3 | 28 x 2 x 6 |
| KM 40551:55 | 9,6 | 95 x 7 |
| KM 40551:56 | 12,8 | 42 x 75 |
| KM 40551:57 | 5,3 | 25 x 25 x 11 |
| KM 40551:58 | 18,3 | 35 x 38 x 13 |
| KM 40551:59 | 9,0 | 56 x 11 x 5 |
| KM 40551:60 | 9,2 | 57 x 20 x 8 |
| KM 40551:61 | 7,7 | 59 x 12 |
| KM 40551:62 | 5,9 | 46 x 7 |
| KM 40551:63 | 5,6 | 26 x 16 x 5 |
| KM 40551:64 | 5,9 | 38 x 22 x 13 |
| KM 40551:65 | 10,7 | 50 x 13 x 6 |
| KM 40551:66 | 31,0 | 40 x 21 x 13 |
| KM 40551:67 | 1,5 | 18 x 10 |
| KM 40551:68 | 0,7 | 15 x 8 x 3 |
| KM 40551:69 | 1,7 | 12 x 8 x 7 |
| KM 40551:70 | 0,6 | 21 x 9 x 3 |
| KM 40551:71 | 2,9 | 19 x 7 x 7 |
| KM 40551:72 | 0,9 | 10 x 8 x 6 |
| KM 40551:73 | 4,7 | 22 x 11 x 5 |
| KM 40551:74 | 1,6 | 12 x 7 x 7 |
| KM 40551:75 | 1,0 | 23 x 9 x 3 |
| KM 40551:81 | 5,8 | 32 x 15 x 9 |

## Desalination charts

| Batch 1 | | | |
|---|---|---|---|
| **Objects in batch** | **Weight before treatment (g)** | **Objects in batch** | **Weight before treatment (g)** |
| KM 40551:1 | 20,9 | KM 40551:54 | 6,2 |
| KM 40551:2 | 5,5 | KM 40551:55 | 11,5 |
| KM 40551:3 | 1,4 | KM 40551:56 | 17,2 |
| KM 40551:4 | 6,1 | KM 40551:57 | 7,6 |
| KM 40551:5 | 1,7 | KM 40551:58 | 20,7 |
| KM 40551:6 | 5,9 | KM 40551:59 | 12,0 |
| KM 40551:7 | 10,9 | KM 40551:60 | 14,1 |
| KM 40551:8 | 4,9 | KM 40551:61 | 9,9 |
| KM 40551:21 | 14,1 | KM 40551:62 | 8,8 |
| KM 40551:22 | 4,1 | KM 40551:63 | 7,1 |
| KM 40551:27 | 6,8 | KM 40551:64 | 8,0 |
| KM 40551:28 | 33,9 | KM 40551:65 | 16,7 |
| KM 40551:31 | 1,3 | KM 40551:66 | 35,7 |
| KM 40551:32 | 6,5 | KM 40551:67 | 2,3 |
| KM 40551:33 | 14,2 | KM 40551:68 | 1,4 |
| KM 40551:39 | 7,8 | KM 40551:69 | 2,0 |
| KM 40551:40 | 3,1 | KM 40551:70 | 1,7 |
| KM 40551:47 | 8,4 | KM 40551:71 | 4,9 |
| KM 40551:52 | 31,9 | KM 40551:72 | 1,6 |
| KM 40551:53 | 4,1 | KM 40551:81 | 6,8 |

| Changes of solution | |
|---|---|
| **Batch start** | 18.11.2015 |
| 1. change | 1.12.2015 |
| 2. change | 16.12.2015 |
| 3. change | 7.1.2016 |
| 4. change | 20.1.2016 |
| 5. change | 3.2.2016 |
| 6. change | 18.2.2016 |
| **Batch end** | 2.3.2016 |

| Washing | |
|---|---|
| 2.3.2016 | |
| 12:45 | pH 4-5 |
| 20:15 | pH 11 |
| 3.3.2016 | |
| 8:30 | pH 9 |
| 19:10 | pH 7 |
| 4.3.2016 | |
| 10:40 | pH 6-7 |
| 16:00 | pH 5-6 |

| Drying |
|---|
| 4.3.2016,16:40 - 7.4.2016, 11:45. T: 110°C |

| Total weight (g) | Batch solution volume (l) |
|---|---|
| 389,7 | 3 |

| Batch 2 | |
|---|---|
| **Objects in batch** | **Weight before treatment (g)** |
| KM 39993:2 | 20,3 |
| KM 39993:3 | 18,8 |
| KM 39993:4 | 45,4 |
| KM 39993:5 | 26,3 |
| KM 39993:6 | 31,2 |
| KM 39993:7 | 50,1 |
| KM 39993:8 | 50,1 |
| KM 39994:2 | 40,3 |
| KM 39994:3 | 144,6 |
| KM 39994:4 | 10,4 |
| KM 39994:5 | 9,6 |
| KM 39994:6 | 29,1 |
| KM 39994:7 | 65,9 |
| KM 39994:8 | 9,1 |
| KM 39995:1 | 91,9 |
| KM 39995:2 | 13,6 |
| KM 39995:3 | 13,8 |
| KM 39995:4 | 15,1 |
| KM 39995:5 | 12,7 |
| KM 39995:6 | 128,9 |
| KM 39995:7 | 31 |
| KM 39995:8 | 9,1 |
| KM 39995:9 | 9,1 |
| KM 39996:1 | 73,1 |

| Changes of solution | |
|---|---|
| **Batch start** | 18.11.2015 |
| 1. change | 1.12.2015 |
| 2. change | 16.12.2015 |
| 3. change | 7.1.2016 |
| 4. change | 20.1.2016 |
| **Batch end** | 3.2.2016 |

| Washing | |
|---|---|
| **3.2.2016** | |
| 13:00 | pH 4-5 |
| 20:00 | pH 10 |
| **4.2.2016** | |
| 10:45 | pH 9 |
| 20:15 | pH 7 |
| **5.2.2016** | |
| 10:45 | pH 6-7 |
| 20:00 | pH 6 |

| Drying |
|---|
| 5.2.2016, 20:15 - 8.2.2016, 15:00. T: 110 °C |

| Total weight (g) | Batch solution volume (l) |
|---|---|
| 949,5 | 6 |

| Batch 3 | |
|---|---|
| **Objects in batch** | **Weight before treatment (g)** |
| KM 39993:1 | 213,2 |
| KM 39994:1 | 189,3 |

| Drying |
|---|
| 27.1.2016, 19:00 - 29.1.2016, 11:15. T: 110 °C |

| **Total weight (g)** | **Batch solution volume (l)** |
|---|---|
| 402,5 | 3 |

| Changes of solution | |
|---|---|
| **Batch start** | 18.11.2015 |
| 1. change | 1.12.2015 |
| 2. change | 16.12.2015 |
| 3. change | 7.1.2016 |
| **Batch end** | 25.1.2016 |

| Washing | |
|---|---|
| **25.1.2016** | |
| 11:00 | pH 4-5 |
| 19:30 | pH 8-9 |
| **26.1.2016** | |
| 11:00 | not measured |
| 19:40 | pH 6-7 |
| **27.1.2016** | |
| 12:40 | pH 5 |
| 19:00 | pH 4-5 |

**Chloride measurement results**

During sample preparation 0,5 ml $HNO_3$ solution was added to each 20 ml sample. This has been compensated in the Method 1 (direct IC) results by recalculating the values with the following formula:

$$cCl = \frac{20,5}{20} \times measured\ cCl$$

The diagrams display the corrected results. Original measured values can be found in appendix x.

| | Aquamerck ® quick test 1.11106.0001 | | | | | | |
|---|---|---|---|---|---|---|---|
| | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 | Sample 7 |
| Batch 1 | 23 | 23 | 28 | 13 | ≤10 | – | – |
| Batch 2 | 160 | 24 | 12 | <8 | <4 | | |
| Batch 3 | 50 | 13 | <8 | <8 | | | |
| Batch 4 | 48 | | | | | | |

| | Ion Chromatograph Metrohm 761 Compact IC | | | | | | |
|---|---|---|---|---|---|---|---|
| | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 | Sample 7 |
| Bach 1 | 10,7 | 17,1 | 21,7 | 11,8 | 9,1 | 8,3 | 4,4 |
| Batch 2 | 192,9 | 18,6 | 10,6 | 3,1 | 1,8 | | |
| Batch 3 | 41,1 | 9,1 | 3,7 | 1,5 | | | |

| Method 1, direct measurement |
|---|
| Method 2, dialysis |

IC chloride measurement charts. Column colour indicates the different methods (light blue – method 1; light grey – method 2).



