

Zeitschrift:	Zeitschrift für schweizerische Archäologie und Kunstgeschichte = Revue suisse d'art et d'archéologie = Rivista svizzera d'arte e d'archeologia = Journal of Swiss archeology and art history
Herausgeber:	Schweizerisches Nationalmuseum
Band:	54 (1997)
Heft:	1: Unser Umgang mit dem Kulturgut : Gegenwart und Zukunft ; Conservation of metal objects in low-pressure hydrogen plasma = Die Niederdruck-Wasserstoffplasma-Methode zur Konservierung von Metallobjekten : Möglichkeiten ihrer Anwendung und Verbesserung
Artikel:	Applications of low pressure plasma treatment at the Swiss National Museum and assessment of the results
Autor:	Schmidt-Ott, Katherina
DOI:	https://doi.org/10.5169/seals-169510

Nutzungsbedingungen

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. [Mehr erfahren](#)

Conditions d'utilisation

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. [En savoir plus](#)

Terms of use

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. [Find out more](#)

Download PDF: 21.02.2026

ETH-Bibliothek Zürich, E-Periodica, <https://www.e-periodica.ch>

Applications of low pressure plasma treatment at the Swiss National Museum and assessment of the results

by KATHARINA SCHMIDT-OTT

Abstract

Low pressure plasma treatment has been applied to metal conservation for several years. With plasma treatment, as in all areas of conservation development, alterations and augmentations are being made along the way. There have been, therefore, different stages of plasma use in Zurich. The results of different treatment parameters for artifacts are discussed. The combination of plasma treatment with other conservation treatments is described and the stability of the differently treated artifacts is assessed. Recent experience and developments with the plasma equipment are described, emphasizing temperature measurements of artifacts themselves.

Zusammenfassung

Die Niederdruckplasma-Methode wird im Bereich der Metallkonservierung seit einigen Jahren angewendet. Wie in der Konservierung allgemein, so sind auch bei der Plasma-Methode, Veränderungen und Entwicklungen notwendig. Es gibt daher in Zürich verschiedene Studien der Anwendung. Die Ergebnisse der zu verschiedenen Zeiten angewandten Behandlungsparameter werden besprochen. Die Anwendung der Plasmamethode in Kombination mit anderen Konservierungs-Massnahmen wird beschrieben, und der Zustand der unterschiedlich behandelten Objekte wird ermittelt. Jüngste Erfahrungen und Entwicklungen, insbesondere die Temperaturmessung direkt am Objekt, werden beschrieben.

Introduction

The application of low-pressure plasma for the cleaning and possible treatment of metal artifacts continues to be an important concept in conservation. Yet experience with the use of the plasma equipment has lead to changes in its application. Its use as a standard treatment procedure, for example for iron artifacts at the Swiss National Museum, has been modified. Some important questions concerning the use of this highly developed technology on archaeological artifacts are:

- Do we damage an artifact more than we conserve it?
- Is the artifact in a more stable state after treatment than it was before?
- Does the method preserve fully the inherent archaeological and metallurgical evidence?
- Is this method actually efficient regarding the relationship of time and cost?



Fig. 1 Artifact from Schleitheim, Hebsack; Kanton Schaffhausen: treated according to parameters used until 1989, corresponds to corrosion scale 0. It has been in a controlled storage environment since 1990.

A comparison of different types of conservation treatments for metal, such as mechanical cleaning, protective coatings, stable storage conditions and various applications of the plasma method, has shown that no single treatment solves all the problems generally encountered with metal artifacts. The investigation of low pressure plasma is part of the search for an appropriate conservation treatment for iron-work and other metals.

First stage of plasma use in iron conservation

Plasma is a well-known physics field and has been applied to metal conservation for several years. Under the supervision of Stanislav Vepřek in the 1980's, it was Jörg Patzscheder at the University of Zurich who first proposed the application of plasma for the cleaning and possible preservation of iron artifacts¹. A collaboration was initiated between the Institute of Inorganic Chemistry at the University and the Swiss National Museum.



Fig. 2 Artifacts from Wartau, Ochsenberg; Kanton St. Gallen (excavated by the University of Zurich): treated according to parameters used until 1993, correspond to corrosion scale 3.

In this early stage of plasma use for iron conservation, and until about 1989, objects underwent a typical treatment that consisted of the following steps²⁻⁴:

- a Two-hour hydrogen-methane plasma application.
- b Mechanical cleaning with scalpel or ultrasonic scaler.
- c 18–20 hours of plasma treatment (approx. 400 °C) using hydrogen, methane, nitrogen and argon.
- d Coating of artifact with microcrystalline wax.

The two-hour hydrogen-methane plasma treatment facilitated mechanical removal of corrosion encrustation by scalpel or ultrasonic scaler. The 18–20 hour plasma treatment was applied in order to remove chlorides and passivate the surface against post-corrosion, a step which has since come into question as a practical or even useful part of the treatment. Temperatures were set around 400 °C and were measured with a mercury thermometer inside a Pyrex glass which penetrated into the radio frequency field. The final step was a coating of the artifacts with microcrystalline wax. Until about 1989 artifacts were treated in this

manner and can be found today in numerous museum collections. The importance of this work was largely acknowledged at the time and the method seemed well developed in its application to daily conservation work. The National Museum's conservation and research staff were fortunate enough to acquire a high-frequency coupled plasma apparatus that was installed on museum premises in 1990⁵.

