Chlorine Determination in Archaeological Wrought Iron by Instrumental Neutron Activation Analysis

Lyndsie Selwyn and Vasilike Argyropoulos

Chlorine Determination in Archaeological Wrought Iron by Instrumental Neutron Activation Analysis

Lyndsie Selwyn* and Vasilike Argyropoulos**

*Canadian Conservation Institute, Department of Canadian Heritage, 1030 Innes Rd., Ottawa, Ontario K1A 0M5, Canada; lyndsie_selwyn@pch.gc.ca

**Technological Educational Institution of Athens, Department of Conservation of Antiquities and Works of Art, Ag. Spyridona, 12210 Athens, Greece; bessie@teiath.gr

One of the challenges in treating chloride-contaminated archaeological iron is determining the effectiveness of conservation treatments. Evaluation of different treatments is possible if it can be determined what fraction of chloride ions is removed by a particular treatment. In this paper, preliminary results are presented of the measurement of the chlorine concentration in small wrought iron artifacts before and after treatment using instrumental neutron activation analysis (INAA). These results are compared to the chloride ion concentrations in the treatment solutions as determined by potentiometric titration. The conservation treatments are based on immersion of the iron samples for 18 weeks in alkaline solutions of either ethylenediamine (5% v/v and 20% v/v) or sodium hydroxide (2% w/v and 0.01% w/v) at 22°C and 50°C. These results illustrate the potential usefulness and limitations of INAA as a non-destructive analytical tool for determining chlorine concentration in small iron artifacts or samples.

Évaluer l'efficacité de la désalinisation représente l'un des défis du traitement des objets archéologiques en fer contaminés par les sels de chlorure. Une comparaison de l'efficacité de divers types de traitements est possible si l'on peut calculer la fraction de chlorures qu'un traitement peut réussir à extraire. Dans cette étude, on présente des résultats préliminaires sur des mesures de la concentration du chlore dans de petits artefacts en fer forgé avant et après traitement, faites au moyen de l'analyse instrumentale par activation neutronique (AIAN). Ces résultats sont comparés à la concentration d'ions de chlorure présents dans les bains de désalinisation, mesurés par titrage potentiométrique. Les traitements de désalinisation testés lors de cette étude incluent l'immersion d'échantillons de fer pendant 18 semaines, à des températures de 22°C ou de 50°C, dans les solutions alcalines suivantes : de l'éthylènediamine à 5 % volume/volume (v/v), ou à 20 % v/v; et de l'hydroxyde de sodium à 2 % poids/volume (p/v) ou à 0,01 % p/v. Les résultats obtenus démontrent le potentiel de l'AIAN, ainsi que ses limites, en tant que technique analytique non-destructive pour déterminer la concentration de chlore dans de petits objets, ou dans des échantillons de fer.

Introduction

Archaeological iron is often contaminated with chlorine, usually in the form of soluble chloride ions or bound within the structure of a solid compound. When dealing with archaeological iron, one challenge is the determination of the amount of chlorine in the object before treatment. One approach is to measure the chlorine concentration by dissolving the iron sample and analyzing the solution for chloride ions.[1-4] The disadvantage with this approach is that the sample is destroyed during analysis. Another approach is to use instrumental neutron activation analysis (INAA) to measure the chlorine concentration. This has the advantage that the sample is not destroyed during analysis. For objects of relatively small size, the entire object can be analyzed non-destructively using this technique. INAA is an analytical technique that may be used to measure the concentration of many elements in a sample without regard to the element's chemical or physical form. INAA has been used in provenance research to determine the geographical source of the materials used in the fabrication of an artifact.[5-9] INAA has also been used to study a single element, such as for the analysis of the chlorine content and distribution in iron meteorites.[10]

In addition to determining the amount of chlorine present in an object before treatment, another issue for archaeological conservators is assessing the efficiency of the conservation treatment used to remove the chlorine. The relative efficiency of treatments is often compared by determining the amount of soluble chloride ions dissolved in treatment solutions using a quantitative technique, such as potentiometric titration.[11,12] This approach allows one to monitor the rate at which chloride ions are diffusing into treatment solutions, but it does not provide any information about the amount of chlorine in the object before treatment or remaining after. A better approach is to use a technique such as INAA to determine the chlorine content before and after treatment. In a few instances, INAA of chlorine has been used for evaluating the effectiveness of plasma treatments for removing chlorine from archaeological iron.[13,14] Kotzamanidi et al. used INAA to measure chlorine in 50 mg samples removed from corroded iron test coupons, before and after plasma treatment.[13] Aoki et al. used INAA to measure chlorine in small archaeological arrowheads, before and after plasma treatment and soxhlet extraction.[14]

This paper reports on the use of INAA to evaluate the effectiveness of two alkaline treatment solutions, sodium hydroxide (NaOH) and ethylenediamine (*EN*), for removing chlorine from archaeological iron. Both wet and dried samples were studied. For comparison purposes, the chloride ion concentration in the treatment solutions, as determined by potentiometric titration, is also presented. This research is part of

a larger study at the Canadian Conservation Institute (CCI) to investigate the effectiveness of 2% w/v NaOH (0.5M) at room temperature and 5% v/v *EN* (0.75M) at 50°C for the treatment of archaeological iron.[15,16] The experiments involving INAA were intended as a quick survey to evaluate the usefulness of the technique as a research tool.

Background on INAA

There is much literature describing the theory and practical details about neutron activation analysis (NAA), an analytical method used for elemental analysis.[17-20] The following is an explanation for readers who may want to use this technique, but are unfamiliar with it.