Batch 1, IC



Batch 2, IC
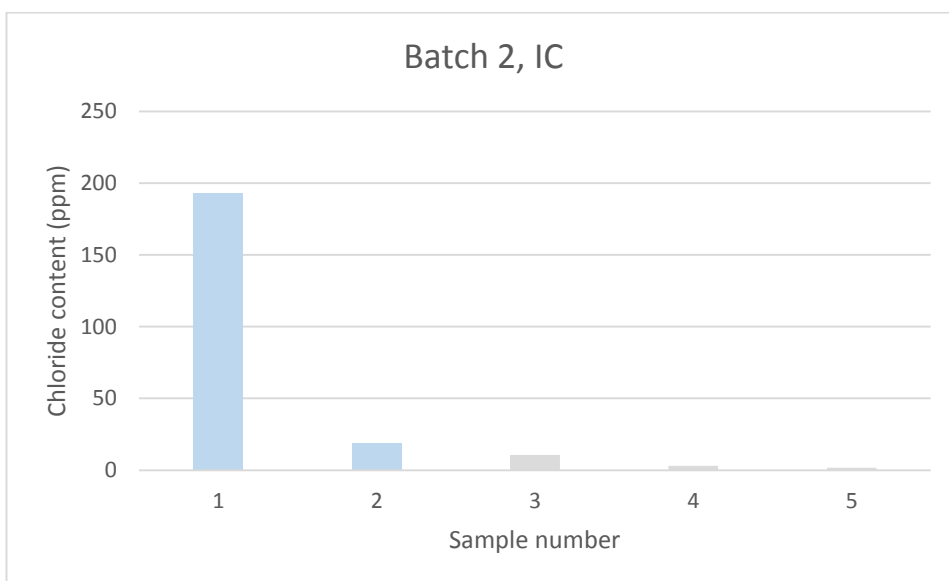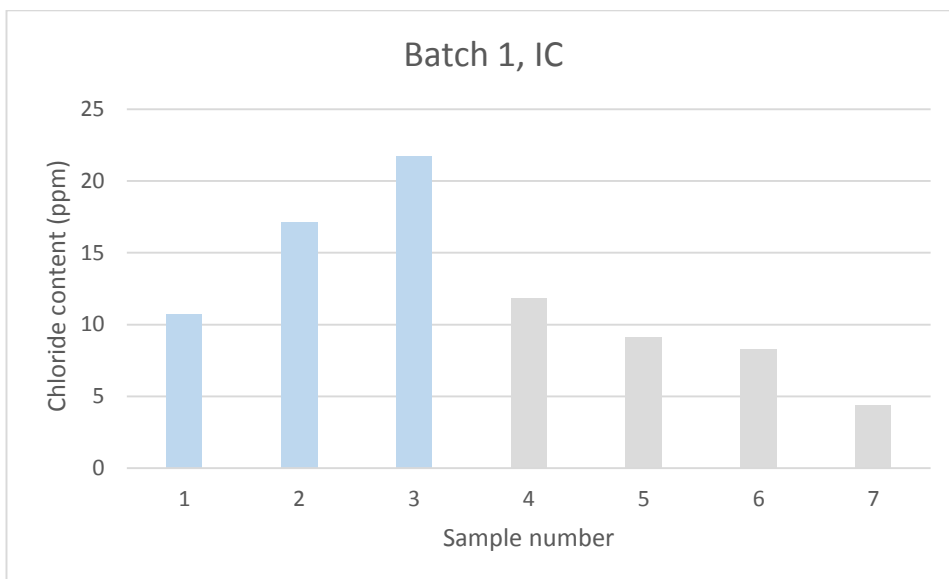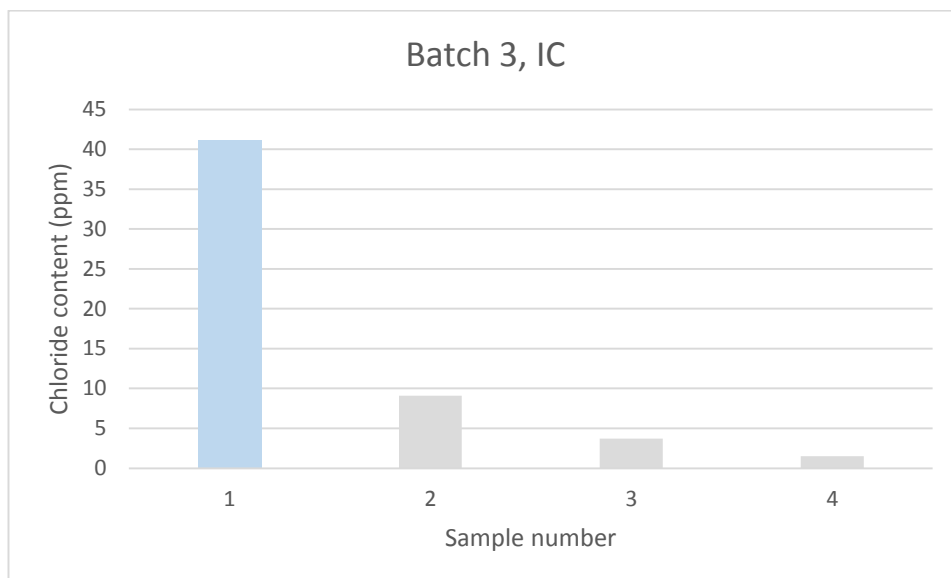
Combined Aquamerck® quick test & IC method 1 result charts. Colour indicates the different methods (green – quick test kit; light grey – IC method 1)

## Batch 2, combined IC + quick test results



## Batch 3, combined IC + quick test



## Total amount of removed chloride
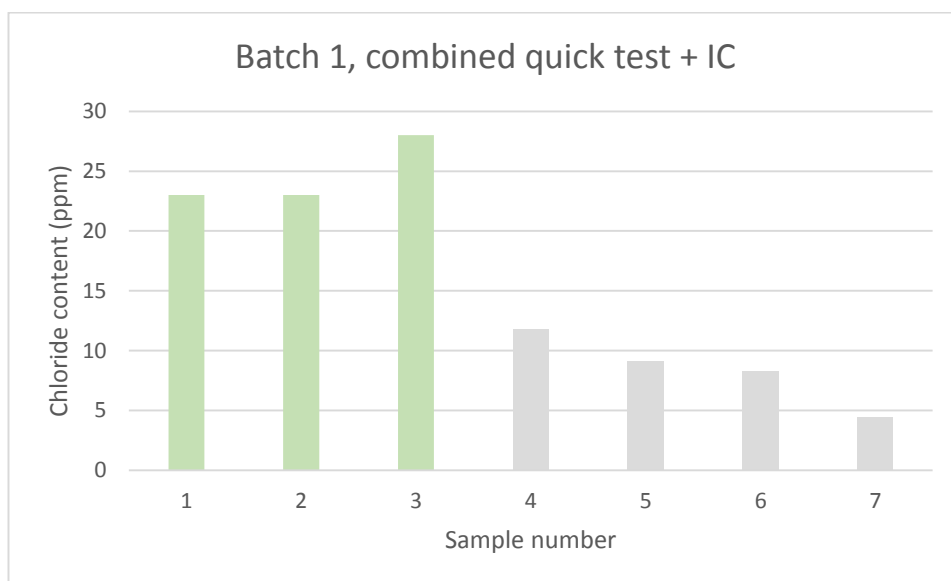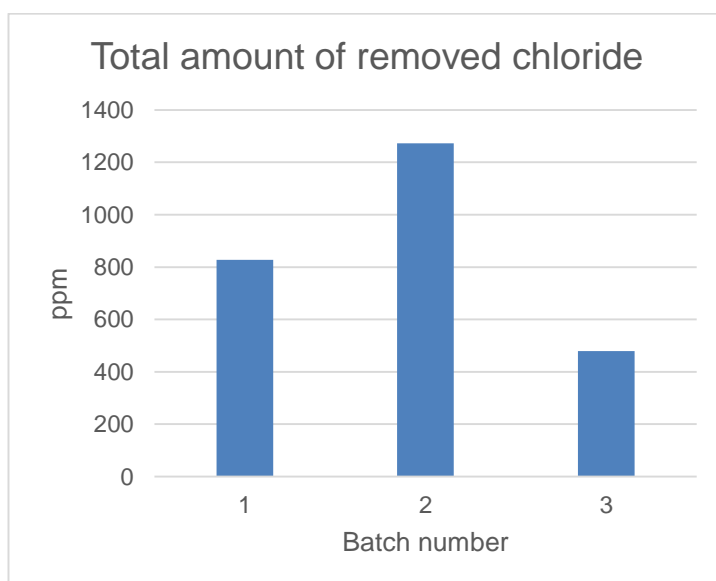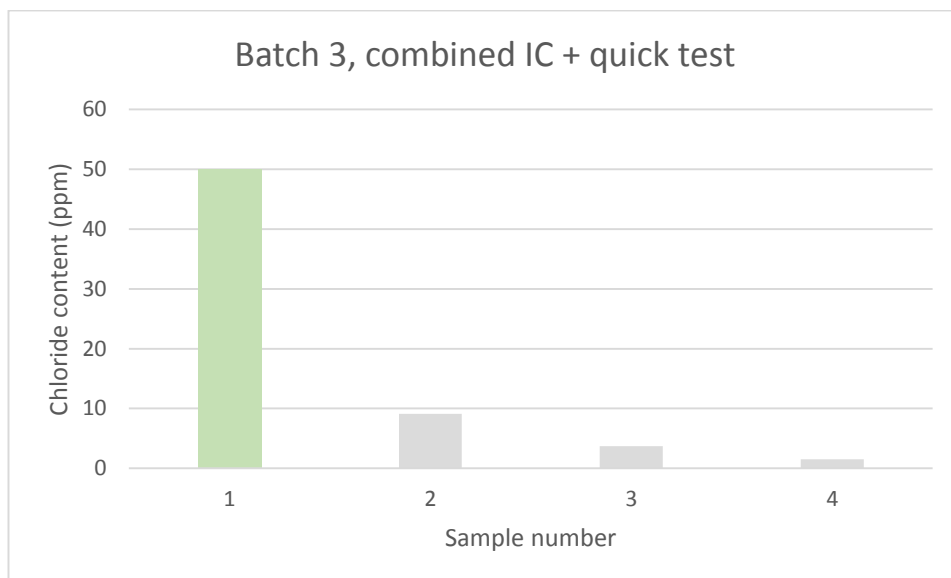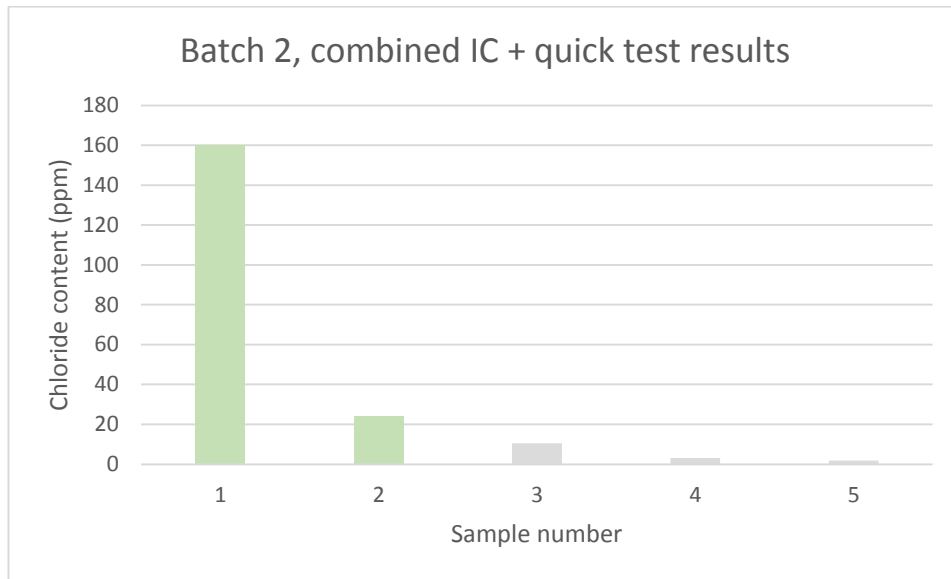
**Standard solution equations**

Preparation of a 2 litre 1000 ppm solution form sodium chloride. A 2 litre 1000 ppm solution will require 2 grams of chloride.