Second stage of plasma use at the Swiss National Museum 1990–1993

The Swiss National Museum's research staff, and metals conservator Jörg Elmer, collaborated in the running of the apparatus for daily use and in the study of its functions. Alterations in temperature, exposure time and other treatment parameters were carried out and the following treatment procedure was formulated:

- a Drying of artifacts in a vacuum oven at around 75 °C prior to plasma treatment.
- b Plasma treatment (7–8 hours) using hydrogen, methane, nitrogen and argon, with the temperature being gradually reduced to an average of 190–260 °C.
- c Mechanical cleaning by ultrasonic scaler or abrasives.
- d Coating of artifact with microcrystalline wax.

It was found at this time that the modified treatment, as detailed above, gave satisfactory results in cleaning and artifact stability⁶. No further changes in treatment were carried out in Zurich at that time. A large number of artifacts were treated in this manner from 1990 to 1993 and are accessible today in various museum collections. In several countries and at a number of different institutions plasma has been used for archaeological conservation, and so there are a variety of plasma treated objects from which to take note.

The treated artifacts are indicative of the effectiveness of plasma treatment and the modifications that have been made. They also speak of the inherent instability of iron. Chlorides have much to do with this instability and the effect that plasma has on chloride removal depends, it seems, on treatment parameters taken⁷⁻⁹.

Patricia Arnoult-Pernot has shown that the effective removal of chlorides (taken from samples made of corrosion products) requires very long treatment times and high temperatures (ranging from 300–450 °C)¹⁰ – conditions that, for all intents and purposes, would be too drastic for archaeological objects. Time and temperature parameters from the first two stages of plasma treatment did partly fall within these high boundaries. But while chloride levels within the objects might have been lessened to a degree, changes to the metallographic information on an artifact were, by today's standards, unacceptable. The use of nitrogen, and especially methane, lead to irreversible colour

changes on original surfaces, and the use of high temperatures could cause metallographic information to change¹¹.

Further alterations and augmentations in the use of the plasma for archaeological artifacts seemed essential; not only were colour changes of concern but so too was overall stability in the long term. The assessment of objects that had undergone various applications of the plasma method became a basis from which to improve the treatment and a corrosion definition scale was introduced to simplify the observations (Table 1):

Corrosion scale	State of artifact
0	no active corrosion observed
1	very few spots (< 1 mm) of active corrosion
2	increased occurrence of small spots (< 1 mm) of active corrosion
3	frequent spots and/or sporadic flaking
4	very active corrosion, numerous flakes
5	extremely corroded, decay of artifact

Table 1 Definition of corrosion scale.

An inspection of objects treated in both first and second plasma stages showed a range of conditions, however, a number of them appeared to be in an unstable condition (Fig. 1-3):

Artifacts treated until 1989 are today, generally, on the corrosion scale of 2-3; those treated according to the parameters used until 1993 are in condition 3-4. Storage conditions will have, of course, a great deal to do with an object's stability and these were often not ideal for the artifacts described. This is a factor that must be included in our observations. There is no doubt, however, that the iron artifacts treated during the first two plasma stages continue to be susceptible to post-corrosion and it would seem that chlorine removal was not successful after all.

Use of plasma at the Swiss National Museum since 1994

Since 1994, changes have been introduced concerning the handling, treatment and storage of objects both before and especially after plasma treatment:

- Pre-drying of artifacts in a vacuum oven at around 75 °C.
- Plasma treatment (approx. 7 hours) using hydrogen and argon, with an average temperature of 120 °C.
- Slow cooling of artifacts in nitrogen.

- Mechanical cleaning by scalpel or micro sandblasting.
- Desalination in alkaline sulphite.
- Completion of mechanical cleaning by micro sandblasting or scalpel.
- Coating of artifact with acrylic resin.
- Dry storage.

Prior to plasma treatment, all artifacts are dried in an oven which is evacuated to a pressure of about 2 mb. This procedure helps to create an even discharge within a very short



Fig. 3 Artifact from Schleitheim, Hebsack; Kanton Schaffhausen: treated according to parameters used until 1989, corresponds to corrosion scale 5. It has been in a controlled storage environment since 1990.