Samples may be liquids, solid pieces, or powders, and many elements can be determined simultaneously. Sample size ranges from small (typically 40 to 400 mg) to solid chunks. The minimum size depends on the element being analyzed and the sensitivity of the equipment being used. The maximum size is limited by the size of the INAA vial used to contain the sample. For example, the largest vials used in the study reported here were 5.5 cm long with a 1.6 cm diameter. In Canada, INAA is currently being carried out at the McMaster University reactor in Hamilton and at SLOWPOKE reactors located at Dalhousie University in Halifax, École Polytechnique in Montreal, Royal Military College of Canada in Kingston, Saskatchewan Research Council in Saskatoon, and University of Alberta in Edmonton. Samples can be submitted to those institutions for INAA and the cost of chlorine analysis in iron ranges from $50 to $100 per sample, depending on the institution. The cost per sample is often lower if several similar samples are submitted at the same time. Instrumental neutron activation analysis (INAA) involves the application of purely instrumental procedures without any chemical separation of the sample. If chemical separations are done to samples after irradiation to remove interferences or to concentrate the elements of interest, the technique is called radiochemical neutron activation analysis (RNAA).

INAA is based on nuclear processes within atoms. Each element in the periodic table has a unique number of protons but the number of neutrons can vary. Atoms having the same number of protons but differing in the number of neutrons are referred to as isotopes. The first step in INAA is to irradiate samples with neutrons, usually with thermalized (mainly low energy) neutrons in a nuclear reactor. During irradiation, radioactivity is induced in the sample because the thermal neutrons react with a small fraction of the atoms in the sample to produce different isotopes, many of which are radioactive.[21] These new radioactive isotopes (radioisotopes) decay with unique half-lives and are usually accompanied by the emission of one or more γ-rays (gamma rays) along with other particles. The γ-rays are characteristic of the element from which they are emitted. The half-life of a radioisotope refers to the time it takes for half the number of atoms of that radioisotope to decay. The radioactive emissions and radioactive decay paths for each element are well known.[18,19,22-24] Elemental analysis by INAA depends on the detection of γ-rays produced by the decay of the radioisotopes formed during neutron irradiation. The radioisotopes eventually decay to form stable elements.[20]

Following neutron irradiation, the sample is removed from the research reactor. After a suitable decay period, which depends on the half-lives of the elements of interest, a γ-ray spectrometer is used to monitor the energies and intensities of the γ-rays emitted by the newly formed radioisotopes in the sample. The characteristic γ-ray energies and half-life of each radioisotope are used to characterize and quantify the elements present in a sample.[19,25] This is done by calculating the relative γ-ray peak intensity for each radioactive isotope detected. The results are then related back to the original concentration of the parent element. Many of the elements in the periodic table have properties suitable for analysis by INAA. Samples can be returned as soon as their radiation levels are negligible.

Neutron Irradiation of Chlorine

Chlorine (Cl) has an atomic number 17 and two stable isotopes exist in nature. One stable isotope,[†] $_{17}Cl^{35}$, has 18 neutrons in the nucleus and a natural abundance of 75.5%.[22,24] The other stable isotope, $_{17}Cl^{37}$, has 20 neutrons in the nucleus and a natural abundance of 24.5%.

When a sample containing the stable (non-radioactive) chlorine isotope $_{17}Cl^{37}$ is bombarded with thermal neutrons in a nuclear reactor, the chlorine nucleus reacts with a neutron (signified by $_0n^1$) and forms an unstable (radioactive) chlorine isotope $_{17}Cl^{38}$. This reaction is the most common one encountered during neutron irradiation of a sample. It is referred to as neutron capture as it involves the absorption of a neutron by the nucleus in an atom. The reaction produces another isotope of the same atom (i.e., the mass number is increased by one because of the absorption of a neutron; the number of protons does not change) and this new isotope is usually unstable and radioactive.[25] For the chlorine isotope $_{17}Cl^{37}$, the neutron capture reaction (n,γ) is represented by:[20,25]

$$_{17}Cl^{37} + {_0n^1} \rightarrow {_{17}Cl^{38}} + \gamma \qquad (1)$$
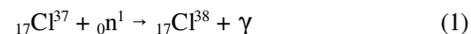
This reaction is accompanied by the essentially simultaneous emission of a γ-ray (called a prompt γ-ray) and possibly other particles [not shown in reaction (1)].

When the radioactive $_{17}Cl^{38}$ isotope undergoes radioactive decay, it undergoes a process known as beta (β) decay. The newly added neutron in the nucleus transforms into a proton and the process is accompanied by the emission of a beta particle β⁻ (an electron) and, usually, γ-rays. As this transformation takes place, the atomic number in the nucleus increases by one unit and the stable argon isotope $_{18}Ar^{38}$ is formed. The mass number remains unchanged. The process is described by the following nuclear reaction:[25]

[†]In the symbols for the isotopes, the number in the subscript refers to the atomic number (the number of protons) and the number in the superscript refers to the mass number (the number of protons and neutrons).

$$_{17}Cl^{38} \rightarrow {_{18}}Ar^{38} + \beta^- + \gamma \qquad (2)$$
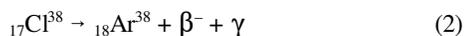
The characteristic γ-rays accompanying this transformation have energies of 1.642 MeV and 2.167 MeV.[19,23,24] The $_{17}Cl^{38}$ isotope is short-lived with a half-life of 37.3 minutes.[23,24]

The other naturally-occurring isotope of chlorine, $_{17}Cl^{35}$, is not suitable for INAA because it forms the radioisotope $_{17}Cl^{36}$ during neutron activation, which has a half-life of 3.0 x 10^5 years[22] and samples would remain radioactive for an unacceptably long time.

Experimental

Archaeological Wrought Iron Samples

Three wrought iron nails from Canadian archaeological sites were used as test samples. Two were kept intact and one was cut into sections for the study. One nail came from a marine site (Gaspe) and the other two were from terrestrial sites (Red Bay and Ferryland). A description of the eight iron samples is given in **Table I**. The following formula was used to estimate the surface area of the samples, assuming they were cylinders and neglecting the areas of the cut surfaces:

$$\text{Area} = \pi \, (\text{diameter}) \, (\text{length}) \qquad (3)$$

where $\pi = 3.1416$.