From

$$\frac{MNaCl}{MCl} \times mCl = mNaCl$$

$M_{NaCl}$ = 58,44 g/mol
$M_{Cl}$ = 35,45 g/mol
$m_{Cl}$ = 2,0 g

We get that 3,29703 grams of sodium chloride is needed. 3,2973 grams measured and dissolved into 2 litres of deionized water.

The rest of the standard solutions were diluted to deionized water as follows:

| The initial Cl-concentration (ppm) | Dilution ratio, solution/deionized water (ml/ml) | The resulting Cl-concentration (ppm) |
|---|---|---|
| 1000 | 5/995 | 5 |
| 1000 | 5/495 | 10 |
| 1000 | 15/885 | 15 |
| 1000 | 5/245 | 20 |
| 1000 | 150/850 | 150 |

| The initial Cl-concentration (ppm) | Dilution ratio, solution/deionized water (ml/ml) | The resulting Cl-concentration (ppm) |
|---|---|---|
| 10 | 10/90 | 1 |
| 150 | 100/100 | 75 |

| The initial Cl-concentration (ppm) | Dilution ratio, solution/deionized water (ml/ml) | The resulting Cl-concentration (ppm) |
|---|---|---|
| 75 | 25/25 | 37,5 |

## Ion chromatography reports

Batch 1, sample 1. Method 2 (dialysis)

```
Report date:        14.4.2016 11:16:20
Printed by:         user

Ident:              Erä 1, näyte 1
Analysis from:      17.3.2016 17:48:33
File:               _2016-03-17_          Last save: 11.4.2016 12:43:01
  Manual peaks!
Method:             Aleksi Pienimäki_dialyysi        Last save: 17.3.2016 13:26:35
Run operator:       user
Analysis number:    61

SAMPLE:             alkaalisulfiitin käyttöliuokset
  :
Vial number:        1
Volume:             20.0 µL
Dilution:           1.00
Amount:             1.0000

COLUMN:             Polyvinyl alcohol
Size:               4.0 x 100 mm
Number:             6.1006.510
Part.size:          5.0 µm

ELUENT:             Na2CO3 3,2 mmol/l / NaHCO3 1 mmol/mol


Flow:               0.70 mL/min
Temperature:        20.0°C
Pressure:           7.0 MPa
```
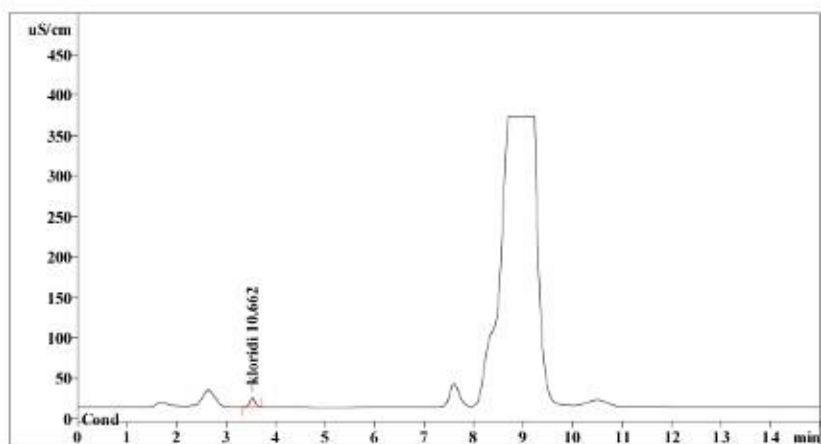


```
Quantitation method:   Custom

No  Retention  Height      Area       Conc.    Name
         min   uS/cm uS/cm*sec        mg/l
 1      3.53   11.49     81.079      10.662    kloridi

This report has been created by IC Net
METROHM LTD
```

Batch 1, sample 2. Method 2 (dialysis)

```
Report date:        14.4.2016 11:17:41
Printed by:         user

Ident:              Erä 1, näyte 2
Analysis from:      17.3.2016 17:20:35
File:               _2016-03-17_            Last save: 11.4.2016 12:43:01
  Manual peaks!
Method:             Aleksi Pienimäki_dialyysi          Last save: 17.3.2016 13:26:35
Run operator:       user
Analysis number:    60

SAMPLE:             alkaalisulfiitin käyttöliuokset
      :

Vial number:        1
Volume:             20.0 µL
Dilution:           1.00
Amount:             1.0000

COLUMN:             Polyvinyl alcohol
Size:               4.0 x 100 mm
Number:             6.1006.510
Part.size:          5.0 µm

ELUENT:             Na2CO3 3,2 mmol/l / NaHCO3 1 mmol/mol


Flow:               0.70 mL/min
Temperature:        20.0°C
Pressure:           6.9 MPa
```
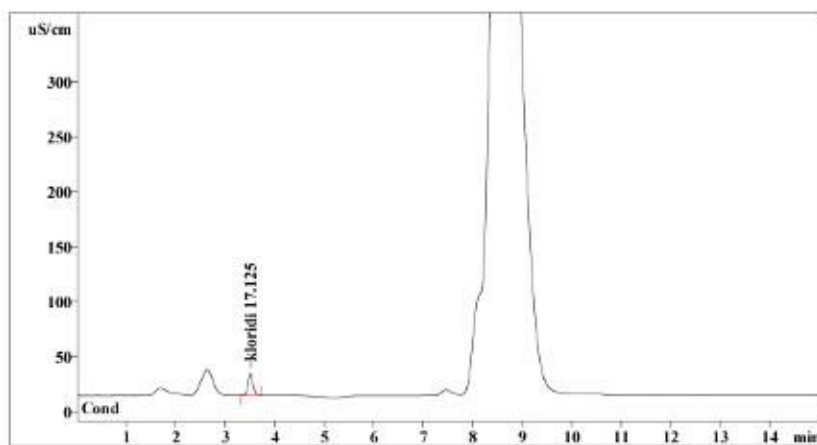


```
Quantitation method:   Custom

No  Retention  Height      Area        Conc.    Name
         min   uS/cm uS/cm*sec         mg/l
 1       3.51  19.58    134.508        17.125   kloridi

This report has been created by IC Net
METROHM LTD
```

Batch 1, sample 3. Method 2 (dialysis)

```
Report date:          14.4.2016 11:18:11
Printed by:           user

Ident:                Erä 1, näyte 3
Analysis from:        17.3.2016 16:51:36
File:                 _2016-03-17_            Last save: 11.4.2016 12:43:01
  Manual peaks!
Method:               Aleksi Pienimäki_dialyysi            Last save: 17.3.2016 13:26:35
Run operator:         user
Analysis number:      59

SAMPLE:               alkaalisulfiitin käyttöliuokset
        :
Vial number:          1
Volume:               20.0 µL
Dilution:             1.00
Amount:               1.0000

COLUMN:               Polyvinyl alcohol
Size:                 4.0 x 100 mm
Number:               6.1006.510
Part.size:            5.0 µm

ELUENT:               Na2CO3 3,2 mmol/1 / NaHCO3 1 mmol/mol


Flow:                 0.70 mL/min
Temperature:          20.0°C
Pressure:             7.4 MPa
```



```
Quantitation method:   Custom

No   Retention  Height      Area      Conc.   Name
          min   uS/cm uS/cm*sec      mg/l
  1       3.53   24.99   175.089     21.735   kloridi

This report has been created by IC Net
METROHM LTD
```

Batch 1, sample 4. Method 1 (direct measurement)

Report date:        15.3.2016 13:47:35
Printed by:         user

Ident:              Erä 1, näyte 4, neljäs ajo
Analysis from:      15.3.2016 11:18:40
File:               2016-03-15_          Last save: 15.3.2016 11:33:38
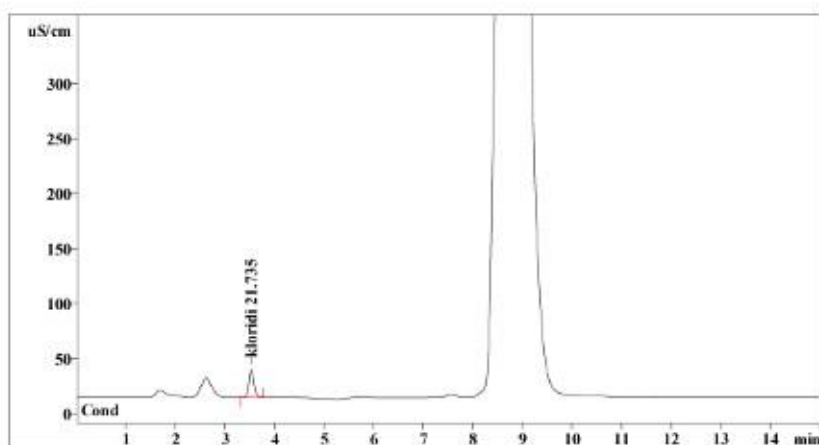Modified!   Manual peaks!
Method:             Aleksi Pienimäki.mtw          Last save: 10.3.2016 13:49:34
Run operator:       user
Analysis number:    22

SAMPLE:             alkaalisulfiitin käyttöliuokset
       :
Vial number:        1
Volume:             20.0 µL
Dilution:           1.00
Amount:             1.0000

COLUMN:             Polyvinyl alcohol
Size:               4.0 x 100 mm
Number:             6.1006.510
Part.size:          5.0 µm

ELUENT:             Na2CO3 3,2 mmol/l / NaHCO3 1 mmol/mol

Flow:               0.70 mL/min
Temperature:        20.0°C
Pressure:           7.1 MPa