<u>Dry Terrestrial Nail (nail #1)</u>: This wrought iron nail had been excavated in 1983 from a wet, saline, and acidic burial site in Red Bay, Labrador and dates to a 16th-century Basque occupation.[26] The nail was from a set of nails collected by CCI from Red Bay and used for experimental purposes. After excavation, the nail was stored in synthetic seawater for one year, followed by hot washing in distilled water until no chloride was detected by potentiometric titration in the wash water.[27] The nail was soaked in acetone to remove the water and then allowed to air dry. This nail was selected for the study because it was assumed to contain chlorides (as hot washing is not effective at removing chlorides) and it was possible to cut the nail.

For the purposes of this study, the nail was cut into six approximately equal sections (samples 1-6) for use as approximately equivalent samples (length ~ 1.4 cm, diameter ~ 0.8 cm). The cuts were made with a Buehler diamond wafering blade in an Isomet 11-1180 low speed saw. A plastic container (for water to wet the blade) was used in place of the metal container to reduce contamination. Care was taken to preserve the corrosion layer on each piece. Bare metal was exposed at both ends of each section except for sections 1 and 2 (the tip and head of the nail, respectively), which had bare metal at only one end. No coating was applied to the exposed ends.

<u>Marine Nail (nail #2)</u>: This wrought iron nail (sample 7) had been excavated in 1980 from an underwater marine shipwreck site located on the east coast of the Gaspe region of Quebec and dates to the late 17th century.[28] The nail was from a set of nails collected by CCI from the Gaspe site and stored for experimental purposes. After excavation, the nail was stored in water until 1993, then frozen. The nail had been removed from a large concretion prior to storage in water, and the iron was covered with only a small amount of surface corrosion.

<u>Freshly Excavated Terrestrial Nail (nail #3)</u>: This wrought iron nail (sample 8) was freshly excavated in 1995 from a wet, saline, and acidic terrestrial site located adjacent to the sea in Ferryland, Newfoundland and dated to the 17th century.[29] The nail was obtained from Cathy Mathias, a conservator at the Memorial University of Newfoundland. A few days after excavation, the nail was sent to CCI in a damp condition. Upon receipt it was stored at room temperature in a zip-locked polyethylene bag.

Table I: Wrought Iron Nail Samples.

Sample	Nail	Description	Approximate Surface Area (cm^2)
1	1	Red Bay, terrestrial, dry, section 1 (tip)	not calculated (untreated control)
2	1	Red Bay, terrestrial, dry, section 2 (head)	4
3	1	Red Bay, terrestrial, dry, section 3	3.5
4	1	Red Bay, terrestrial, dry, section 4	3.8
5	1	Red Bay, terrestrial, dry, section 5	3.8
6	1	Red Bay, terrestrial, dry, section 6	4.5
7	2	Gaspe, marine, stored in water (length 4.4 cm, diameter 0.5 cm)	69
8	3	Ferryland, terrestrial, freshly excavated (length 5.5 cm, diameter 0.4 cm)	117

Table II: Treatment Information for Wrought Iron Samples.

Sample	Description	Treatment Solution	Solution Volume (mL)	Temperature (°C)	pH
1	Red Bay, section 1	-	-	-	-
2	Red Bay, section 2	5% v/v *EN*	40	50	11.7
3	Red Bay, section 3	5% v/v *EN*	35	22	11.7
4	Red Bay, section 4	20% v/v *EN*	38	50	12.6
5	Red Bay, section 5	2% w/v NaOH	38	22	13.2
6	Red Bay, section 6	0.01% w/v NaOH	45	22	11.2
7	Gaspe, marine	5% v/v *EN*	70	50	11.7
8	Ferryland, freshly excavated	5% v/v *EN*	115	50	11.7

Conservation Treatments

The iron samples were treated by immersion in an alkaline solution of either sodium hydroxide (NaOH) or ethylenediamine (*EN*), except for one iron piece (sample 1), which was left untreated. The different solution concentrations and temperatures used for the treatments are listed in **Table II**. Sample 1(untreated) was repeatedly analyzed with INAA to test the consistency of the chlorine content determination. Samples 2, 7, and 8 underwent treatment in 5% v/v *EN* (0.75M) at 50°C (the standard *EN* treatment) to compare the effectiveness of this treatment on different iron samples. Samples 2 to 6 (from the same nail and assumed to have identical chlorine content) were treated with several concentrations of *EN* and NaOH to compare the chlorine removal effectiveness of each treatment. Thus, sample 3 underwent treatment in 5% v/v *EN* at 22°C to test the effect of room temperature compared to 50°C (as used to treat sample 2). Sample 4 underwent treatment in 20% v/v *EN* (3.0M) at 50°C to test the effect of an increased concentration compared to the standard 5% v/v *EN* (as used to treat sample 2). Sample 5 underwent treatment in 2% w/v NaOH (0.5M) at 22°C to compare its effectiveness with the *EN* treatment at a similar temperature (i.e., sample 3). Sample 6 underwent treatment in 0.01% w/v NaOH (0.003M), a treatment condition chosen to compare the effectiveness of the two treatments (NaOH and *EN*) at constant temperature, at approximately the same pH (i.e., sample 3). Sample 5 underwent treatment in 2% w/v NaOH, a higher concentration than sample 6.

The iron samples were placed in 100 mL beakers and the treatment solution added, using 10 mL of solution per square centimetre of the sample's approximate surface area. The solutions were replaced every two weeks for the duration of the 18 weeks of treatment. Treatments at 50°C were heated during normal work hours and left unheated otherwise. After treatment, the samples were hot-washed in deionized water for one day, soaked in acetone for five days, and then air-dried.

Chlorine Analysis by INAA

Samples were analyzed for chlorine at the SLOWPOKE Reactor Facility at the University of Toronto.[30] For irradiation, samples were placed into one of two sizes of polyethylene vials, either a large one (length 5.5 cm, diameter 1.6 cm) or a small one (length 2.5 cm, diameter 1.2 cm). For damp iron samples (samples 7 and 8 before treatment) and for the liquid standards, the lids of the vials were heat-sealed in place with a soldering gun to prevent moisture loss. The samples were irradiated serially in the reactor for one minute at a neutron flux of 1×10^{11} neutrons per square centimetre per second (n cm^{-2} s^{-1}). Following removal from the reactor, they were left for a decay period of between 10 and 30 minutes, and then counted for five minutes using a germanium lithium Ge(Li)-detector-based γ-ray spectrometer. When monitoring specifically for chlorine, data were collected for the 2.167 MeV γ-ray peak generated by $_{17}Cl^{38}$. The results for elemental concentrations were calculated based on the comparator method.[31]

Sample 1 was sent first for irradiation to obtain general information about the chlorine content as well as other elements present in the sample. This information was needed to determine the approximate concentration of chlorine to be used in the chlorine standard as well as to identify the longest-lived radioisotopes generated by the activation process.

Chlorine Standard

A sodium chloride (NaCl) solution of known concentration was included with two sets of iron samples sent to the SLOWPOKE Reactor Facility for INAA to test the precision and accuracy of the analytical procedure. The standard solution contained 1000 parts per million (ppm) chloride ion in water. Approximately 0.5 mL of the solution was weighed in a polyethylene vial and then heat sealed with a soldering gun. The first solution weighed 0.5133 g and the second one weighed 0.5104 g.

Chloride Ion Analysis by Titration

Treatment solutions were analysed for chloride ion content using potentiometric titration with silver nitrate.[11,12] A 30 mL sample was collected prior to each solution change (once every two weeks). For each analysis, 5.00 mL of treatment solution was placed in a 100 mL beaker along with a magnetic stir bar, 45.00 mL of deionized water (Millipore reverse-osmosis and Milli-Q deionized), and 0.50 mL of 5M sodium nitrate [an ionic strength adjuster]. This mixture was then acidified to about pH 5 by adding concentrated nitric acid. Two electrodes, a silver/sulfide electrode (Orion Model 94-16) and a silver/silver chloride double junction reference electrode (Orion Model 90-02), were placed in the solution. The solution was then titrated by adding 2.00 mL quantities of 3.00×10^{-3}M silver nitrate with a digital pipette and recording the potential difference between the two electrodes with a pH/millivolt meter (Orion, Model 811) after each addition. The endpoint of the titration was calculated using a least-squares fitting procedure which included a term for volume correction. As part of each analysis, the chloride ion content was determined in blanks of unused *EN* and NaOH solutions and the results were used to correct the chloride ion contents of the treatment solutions. Repeated analyses of chloride ion standards in sodium hydroxide and ethylenediamine at two chloride ion concentrations (71.0 and 7.1 ppm) gave reproducible results.[32] Based on the standard deviations of these results, a probable error of ±3 ppm was assigned to individual chloride ion measurements.

Results

Initial Test Sample

Table III lists the elements detected during the initial INAA of sample 1 (untreated). The error limits are based on counting statistics and were provided with the results.[33] The chlorine detection limits were <70 ppm (95% confidence) and ≤35 ppm (68% confidence).

Table III: INAA Results from Initial Analysis of Sample 1.

Element	Concentration (ppm)
Cobalt (Co)	65 ± 8
Arsenic (As)	700 ± 30
Manganese (Mn)	165 ± 5
Copper (Cu)	≤ 50*
Sodium (Na)	≤ 30*
Vanadium (V)	134 ± 4
Aluminum (Al)	110 ± 4
Chlorine (Cl)	1550 ± 30

* 68% confidence limit

The longest-lived radioisotope measured in this first sample was arsenic $_{33}As^{76}$ which has a half-life of 26.3 hours.[23,24] This means that the radioactivity given off by the sample will decrease significantly a week or two after irradiation, allowing the sample to be safely handled. The samples were returned after approximately six weeks, when the radiation levels were negligible.

Chlorine Standard

The two standards containing 1000 ppm chlorine gave INAA results of 1072 ± 40 ppm, and 1100 ± 40 ppm chlorine. These results indicate that the measurements are precise, falling within the ± 40 ppm error limits. However, the results also indicate a measurement inaccuracy of about 9% given the measured average was 1086 ± 40 ppm, while the known concentration of the standard was 1000 ppm.

Control Sample

Table IV contains results for the detection of chlorine measured four times in sample 1. This sample was analyzed once at the beginning to test the possibility of using INAA, and then included with the three sample sets sent later for INAA. The mean value of these four measurements is 1540 ppm with a sample standard deviation of 60 ppm. This reflects a precision of about 4% for sequentially determining chlorine at this concentration level.

Iron Samples

For samples 2 to 5 (from nail #1), the treatment solutions were light orange during the first 2-week period of immersion, and colourless and transparent during the remaining 2-week periods. This indicated either minor initial corrosion or that the loose surface corrosion was washed off in the first two weeks. For sample 6 (also from nail #1), the treatment solutions for most of the 2-week periods of immersion were light orange, and orange-red flocculent material appeared at the exposed metal surface, indicating active corrosion.

The *EN* treatment solutions used for sample 7 (nail #2) and sample 8 (nail #3) became murky with an orange or red-brown suspension of particulate matter during each 2-week period of immersion. The solutions were dark brown during the first few 2-week periods, and then were a lighter orange colour for later

Table IV: Results from Four Different INAA of Sample 1.