Quantitation method:    Custom

No  Retention  Height       Area        Conc.   Name
           min    uS/cm  uS/cm*sec       mg/l
 1       3.37    21.52    145.737       11.492   kloridi

This report has been created by IC Net
 METROHM LTD

Batch 1, sample 5. Method 1 (direct measurement)



```
Report date:          15.3.2016 13:41:44
Printed by:           user

Ident:                Erä 1, näyte 5
Analysis from:        15.3.2016 11:51:28
File:                 _2016-03-15_              Last save: 15.3.2016 12:08:58
   Manual peaks!
Method:               Aleksi Pienimäki.mtw           Last save: 15.3.2016 11:49:53
Run operator:         user
Analysis number:      25

SAMPLE:               alkaalisulfiitin käyttöliuokset
       :
Vial number:          1
Volume:               20.0 µL
Dilution:             1.00
Amount:               1.0000

COLUMN:               Polyvinyl alcohol
Size:                 4.0 x 100 mm
Number:               6.1006.510
Part.size:            5.0 µm

ELUENT:               Na2CO3 3,2 mmol/l / NaHCO3 1 mmol/mol


Flow:                 0.70 mL/min
Temperature:          20.0°C
Pressure:             7.5 MPa
```
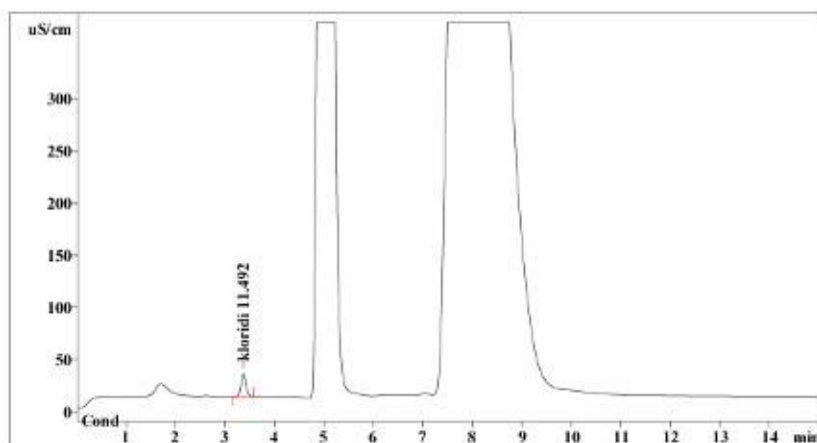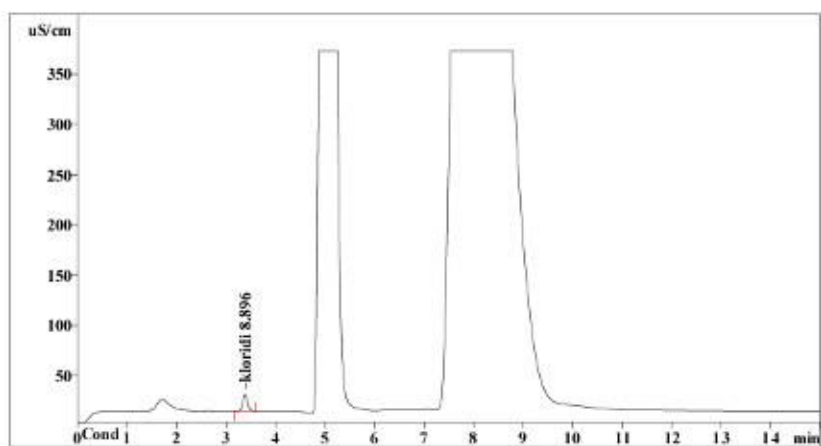
Quantitation method:   Custom

| No | Retention min | Height uS/cm | Area uS/cm*sec | Conc. mg/l | Name |
|----|----|----|----|----|----|
| 1 | 3.39 | 16.30 | 110.355 | 8.896 | kloridi |

This report has been created by IC Net
METROHM LTD

Batch 1, sample 6. Method 1 (direct measurement)

```
Report date:          15.3.2016 13:48:31
Printed by:           user

Ident:                Erä 1, näyte 6
Analysis from:        15.3.2016 12:23:28
File:                 _2016-03-15_              Last save: 15.3.2016 13:45:05
  Manual peaks!
Method:               Aleksi Pienimäki.mtw             Last save: 15.3.2016 12:08:57
Run operator:         user
Analysis number:      28

SAMPLE:               alkaalisulfiitin käyttöliuokset
       :
Vial number:          1
Volume:               20.0 µL
Dilution:             1.00
Amount:               1.0000

COLUMN:               Polyvinyl alcohol
Size:                 4.0 x 100 mm
Number:               6.1006.510
Part.size:            5.0 µm

ELUENT:               Na2CO3 3,2 mmol/l / NaHCO3 1 mmol/mol


Flow:                 0.70 mL/min
Temperature:          20.0°C
Pressure:             7.1 MPa
```



```
Quantitation method:  Custom

No  Retention  Height      Area        Conc.    Name
           min  uS/cm  uS/cm*sec       mg/l
 1      3.37   15.00    100.288        8.135   kloridi

This report has been created by IC Net
METROHM LTD
```

Batch 1, sample 7. Method 1 (direct measurement)

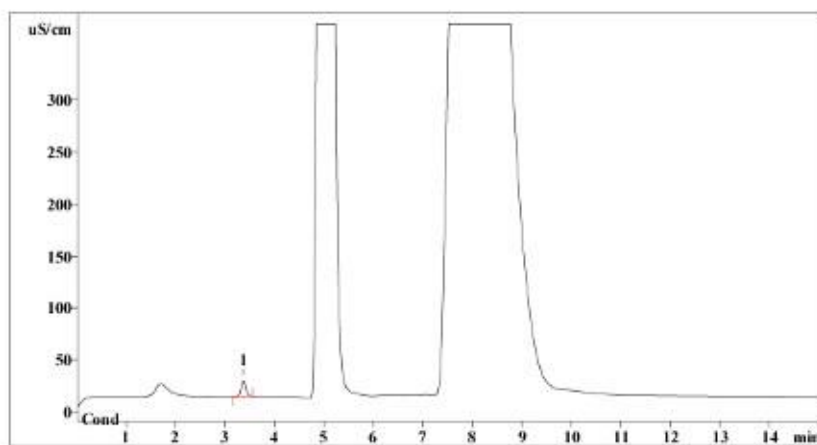Report date:        15.3.2016 13:49:53
Printed by:         user

Ident:              Erä 1, näyte 7
Analysis from:      15.3.2016 13:32:53
File:               _2016-03-15_              Last save: 15.3.2016 13:47:51
Modified!  Manual peaks!
Method:             Aleksi Pienimäki.mtw            Last save: 15.3.2016 12:08:57
Run operator:       user
Analysis number:    30

SAMPLE:             alkaalisulfiitin käyttöliuokset
     :
Vial number:        1
Volume:             20.0 µL
Dilution:           1.00
Amount:             1.0000

COLUMN:             Polyvinyl alcohol
Size:               4.0 x 100 mm
Number:             6.1006.510
Part.size:          5.0 µm

ELUENT:             Na2CO3 3,2 mmol/l / NaHCO3 1 mmol/mol


Flow:               0.70 mL/min
Temperature:        20.0°C
Pressure:           7.1 MPa



Quantitation method:   Custom

No  Retention  Height      Area       Conc.   Name
          min    uS/cm uS/cm*sec       mg/l
 1      3.37     7.50     50.902       4.254   kloridi

This report has been created by IC Net
METROHM LTD

Batch 2, sample 1. Method 2 (dialysis)

```
Report date:        14.4.2016 11:18:37
Printed by:         user

Ident:              Erä 2, näyte 1
Analysis from:      17.3.2016 15:23:40
File:               _2016-03-17_              Last save: 11.4.2016 12:43:01
  Manual peaks!
Method:             Aleksi Pienimäki_dialyysi            Last save: 17.3.2016 13:26:35
Run operator:       user
Analysis number:    56

SAMPLE:             alkaalisulfiitin käyttöliuokset
      :
Vial number:        1
Volume:             20.0 µL
Dilution:           1.00
Amount:             1.0000

COLUMN:             Polyvinyl alcohol
Size:               4.0 x 100 mm
Number:             6.1006.510
Part.size:          5.0 µm

ELUENT:             Na2CO3 3,2 mmol/l / NaHCO3 1 mmol/mol


Flow:               0.70 mL/min
Temperature:        20.0°C
Pressure:           7.4 MPa
```
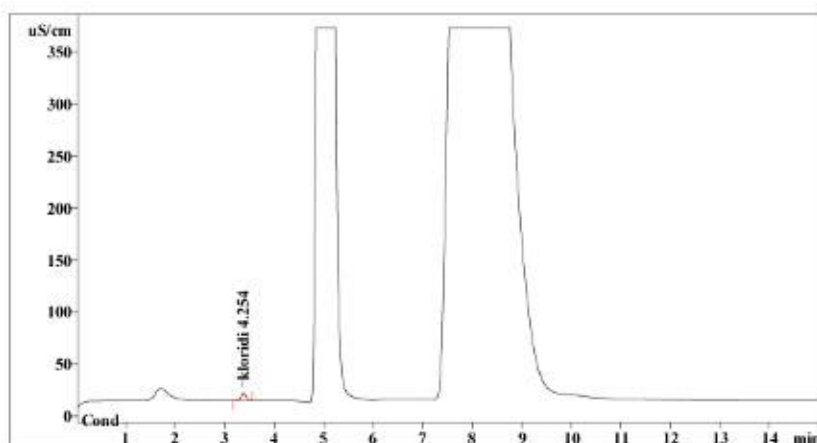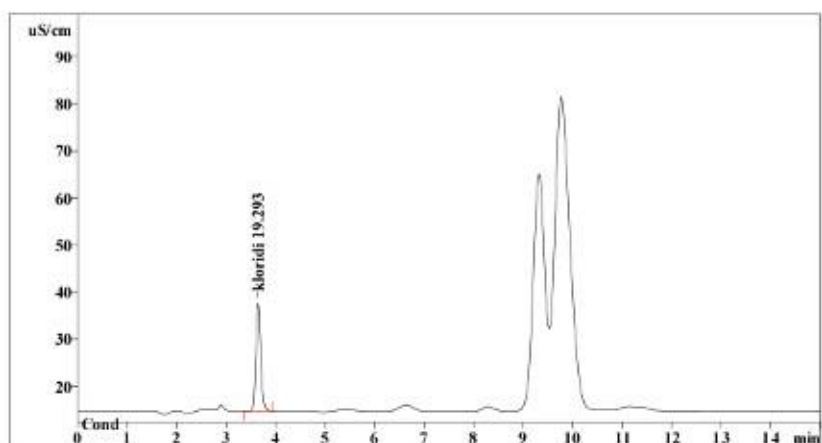


```
Quantitation method:    Custom

No   Retention   Height      Area        Conc.   Name
           min   uS/cm  uS/cm*sec        mg/l
 1       3.65    22.84    153.306       19.293   kloridi

This report has been created by IC Net
METROHM LTD
```