Sample 1 (tip of Red Bay nail)	Chlorine Concentration (ppm)
irradiation 1	1550 ± 30
irradiation 2	1460 ± 40
irradiation 3	1550 ± 50
irradiation 4	1600 ± 40

Table V: Results for Chlorine Analysis by INAA and Chloride Ion Analysis by Titration.*

Sample No.	Treatment Solution	Weight (g)	Chlorine in Sample [INAA] (ppm)	Chlorine Removed [INAA] (mg)	Chloride Ion in Solution (mg)
1	control	0.8625	1540 ± 60	-	-
2	5% v/v *EN* 50°C pH = 11.7	6.6986 before 6.6954 after 0.0032 loss	2200 ± 40 before 1270 ± 40 after 930 ± 80 loss (42%)	6.2 ± 0.5	3.8 ± 0.4
3	5% v/v *EN* 22°C pH = 11.7	6.3968 before 6.3710 after 0.0258 loss	1810 ± 40 before 840 ± 30 after 970 ± 70 loss (54%)	6.2 ± 0.5	7.4 ± 0.3
4	20% v/v *EN* 50°C pH = 12.6	5.8928 before 5.8670 after 0.0258 loss	2140 ± 50 before 700 ± 30 after 1440 ± 80 loss (67%)	8.5 ± 0.5	10.3 ± 0.3
5	2% w/v NaOH 22°C pH = 13.2	5.1768 before 5.1664 after 0.0104 loss	2740 ± 60 before 970 ± 30 after 1770 ± 90 loss (65%)	9.2 ± 0.5	11.2 ± 0.3
6	0.01% w/v NaOH 22°C pH = 11.2	4.3559 before 4.2403 after 0.1156 loss	1280 ± 40 before 180 ± 20 after 1100 ± 60 loss (86%)	4.8 ± 0.3	7.3 ± 0.4
7	5% v/v *EN* 50°C pH = 11.7	8.0373 before 6.2751 after 1.7622 loss	4160 ± 50 before ≤13** after 4147 ± 52 loss (99.8%)	35.4 ± 0.4	38.9 ± 0.6
8	5% v/v *EN* 50°C pH = 11.7	7.9771 before 4.9949 after 2.9822 loss	2980 ± 50 before ≤24** after 2956 ± 50 loss (99.5%)	23.6 ± 0.4	9.4 ± 1.0

*   The table lists chlorine in the sample and chloride ion in solution for the iron samples, before and after treatment. "Loss" refers to the difference between the weights (column 3) or chlorine concentration (column 4) before and after treatment.

**   68% confidence limit.

2-week periods. For sample 7, the black layer (presumably magnetite) appeared to be continuously stripped by the *EN* solution. For sample 8, the outer red-brown corrosion layer fell off during treatment and the underlying black layer also appeared to be continuously stripped by the *EN* solution.

Table V contains results from INAA and titration for the wrought iron samples before and after treatment. The table lists the sample number, the treatment solution associated with the sample, and the sample weights "before" and "after" treatment, along with the differences between before and after weights (labelled "loss" in the table). Column 4 lists the results from INAA for the concentration (in ppm) of chlorine in the samples before and after treatment. This concentration was then converted to weight (in mg) in column 5 using the weights of the samples and the following definition for ppm for a solid:[34]

$$ppm = \frac{\text{weight of solute (mg Cl)}}{\text{weight of sample (mg sample)}} \times 10^6 \qquad (4)$$

The final column in **Table V** lists the total amount of chloride ions (in mg) dissolved in the treatment solutions for the samples

after the 18 weeks of treatment. During treatment, the chloride ion concentration (in ppm) in the treatment solution was determined by titration every two weeks. This concentration was then converted to weight (in mg) using the volume of the treatment solutions and the following definition for ppm for a liquid:[34]

$$ppm = \frac{\text{weight of solute (mg Cl)}}{\text{volume of solution (L)}} \qquad (5)$$

This definition holds for solutions where the solvent is water, the quantity of solute is small, and the density of the solution is assumed to be 1.00 g mL^{-1}. The results are graphed in **Figure 1**. For each sample, data points are the sum of the amount of chloride ions in each solution up to that time.

Figure 2 contains a bar graph showing the weight of chlorine removed from each sample. The largest weight of chlorine was removed from sample 7 (nail #2, marine, stored in water). The graph compares the amount of chlorine removed from the samples (determined by INAA) with the total amount of chloride ion dissolved in the full set of sequential treatment solutions (determined by titration). As shown in **Figure 2** the total amount
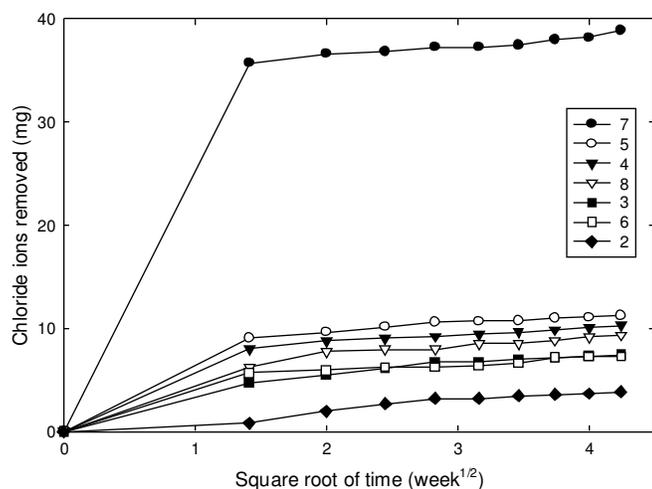
Figure 1. Cumulative weight of chloride ions (determined by titration) removed from the wrought iron samples against the square root of time. The error in each data point was calculated by summing the squares of the error for each measurement and then taking the square root. The error bars are not shown because they are approximately the same size as the symbols.
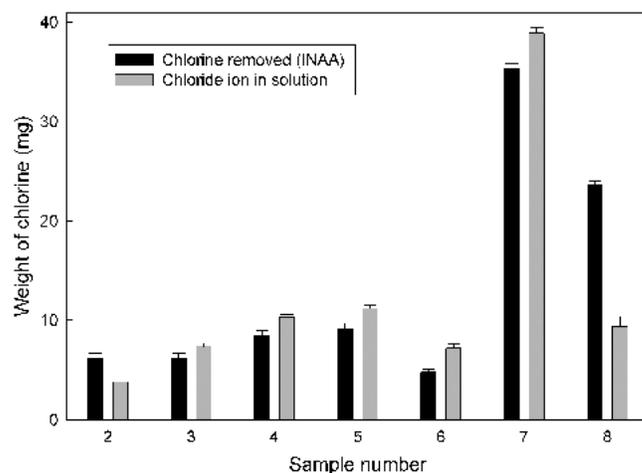
Figure 2. Total weight of chlorine removed from the wrought iron samples after 18 weeks of treatment. The height of the solid bars represents the difference between the weights of chlorine before and after treatment (determined by INAA), and the height of the shaded bars represents the total weights of chloride ions in the 18-week sequence of treatment solutions (determined by titration).

of chlorine determined by INAA and the total amount of dissolved chloride ions determined by titration are related, and the relative values of the results within most sets show a similar trend.

Discussion

Monitoring Chlorine Concentration in Iron Samples by INAA

The chlorine content in seven wrought iron samples was measured before and after treatment. Of these seven treated samples, five still contained significant chlorine after 18 weeks of treatment. Thus, the INAA results presented in this paper show that this analytical technique is useful for detecting chlorine remaining in samples of archaeological iron after treatment. The main advantage of INAA is that the artifact or sample is not destroyed during analysis and the amount of chlorine can be measured in the same piece before and after treatment. It would be particularly useful on experimental material designed to research treatment effectiveness.

The main restriction in using INAA to study whole objects is that the object must be small enough to fit into the containers used at the research reactor. For the experiments reported here, two of the samples were small nails and the other samples were pieces cut from a nail. These fit into the larger polyethylene containers (length 5.5 cm, diameter 1.6 cm) used at the SLOWPOKE reactor in Toronto, thus allowing the complete object (or cut sample) to be analyzed repeatedly.

Unfortunately, INAA is inappropriate as a tool for monitoring the progress of a treatment because of the wait time before the sample can be returned and treatment continued. During irradiation, radioactivity may be induced in several different elements, each having a different half-life. After irradiation, the

sample cannot be returned until this induced radioactivity has decayed to a negligible level.

Another disadvantage is that INAA cannot distinguish whether the chlorine is present as soluble chloride ions or bound within the structure of a solid compound, such as in akaganéite (β-FeOOH).[35] The form of the chlorine is important since conservation treatments for archaeological iron address ways to remove soluble chloride ions, but not akaganéite. Further research is needed to determine how akaganéite is affected by alkaline solutions, although it is known that it is not possible to remove the bound chlorine from akaganéite by washing in water.[36] There is still some debate as to whether the presence of akaganéite can cause further damage to iron if it transforms to another iron oxyhydroxide and releases soluble chloride ions.[37] Further research in this area is needed.

Monitoring Chloride Ion Concentration in Treatment Solutions by Titration

The potentiometric titration results reported in this paper demonstrate that this analytical technique is useful for monitoring the concentration of chloride ions in the treatment solutions and for determining the total amount removed by the treatment. For each treatment solution, the chloride ion concentration was determined every two weeks (prior to each solution change) for the 18 weeks of treatment.

The advantage of the titration technique is that it is relatively easy and quick (in comparison to INAA) to monitor the chloride ion concentration in the treatment solution as a function of time. For the seven treated samples, the titration results (**Figure 1**) showed that most of the chloride ions were removed during the first two weeks of immersion, and that during the last two weeks

of immersion, the chloride ion concentration was low ($\leq$ 10 ppm). Archaeological conservators usually decide to stop treatment when low chloride ion concentrations are detected in consecutive treatment solutions. Low chloride ion concentrations are reported to be about 50 ppm by North,[38] 20 ppm by Watkinson,[1] and 10 ppm by Riss.[39]

A disadvantage in using titration only to monitor the chloride ion concentration in the treatment solution is that it does not provide information about how much chlorine remains in the object after treatment. Low levels of chloride ions in consecutive treatment solutions indicate a low diffusion rate of soluble chloride ions from an object. They can give a conservator a false sense of security because the low levels imply that the treatment is finished. However, as demonstrated by the INAA results presented for the seven samples after treatment, significant chlorine can remain. More research is needed to determine how much chlorine needs to be removed from chlorine-contaminated archaeological iron in order to ensure its stability.

Effectiveness of Treatment Solutions

A range of treatment conditions (different chemicals, concentrations, and temperature) was selected for treating the archaeological iron samples. These experiments were chosen to provide a quick survey of several variables rather than a comprehensive study. Only one nail for each type of experiment was tested, and so the following interpretation should be considered preliminary. Higher pH solutions (for both *EN* and NaOH) were more effective at removing chlorine than lower pH solutions. A lower temperature (22°C instead 50°C) did not have any significant effect for the *EN* solution. The ability of *EN* to strip off corrosion products and cause rapid iron corrosion was also noted (samples 7 and 8 corroded rapidly). This dangerous behaviour has been observed by others,[27,40,41] and is due to the ability of the neutral *EN* molecule to form soluble complexes with iron(II) ions.[16] Nail #1 (samples 1 to 6) had been allowed to dry after its initial treatment by hot washing in water and before the treatment listed in **Table II**. It may be that if the archaeological iron samples had been kept wet prior to treatment, then the alkaline solutions would have been more successful at removing chloride ions, as demonstrated by González et al.[4]

Sources of Error

As shown in **Figure 2**, for samples 3 to 7, more chloride ions were detected in solution by titration than were removed from the iron as measured by INAA. In addition, if the 9% accuracy error (from the chlorine standards) is taken into account, then the INAA results for the samples would all decrease by that much, making the discrepancy between the two methods even larger. The reason for the difference in the results is not known. More work needs to be done on analyzed standard materials to check the accuracy of the two methods and determine if the differences are due to human error or systematic errors. For example, it would be useful to cross-calibrate the two techniques by analyzing the same standard.

For samples 2 and 8, lower chloride ion concentrations were detected in solution compared to the amounts removed from the iron as determined from the INAA results. A source of error in studying chlorine in corroded archaeological iron is loss of material during repeated handling. Archaeological iron is covered with corrosion products that may be easily knocked off and possibly lost when transferring objects between containers. Moreover, the outer corrosion products may be removed during treatment. The chlorine may be trapped within these corrosion products, either as chloride ions dissolved in pore water or else bound in a solid compound. For these two samples, chloride-contaminated corrosion products were likely removed from the beaker when the treatment solution was changed before all the soluble chloride ions had diffused into solution. This would explain why more chloride ions were removed from the iron (as measured by INAA) than were present in the solution (as measured by titration).