Batch 2, sample 2. Method 2 (dialysis)

```
Report date:        14.4.2016 11:19:04
Printed by:         user

Ident:              Erä 2, näyte 2
Analysis from:      17.3.2016 16:20:17
File:               _2016-03-17_              Last save: 11.4.2016 12:43:01
  Manual peaks!
Method:             Aleksi Pienimäki_dialyysi          Last save: 17.3.2016 13:26:35
Run operator:       user
Analysis number:    58

SAMPLE:             alkaalisulfiitin käyttöliuokset
        :
Vial number:        1
Volume:             20.0 µL
Dilution:           1.00
Amount:             1.0000

COLUMN:             Polyvinyl alcohol
Size:               4.0 x 100 mm
Number:             6.1006.510
Part.size:          5.0 µm

ELUENT:             Na2CO3 3,2 mmol/l / NaHCO3 1 mmol/mol


Flow:               0.70 mL/min
Temperature:        20.0°C
Pressure:           6.9 MPa
```
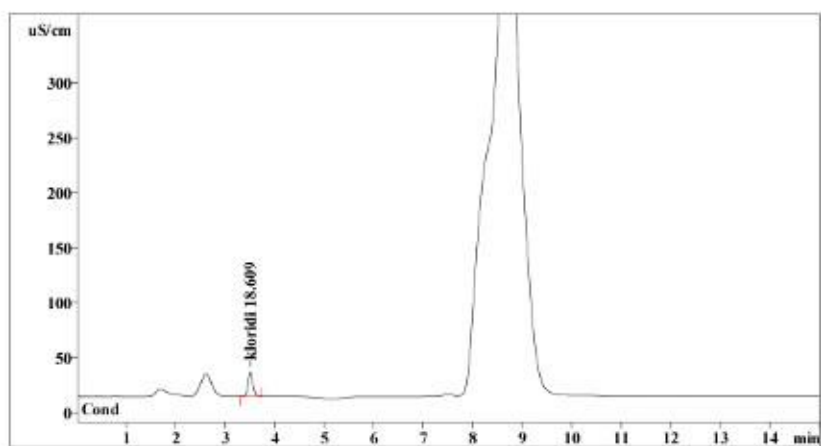


```
Quantitation method:   Custom

No  Retention  Height      Area        Conc.   Name
           min    uS/cm  uS/cm*sec       mg/l
  1      3.50   21.61   147.322       18.609  kloridi

This report has been created by IC Net
METROHM LTD
```

Batch 2, sample 3. Method 1 (direct measurement)

Report date:          15.3.2016 15:54:13
Printed by:           user

Ident:                Erä 2, näyte 3
Analysis from:        15.3.2016 15:15:55
File:                 2016-03-15_              Last save: 15.3.2016 15:30:53
Modified!  Manual peaks!
Method:               Aleksi Pienimäki.mtw            Last save: 15.3.2016 15:01:35
Run operator:         user
Analysis number:      37

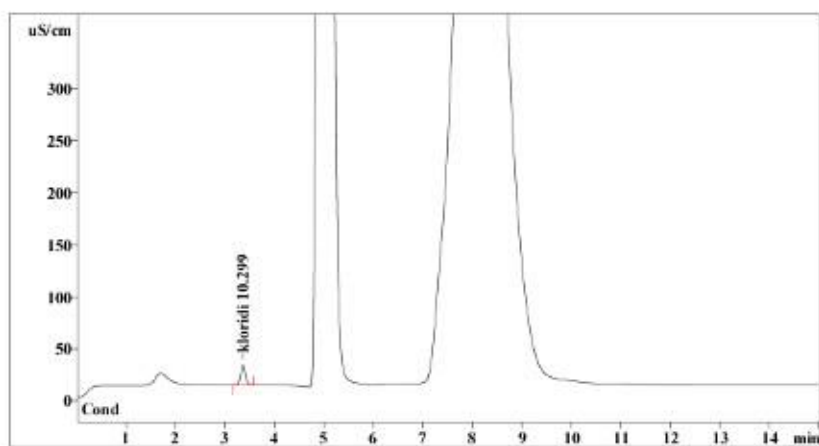SAMPLE:               alkaalisulfiitin käyttöliuokset
      :
Vial number:          1
Volume:               20.0 µL
Dilution:             1.00
Amount:               1.0000

COLUMN:               Polyvinyl alcohol
Size:                 4.0 x 100 mm
Number:               6.1006.510
Part.size:            5.0 µm

ELUENT:               Na2CO3 3,2 mmol/l / NaHCO3 1 mmol/mol


Flow:                 0.70 mL/min
Temperature:          20.0°C
Pressure:             7.2 MPa



Quantitation method:  Custom

No  Retention  Height     Area        Conc.   Name
        min    uS/cm  uS/cm*sec       mg/l
 1      3.36   19.23   129.261        10.299  kloridi

This report has been created by IC Net
METROHM LTD

Batch 2, sample 4. Method 1 (direct measurement)

```
Report date:          15.3.2016 15:01:18
Printed by:           user

Ident:                Erä 2, näyte 4
Analysis from:        15.3.2016 14:42:52
File:                 2016-03-15_              Last save: 15.3.2016 14:57:50
Modified!  Manual peaks!
Method:               Aleksi Pienimäki.mtw           Last save: 15.3.2016 14:27:24
Run operator:         user
Analysis number:      35

SAMPLE:               alkaalisulfiitin käyttöliuokset
    :
Vial number:          1
Volume:               20.0 µL
Dilution:             1.00
Amount:               1.0000

COLUMN:               Polyvinyl alcohol
Size:                 4.0 x 100 mm
Number:               6.1006.510
Part.size:            5.0 µm

ELUENT:               Na2CO3 3,2 mmol/l / NaHCO3 1 mmol/mol


Flow:                 0.70 mL/min
Temperature:          20.0°C
Pressure:             7.1 MPa
```
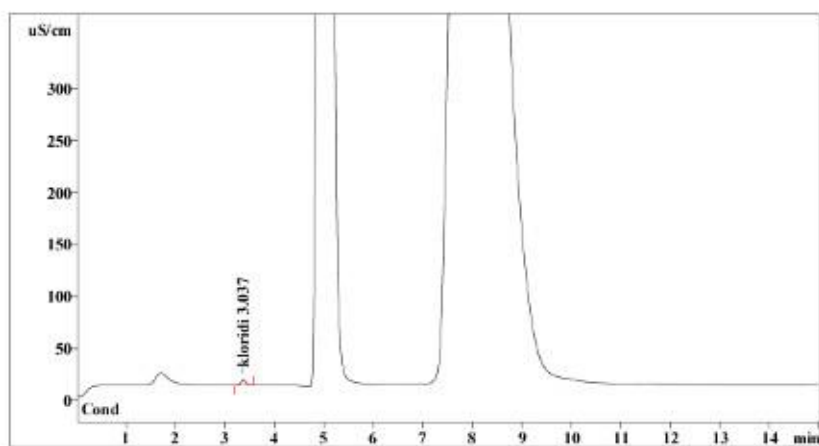


```
Quantitation method:   Custom

No  Retention  Height      Area       Conc.    Name
         min   uS/cm uS/cm*sec        mg/l
 1       3.37   5.23    36.018         3.037   kloridi

This report has been created by IC Net
METROHM LTD
```

Batch 2, sample 5. Method 1 (direct measurement)

```
Report date:          15.3.2016 14:26:57
Printed by:           user

Ident:                Erä 2, näyte 5
Analysis from:        15.3.2016 14:08:14
File:                 2016-03-15_            Last save: 15.3.2016 14:23:12
Modified!  Manual peaks!
Method:               Aleksi Pienimäki.mtw            Last save: 15.3.2016 13:50:17
Run operator:         user
Analysis number:      33

SAMPLE:               alkaalisulfiitin käyttöliuokset
       :
Vial number:          1
Volume:               20.0 µL
Dilution:             1.00
Amount:               1.0000

COLUMN:               Polyvinyl alcohol
Size:                 4.0 x 100 mm
Number:               6.1006.510
Part.size:            5.0 µm

ELUENT:               Na2CO3 3,2 mmol/l / NaHCO3 1 mmol/mol


Flow:                 0.70 mL/min
Temperature:          20.0°C
Pressure:             7.5 MPa
```
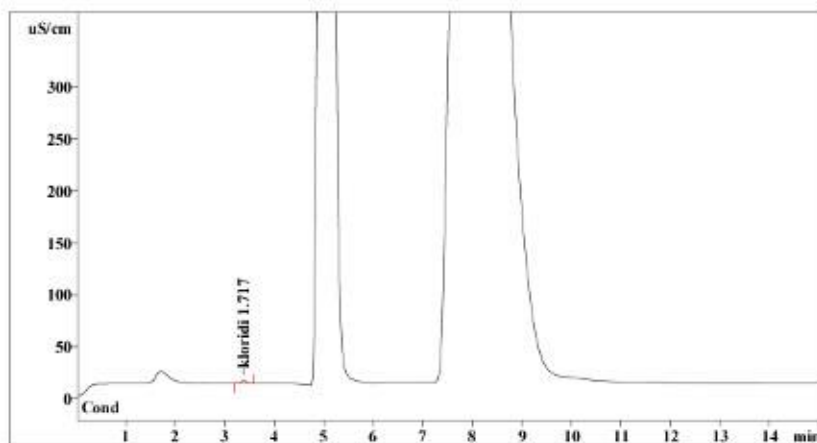


```
Quantitation method:   Custom

No  Retention  Height     Area       Conc.   Name
           min   uS/cm uS/cm*sec       mg/l
 1      3.38     2.85    20.173       1.717   kloridi

This report has been created by IC Net
 METROHM LTD
```

Batch 3, sample 1. Method 2 (dialysis)

Report date:        14.4.2016 11:19:25
Printed by:         user

Ident:              Erä 3, näyte 1
Analysis from:      17.3.2016 15:52:18
File:               _2016-03-17_              Last save: 11.4.2016 12:43:01
  Manual peaks!
Method:             Aleksi Pienimäki_dialyysi         Last save: 17.3.2016 13:26:35
Run operator:       user
Analysis number:    57

SAMPLE:             alkaalisulfiitin käyttöliuokset
  :
Vial number:        1
Volume:             20.0 µL
Dilution:           1.00
Amount:             1.0000

COLUMN:             Polyvinyl alcohol
Size:               4.0 x 100 mm
Number:             6.1006.510
Part.size:          5.0 µm

ELUENT:             Na2CO3 3,2 mmol/l / NaHCO3 1 mmol/mol

Flow:               0.70 mL/min
Temperature:        20.0°C
Pressure:           6.9 MPa
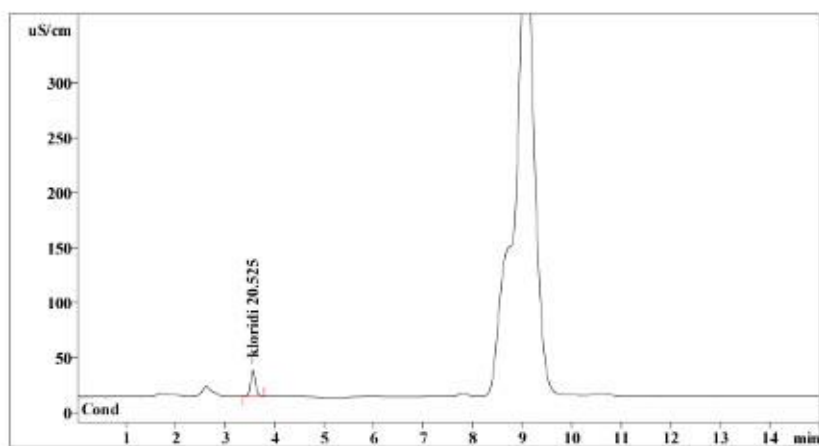


Quantitation method:    Custom

No  Retention  Height      Area       Conc.   Name
           min  uS/cm uS/cm*sec        mg/l
 1      3.56   23.82   164.210     20.525  kloridi

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METROHM LTD

Batch 3, sample 2. Method 1 (direct measurement)

```
Report date:          15.3.2016 17:20:46
Printed by:           user

Ident:                Erä 3, näyte 2
Analysis from:        15.3.2016 17:03:38
File:                 2016-03-15_                Last save: 15.3.2016 17:18:36
Modified!  Manual peaks!
Method:               Aleksi Pienimäki.mtw            Last save: 15.3.2016 15:54:34
Run operator:         user
Analysis number:      44

SAMPLE:               alkaalisulfiitin käyttöliuokset
       :
Vial number:          1
Volume:               20.0 µL
Dilution:             1.00
Amount:               1.0000

COLUMN:               Polyvinyl alcohol
Size:                 4.0 x 100 mm
Number:               6.1006.510
Part.size:            5.0 µm

ELUENT:               Na2CO3 3,2 mmol/l / NaHCO3 1 mmol/mol


Flow:                 0.70 mL/min
Temperature:          20.0°C
Pressure:             7.2 MPa
```
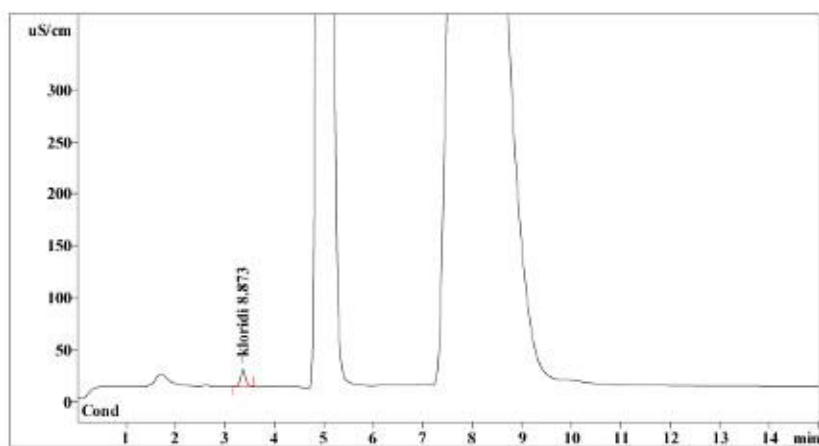


```
Quantitation method:  Custom

No  Retention  Height      Area        Conc.   Name
          min  uS/cm  uS/cm*sec         mg/l
 1       3.36  16.43   110.045         8.873   kloridi

This report has been created by IC Net
METROHM LTD
```

Batch 3, sample 3. Method 1 (direct measurement)

```
Report date:          15.3.2016 17:12:13
Printed by:           user

Ident:                Erä 3, näyte 3
Analysis from:        15.3.2016 15:52:41
File:                  2016-03-15_              Last save: 15.3.2016 16:07:39
Modified!  Manual peaks!
Method:               Aleksi Pienimäki.mtw            Last save: 15.3.2016 15:01:35
Run operator:         user
Analysis number:      40

SAMPLE:               alkaalisulfiitin käyttöliuokset
         :
Vial number:          1
Volume:               20.0 µL
Dilution:             1.00
Amount:               1.0000

COLUMN:               Polyvinyl alcohol
Size:                 4.0 x 100 mm
Number:               6.1006.510
Part.size:            5.0 µm

ELUENT:               Na2CO3 3,2 mmol/l / NaHCO3 1 mmol/mol


Flow:                 0.70 mL/min
Temperature:          20.0°C
Pressure:             7.5 MPa
```
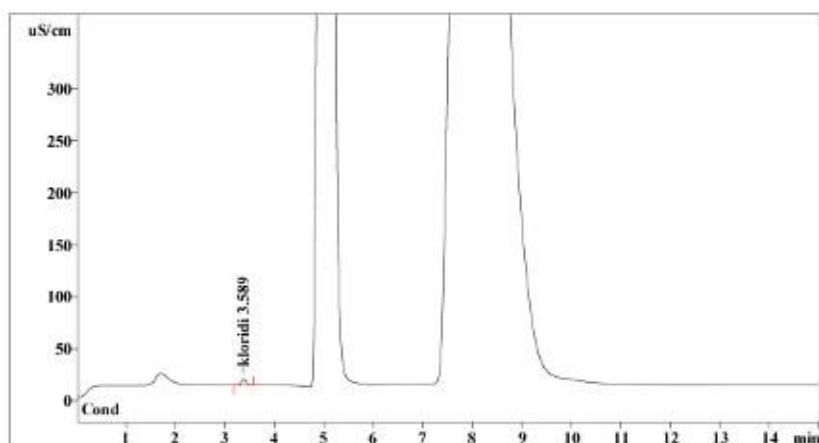


```
Quantitation method:   Custom

No  Retention  Height      Area       Conc.   Name
          min   uS/cm uS/cm*sec        mg/l
 1       3.38    6.12    42.743        3.589  kloridi

This report has been created by IC Net
METROHM LTD
```

Batch 3, sample 4. Method 1 (direct measurement)

Report date:          15.3.2016 17:10:41
Printed by:           user

Ident:                Erä 3, näyte 4
Analysis from:        15.3.2016 16:30:25
File:                 _2016-03-15_              Last save: 15.3.2016 16:45:23
Modified!  Manual peaks!
Method:               Aleksi Pienimäki.mtw            Last save: 15.3.2016 15:54:34
Run operator:         user
Analysis number:      42

SAMPLE:               alkaalisulfiitin käyttöliuokset
    :
Vial number:          1
Volume:               20.0 µL
Dilution:             1.00
Amount:               1.0000

COLUMN:               Polyvinyl alcohol
Size:                 4.0 x 100 mm
Number:               6.1006.510
Part.size:            5.0 µm

ELUENT:               Na2CO3 3,2 mmol/l / NaHCO3 1 mmol/mol


Flow:                 0.70 mL/min
Temperature:          20.0°C
Pressure:             7.1 MPa
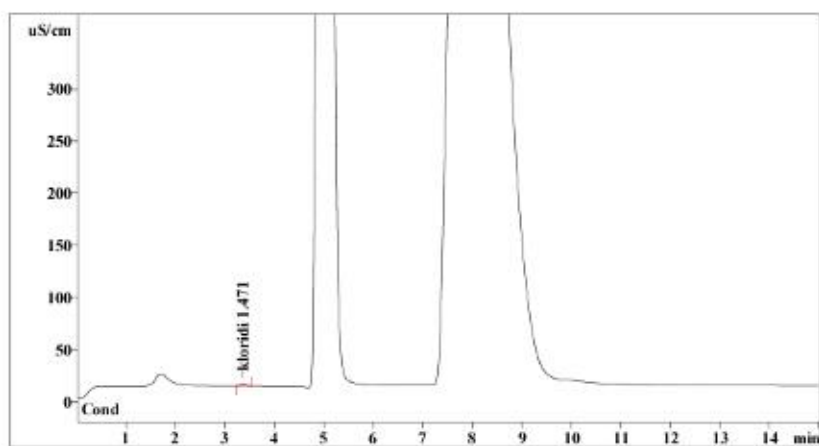


Quantitation method:   Custom

No  Retention  Height      Area       Conc.    Name
          min   uS/cm  uS/cm*sec       mg/l
 1      3.37    2.53     17.256        1.471    kloridi