Conclusions

Results are presented of a survey investigation into the use of instrumental neutron activation analysis as a non-destructive analytical tool in determining the chlorine concentration in small wrought iron nails. Results are also presented of the use of potentiometric titration for monitoring the chloride ion concentration in various treatment solutions.

INAA can be a useful tool for studying iron treatments in certain instances because it can be used to measure the chlorine concentration before and after treatment, thus allowing the effectiveness of the treatments to be determined. INAA is limited by the maximum sample size (determined by the size of the INAA container) and by the wait time (determined by the radioactivity induced in the sample by irradiation). Potentiometric titration is a proven useful tool for monitoring the progress of iron treatments by following the chloride ion concentration in treatment solutions. A disadvantage in using titration only to monitor the chloride ion concentration in the treatment solution is that it does not provide information about how much chlorine remains in the object after treatment.

Low levels of chloride ions in the solution are often assumed to indicate that the treatment is finished. However, as demonstrated by the INAA results presented here, significant chlorine can remain in the object after treatment, either as soluble chloride ions trapped within the corrosion products, or as chlorine bound within insoluble corrosion products. Thus, a combination of INAA and potentiometric titration can provide a more complete picture about the effectiveness of archaeological iron treatments than using only one of these analytical methods.

Materials

Chlorine standard, based on NaCl (1000 ppm, 1 mL = 1 mg Cl): Fisher Scientific Company, 112 Colonnade Road, Ottawa, ON K2E 7L6, 1-800-234-7437 or (613) 226-3273.

Ethylenediamine (98-100%): Fisher Scientific Company.

Nitric acid (ACS certified): Fisher Scientific Company.

Silver nitrate (ACS certified): Fisher Scientific Company.

Sodium hydroxide (ACS certified): Fisher Scientific Company.

Sodium nitrate (ACS certified): Fisher Scientific Company.

Notes and References

1. Watkinson, David, "Degree of Mineralization: Its Significance for the Stability and Treatment of Excavated Ironwork," *Studies in Conservation*, vol. 28, no. 2, 1983, pp. 85-90.

2. Watkinson, David, "Chloride Extraction from Archaeological Iron: Comparative Treatment Efficiencies," in: *Archaeological Conservation and Its Consequences*, edited by Ashok Roy and Perry Smith (London: International Institute for Conservation of Historic and Artistic Works of Art, 1996), pp. 208-212.

3. Al-Zahrani, Abdulnasar A., "Chloride Ion Removal from Archaeological Iron and β-FeOOH," PhD Thesis (Cardiff: University of Wales, 1999).

4. González, Néstor G., de Viviés, Philippe, Drews, Michael J. and Mardikian, Paul, "Characterizing the Chloride in the Wrought Iron Rivets from the Hunley," in: *NACE Northern Area Eastern Conference*, Ottawa, Sept. 15-17, 2003 (Ottawa: NACE Canadian National Capital Section, 2003). (Proceedings on CD).

5. Hancock, R.G.V., "Some Aspects of the Analysis of Ancient Artifacts by Neutron Activation," *Journal of the International Institute for Conservation - Canadian Group*, vol. 3, no. 2, 1978, pp. 21-27.

6. Neff, H. and Glascock, M.D., "The State of Nuclear Archaeology in North America," *Journal of Radioanalytical and Nuclear Chemistry*, vol.196, no. 2, 1995, pp. 275-286.

7. Levine, Mary Ann, "Determining the Provenance of Native Copper Artifacts from Northeastern North America: Evidence from Instrumental Neutron Activation Analysis," *Journal of Archaeological Science*, vol. 34, no. 4, 2007, pp. 572-587.

8. Argyropoulos, Vasilike, "A Characterization of the Compositional Variations of Roman Samian Pottery Manufactured at the Lezoux Production Centre," *Archaeometry*, vol. 37, no. 2, 1995, pp. 271-285.

9. Hancock, R.G.V., Pavlish, L.A., Farquhar, R.M., Salloum, R., Fox, W.A. and Wilson, G.C., "Distinguishing European Trade Copper and North-Eastern North American Native Copper," *Archaeometry*, vol. 33, no. 1, 1991, pp. 69-86.

10. Berkey, E. and Fisher, D.E., "The Abundance and Distribution of Chlorine in Iron Meteorites," *Geochimica et Cosmochimica Acta*, vol. 31, September - December, 1967, pp. 1543-1558.

11. Costain, Charlie, "Measurement of Chlorides in Treatment Solutions," *ICOM Committee for Conservation, Metals Working Group Newsletter*, vol. 1, 1985, pp. 4-7, and erratum in following newsletter.

12. Selwyn, Lyndsie S., "Analysis of the Chloride Ion Concentration in Aqueous Solutions by Potentiometric Titration", *CCI Research Report*, no. 2 (Ottawa: Canadian Conservation Institute, 2001).

13. Kotzamanidi, I., Sarris, E.M., Vassiliou, P., Kollia, C., Kanias, G.D., Varoufakis, G.J., and Filippakis, S.E., "Effect of Heat Treatment in Reducing Plasma Environments on Chloride Ion Removal and Corrosion of Oxidised Steel Artefacts," *British Corrosion Journal*, vol. 34, no. 4, 1999, pp. 285-291.

14. Aoki, Shigeo, Hirao, Yoshimitsu, Hirai, Shoji and Kubota, Harutoshi, "Stabilization of Archaeological Iron," in: *Current Problems in the Conservation of Metal Antiquities*, edited by Shigeo Aoki (Tokyo: Tokyo National Research Institute of Cultural Properties, 1993), pp. 107-119.