This report has been created by IC Net
METROHM LTD

# XRF-analysis report, KM 39993-5 white metal coating

XRF-MITTAUS, TULOSTETTU RAPORTTI

| Nimi | Luokka | | | Päivämäärä | | Kellonaika | Kesto |
|------|--------|--|--|-----------|--|-----------|-------|
| KM39993:5-3mitraus | Alloy_LE_FP | | | 5.4.2016 | | 12.04.32 | 10,5 s |

| Alkuaine | Si % | Ti % | Fe % | Zn % | Sn % | Pb % |
|----------|------|------|------|------|------|------|
| | 0,76 | 0,22 | 93,00 | 0,06 | 4,73 | 1,24 |
| ± | 0,189 | 0,037 | 0,338 | 0,017 | 0,116 | 0,046 |

Vertailunäyte:
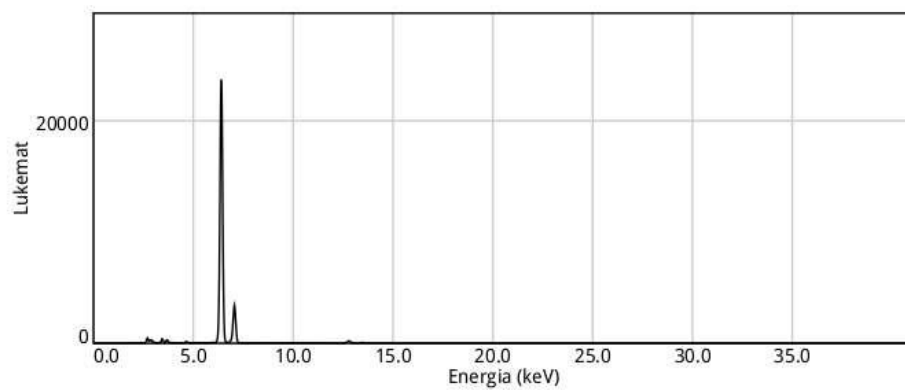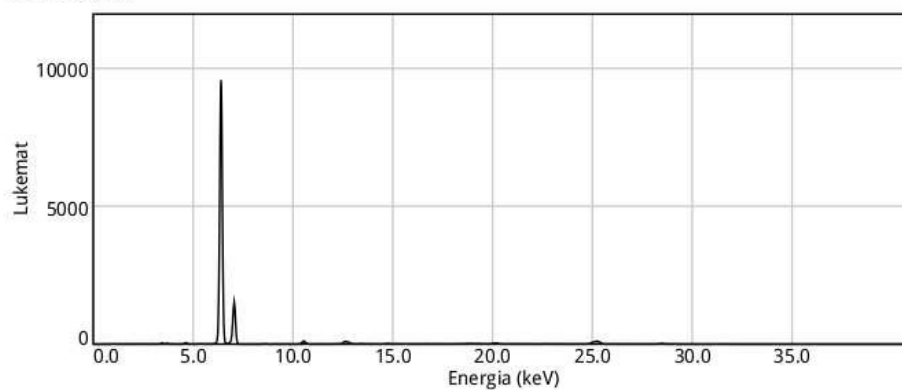
**Pictures before and after conservation. In natural size unless otherwise stated.**

KM 39993:1

KM 39993:2 before conservation

KM 39994:2 after conservation

KM 39993:3 before conservation

KM 39993:3 after conservation

KM 39993:4 before conservation

KM 39993:4 after conservation

KM 39993:5 before conservation



KM 39993:5 after conservation

KM 39993:6 before conservation





KM 39993:6 after conservation

KM 39993:7 before conservation

KM 39993:7 after conservation

KM 39993:8 before conservation

KM 39993:8 after conservation

KM 39994:1 before and after conservation, scale 1:2

KM 39994:1 socket details after conservation

KM 39994:2 before conservation

KM 39994:2 after conservation

Scale 1:2

KM 39994:3 after conservation

KM 39994:3 before conservation

Natural size

KM 39994:4 before conservation

KM 39994:4 after conservation

KM 39994:5 before conservation

KM 39994:5 after conservation
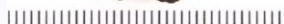
KM 39994:6 before conservation

KM 39994:6 after conservation

KM 39994:7 before conservation

KM 39994:7 after conservation

KM 39994:7 before conservation

KM 39994:7 after conservation

KM 39994:8 before conservation

KM 39994:8 after conservation

Scale 2:3

KM 39995:2 before conservation

KM 39995:2 after conservation

KM 39995:3 before conservation

KM 39995:3 after conservation

KM 39995:4 before conservation

KM 39995:4 after conservation

KM 39995:5 before conservation

KM 39995:5 after conservation

Scale 1:2

KM 39995:6 before conservation

KM 39995:6 after conservation

KM 39995:7 before conservation

KM 39995:7 after conservation

KM 39995:8 before conservation

KM 39995:8 after conservation

KM 39995:9 before conservation

KM 39995:9 after conservation

KM 39996:1 before conservation

KM 39996:1 after conservation

KM 40551:1 before conservation

KM 40551:1 after conservation

KM 40551:2 before conservation

KM 40551:2 after conservation

KM 40551:3 before conservation

KM 40551:3 after conservation

KM 40551:4 before conservation

KM 40551:4 after conservation

KM 40551:5 before conservation
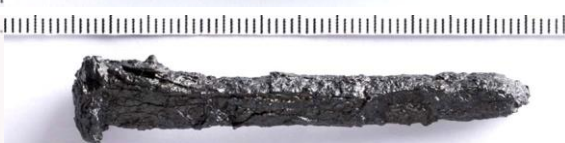
KM 40551:5 after conservation

KM 40551:6 before conservation

KM 40551:6 after conservation

KM 40551:7 before conservation

KM 40551:7 after conservation

KM 40551:8 before conservation

KM 40551:8 after conservation

KM 40551:21 before conservation

KM 40551:21 after conservation

KM 40551:22 before conservation

KM 40551:22 after conservation

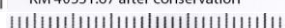KM 40551:27 before conservation

KM 40551:27 after conservation

KM 40551:28 before conservation

KM 40551:28 after conservation

KM 40551:31 before conservation

KM 40551:31 after conservation

KM 40551:32 before conservation

KM 40551:32 after conservation

KM 40551:33 before conservation
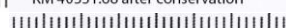
KM 40551:33 after conservation

KM 40551:34 before conservation

KM 40551:34 after conservation

KM 40551:39 before conservation

KM 40551:39 after conservation

KM 40551:40

KM 40551:44 before conservation

KM 40551:40 after conservation

KM 40551:44 after conservation

KM 40551:47 before conservation

KM 40551:51 before conservation

KM 40551:47 after conservation

KM 40551:51 after conservation

KM 40551:52 before conservation

KM 40551:52 after conservation

KM 40551:53 before conservation

KM 40551:53 after conservation

KM 40551:54 before conservation

KM 40551:54 after conservation

KM 40551:55 before conservation

KM 40551:55 after conservation

KM 40551:56 before conservation

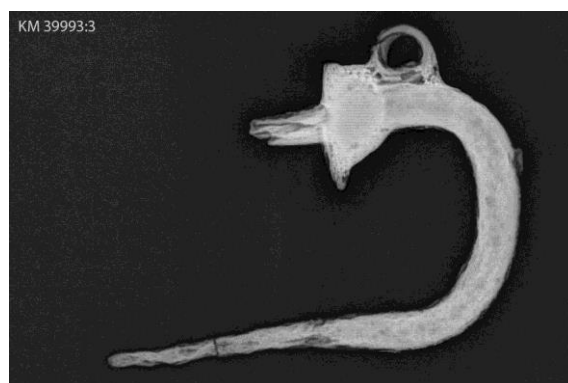KM 40551:56 after conservation

KM 40551:57 before conservation

KM 40551:57 after conservation

KM 40551:58 before conservation

KM 40551:58 after conservation

KM 40551:59 before conservation

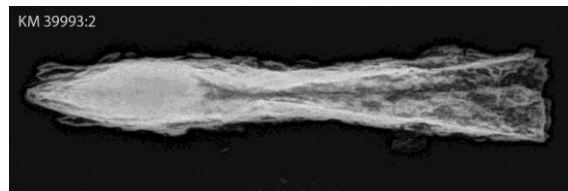KM 40551:59 after conservation

KM 40551:60 before conservation

KM 40551:60 after conservation

KM 40551:61 before conservation

KM 40551:61 after conservation

KM 40551:62 before conservation

KM 40551:62 after conservation

KM 40551:63 before conservation

KM 40551:63 after conservation

KM 40551:64 before conservation

KM 40551:64 after conservation
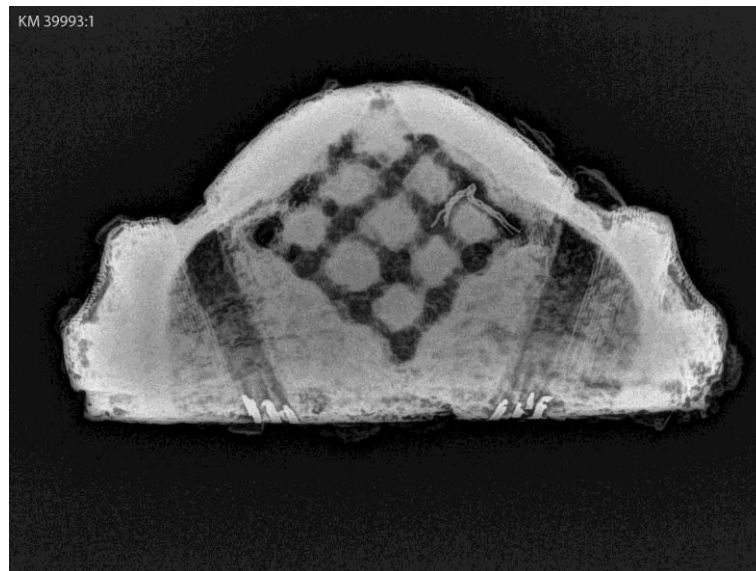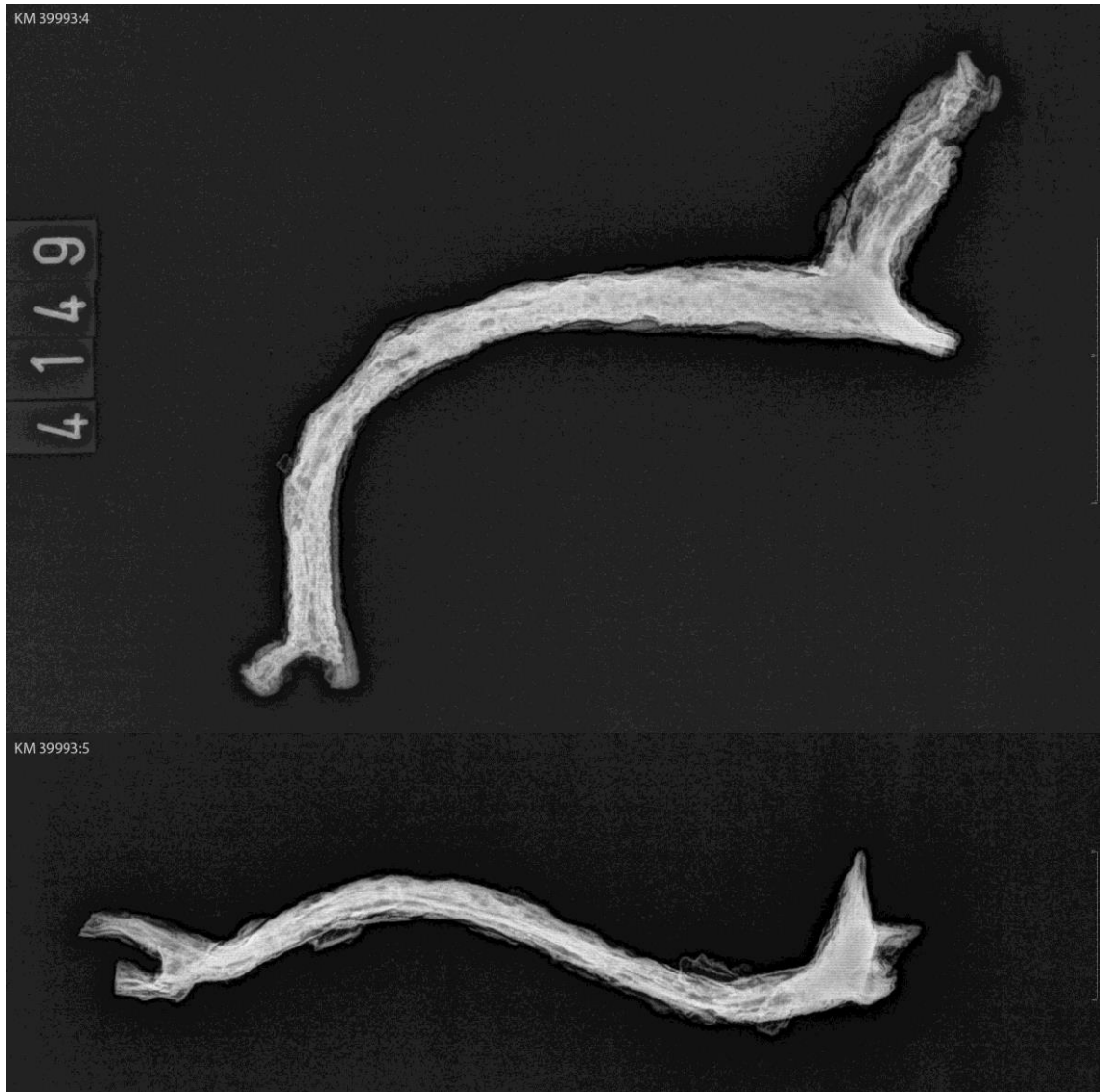
KM 40551:65 before conservation

KM 40551:65 after conservation

KM 40551:66 before conservation

KM 40551:66 before conservation

KM 40551:66 after conservation

KM 40551:66 after conservation

KM 40551:67 before conservation

KM 40551:67 after conservation

KM 40551:68 before conservation

KM 40551:68 after conservation

KM 40551:69 before conservation

KM 40551:69 after conservation

KM 40551:70 before conservation

KM 40551:70 after conservation

KM 40551:71 before conservation

KM 40551:71 after conservation

KM 40551:72 before conservation

KM 40551:72 after conservation

KM 40551:73 before conservation

KM 40551:73 after conservation

KM 40551:74 before conservation

KM 40551:74 after conservation

KM 40551:75 before conservation

KM 40551:75 after conservation

KM 40551:81 before conservation
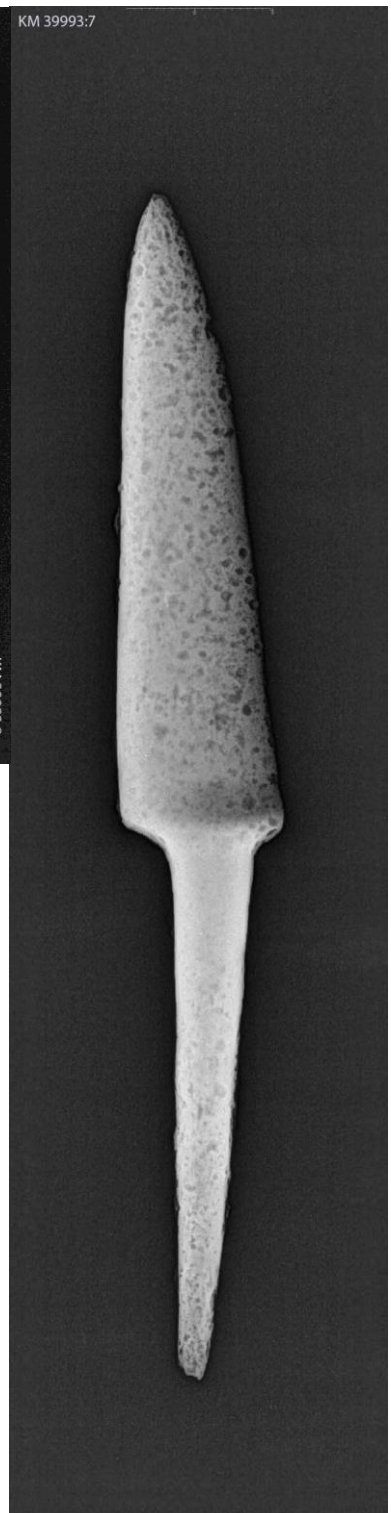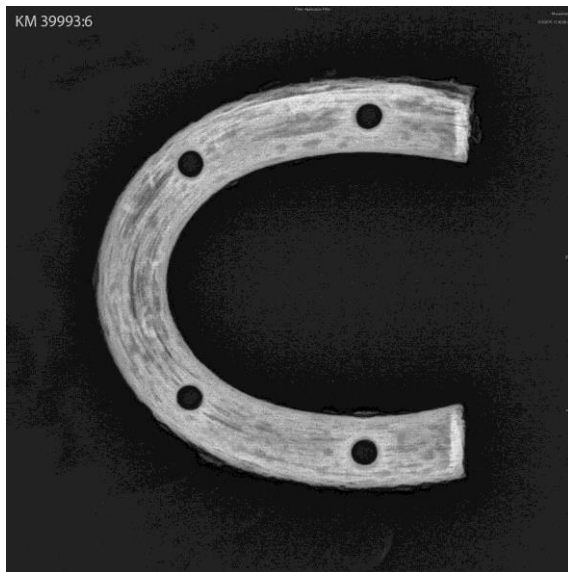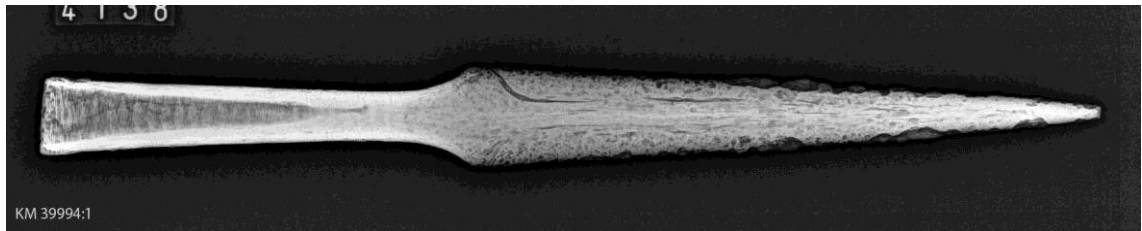
KM 40551:81 after conservation

**X-ray pictures**

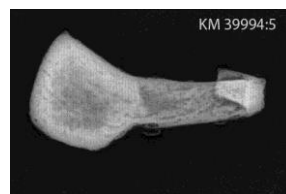In natural size unless otherwise stated. Rhythm Review, version 5.1 (Spa12) (0.93), viewing program Flash filter used.
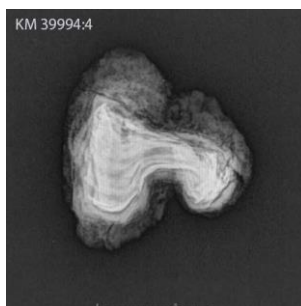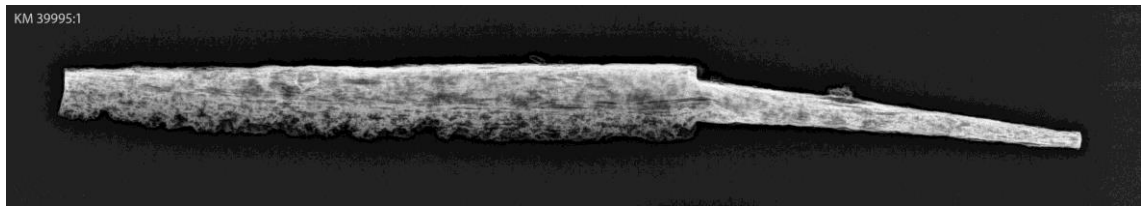
KM 39993:6

KM 39993:8

KM 39993:7

Scale 1:2



Natural size

KM 39994:3



KM 39994:4



KM 39994:5



KM 39994:6

Sale 1:3



Natural size

KM 39995:6



KM 39995:7



KM 39995:8



KM 39995:9

KM 40551:39

KM 40551:40

KM 40551:44

KM 40551:47

KM 40551:51

KM 40551:52

KM 40551:53

KM 40551:54

KM 40551:55

KM 40551:56

KM 40551:57

KM 40551:58

KM 40551:59

KM 40551:60