15. Argyropoulos, Vasilike, Selwyn, Lyndsie S. and Logan, Judith A., "Developing a Conservation Treatment Using Ethylenediamine as a Corrosion Inhibitor for Wrought Iron Objects Found at Terrestrial Archaeological Sites," in: *Metal 95: Proceedings of the International Conference on Metals Conservation*, edited by Ian D. MacLeod, Stéphane L. Pennec and Luc Robbiola (London: James & James, 1997) pp. 153-158.

16. Selwyn, Lyndsie S. and Argyropoulos, Vasilike, "Removal of Chloride and Iron Ions from Archaeological Wrought Iron with Sodium Hydroxide and Ethylenediamine Solutions," *Studies in Conservation*, vol. 50, no. 2, 2005, pp. 81-100.

17. Muecke, G.K., ed., *Short Course in Neutron Activation Analysis in the Geosciences, Short Course Handbook*, vol. 5 (Toronto: Mineral Association of Canada, 1980).

18. de Soete, Damiaan, Gijbels, Renaat and Hoste, J., *Neutron Activation Analysis* (London: Wiley-Interscience, 1972).

19. Landsberger, Sheldon, "Delayed Instrumental Neutron Activation Analysis," in: *Chemical Analysis by Nuclear*

Methods, edited by Zeev B. Alfassi (Chichester: John Wiley & Sons, 1994), pp. 121-162.

20. Pollard, A. Mark and Heron, Carl, *Archaeological Chemistry* (Cambridge: The Royal Society of Chemistry, 1996), pp. 54-61.

21. Haskin, L.A., "An Overview of Neutron Activation Analysis in Geochemistry," in: *Short Course in Neutron Activation Analysis in the Geosciences*, *Short Course Handbook*, vol. 5, edited by G. K. Muecke (Toronto: Mineral Association of Canada, 1980), pp. 1-19.

22. Friedlander, Gerhart, Kennedy, Joseph W. and Miller, Julian M., *Nuclear and Radiochemistry*, 2nd ed. (New York: John Wiley & Sons, 1964), pp. 535-566.

23. Glascock, Michael D., *Tables for Neutron Activation Analysis* (Columbia, MO: University of Missouri, 1988).

24. Leclerc, J.C. and Cornu, A., *Neutron Activation Analysis Tables* (London: Heyden, 1974).

25. Dostal, J. and Elson, C., "General Principles of Neutron Activation Analysis," in: *Short Course in Neutron Activation Analysis in the Geosciences*, *Short Course Handbook*, vol. 5, edited by G. K. Muecke (Toronto: Mineral Association of Canada, 1980), pp. 21-42.

26. Tuck, James A. and Grenier, Robert, *Red Bay, Labrador: World Whaling Capital A.D. 1550-1600* (St. John's: Atlantic Archaeology, 1989).

27. Costain, Charles G., "Evaluation of Storage Solutions for Archaeological Iron," *Journal of the Canadian Association for Conservation*, vol. 25, 2000, pp. 11-20.

28. Lépine, André, "Archéologie Sous-Marine: Épave d'un Vaisseau Ancien dans la Baie de Gaspé," *Gaspésie*, vol. 12, no. 1, 1984, pp. 12-25.

29. Tuck, James A., "Archaeology at Ferryland, Newfoundland," *Newfoundland Studies*, vol. 9, no. 2, 1993, pp. 294-310.

30. INAA of the iron samples was carried out prior to the permanent shut down of the Toronto SLOWPOKE reactor at the end of 1998. The cost was $20 per sample.

31. Hancock, R.G.V., "Low Flux Multielement Instrumental Neutron Activation Analysis in Archaeometry," *Analytical Chemistry*, vol. 48, no. 11, 1976, pp. 1443-1445.

32. Selwyn, Lyndsie, "Supplementary Information," CPMR Report, Proteus # 86672 (Ottawa: Canadian Conservation Institute, 2004). Unpublished report.

33. Hancock, Ron (Director, SLOWPOKE Reactor Facility, University of Toronto), personal communication, 1996.

34. Skoog, Douglas A., West, Donald M. and Holler, F. James, *Fundamentals of Analytical Chemistry*, 5th ed. (New York: Saunders College Publishing, 1988), p. 96.

35. Selwyn, Lyndsie S., Sirois, P. Jane and Argyropoulos, Vasilike, "The Corrosion of Excavated Archaeological Iron with Details on Weeping and Akaganéite," *Studies in Conservation*, vol. 44, no. 4, 1999, pp. 217-232.

36. Ståhl, Kenny, Nielsen, Kurt, Jiang, Jianzhong, Lebech, Bente, Hanson, Jonathan C., Norby, Poul and van Lanschot, Jettie, "On the Akaganéite Crystal Structure, Phase Transformations and Possible Role in Post-Excavational Corrosion of Iron Artifacts," *Corrosion Science*, vol. 45, no. 11, 2003, pp. 2563-2575.

37. Selwyn, Lyndsie, "Overview of Archaeological Iron: The Corrosion Problem, Key Factors Affecting Treatment, and Gaps in Current Knowledge," in: *Metal 04: Proceedings of the International Conference on Metals Conservation*, 4-8 October 2004, edited by John Ashton and David Hallam (Canberra: National Museum of Australia, 2004), pp. 294-306.

38. North, Neil A., "Conservation of Metals," in: *Conservation of Marine Archaeological Objects*, edited by Colin Pearson (London: Butterworths, 1987), pp. 207-252.

39. Riss, Dan, "Desalinization: Passive Alkaline Soak," *National Park Service Conserve O Gram no. 6/2*, 1993, pp. 1-2. <http://www.cr.nps.gov/museum/publications/ conserveogram/06-02.pdf>. Accessed January 2007.

40. Busse, Enno, "The Manitoba North Cannon Stabilization Project," in: *Metal 95: Proceedings of the International Conference on Metals Conservation*, 25-28 September 1995, edited by Ian D. MacLeod, Stéphane L. Pennec and Luc Robbiola (London: James & James, 1997), pp. 263-268.

41. Brown, Carol E., "Ethylene-diamine Treatment of Iron," *Conservation News*, vol. 27, 1985, p. 38.