time. Keeping in mind the inherent nature of an artifact and the information it contains, treatment must neither destroy nor alter such information. Treatment temperatures have not been raised, but reduced. The use of methane and nitrogen gas has also been discontinued because of the colour changes caused as well as the alterations of metallurgical information to the metal surface that occur through the introduction of carbon and nitride. It has also been found that passivation of the surface against post-corrosion does not occur to a substantial enough degree to prove practical. Further research is still necessary. For the time being, plasma treatment is being applied to facilitate the removal of corrosion encrustation and to facilitate chloride removal in conjunction with other desalination methods. It has become standard that, following plasma treatment and mechanical cleaning with a scalpel and micro sandblasting, iron artifacts undergo a desalination in alkaline sulphite. Comparing the effectiveness of desalination for iron artifacts in alkaline sulphite with and without plasma pre-treatment, has shown that chlorine removal is increased and desalination time reduced if both treatments are combined. After desalination and mechanical cleaning, the artifacts are coated with an acrylic resin. *Paraloid B72* has been the standard resin

used for the last eight months; prior to that it was B48 N¹². The decision to coat artifacts with an acrylic resin, rather than the microcrystalline wax used as standard before this, was made because of the better reversibility properties of the acrylic resins and for the aesthetic appearance they give.



Fig. 4 Artifacts from Uster-Nänikon, Bühl, Kanton Zurich: treated in 1993 (without desalination, etc.); 2 years after conservation was completed.

For the assembly of fragments during cleaning, *Technovit 5071* resin, a methylmethacrylate, is used. This embedding material has the advantages of a fast curing time (2–3 minutes), strength as an adhesive, resilience over long periods of immersion in alkaline sulphite, resistance to high temperatures (100 °C), and good reversibility. It is soluble in acetone and works well in conjunction with *Paraloid*.

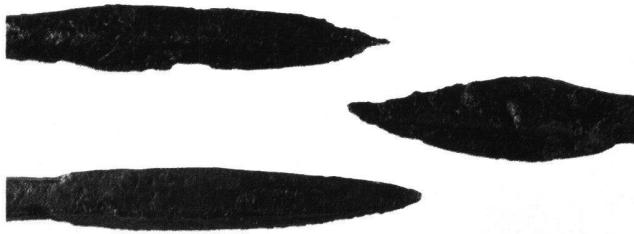


Fig. 5 Artifacts from Uster-Nänikon, Bühl, Kanton Zurich: treated according to steps applied since 1994; 1 year and 10 months after conservation was completed.

Only artifacts with no visible organic remains are treated with the plasma method at our laboratory. When non-mineralised organic remains are involved, plasma treatment will lead to extreme drying (e.g. of wood, textile) resulting

in shrinkage and colour changes¹³. Artifacts are stored with silica-gel as a matter of rule. An ongoing effort is being given to advise other institutions regarding adequate storage and handling for conserved metal artifacts. The following photographs show artifacts treated at different times in the archaeological conservation laboratory of the Swiss National Museum (Fig.4,5):

These artifacts are representative of nearly 400 pieces treated in total and coming from the same site. For all of these objects, storage conditions after conservation have not been ideal. Since 1994, over a thousand iron artifacts have been treated with the combination plasma-desalination treatment and to date all seem to be in stable condition.

Along with the modifications brought to the plasma treatment, we have also been developing temperature measuring devices which help us with our understanding of the effect of the plasma-treatment on artifacts. The temperature of the object itself (not just the surrounding area of the chamber) is important because of the metallographic changes that apparently take place during treatment and the subsequent alteration of information contained within the metallographic structure. It is important to note that until recently we have not been able to accurately determine these temperatures during treatment. A thermocouple with a high frequency filter was built in 1996 for this purpose¹⁴ and during treatment it is in direct contact with the artifact.

Fig. 6 shows the different temperatures now measured during plasma treatment:

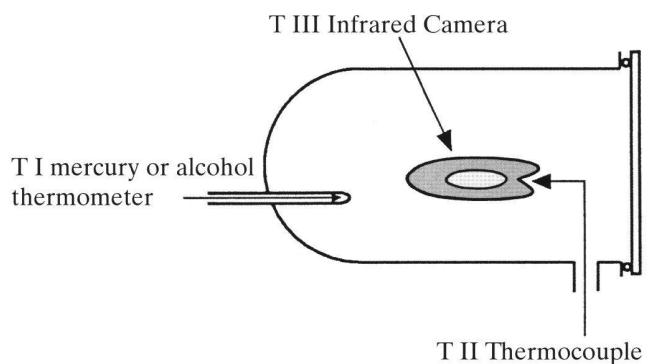


Fig. 6 Present temperature measurements during plasma treatment T I-T III:
 – T I: mercury or alcohol thermometer inside Pyrex glass tube.
 – T II: thermocouple in direct contact with an artifact.
 – T III: Infrared-camera focused on artifact surface.

Temperature measurements prior to our most recent determinations were not of the artifacts themselves but of the wall of a Pyrex glass tube within the ionised gas (Fig. 6: T I). The heating of the tube is mainly caused by dielectric

energy loss in the Pyrex. The temperature of a mercury or alcohol thermometer T I is, therefore, a relative measure for deposited radio frequency energy. While this temperature reading has been the one worked with for years, it is more to our purposes to know the temperature of the sample itself (Fig. 6: T II and T III). When comparing the temperature of an artifact with a metal core to that of a Pyrex glass tube, several points have to be considered:

It turns out that the temperature T I measured with an alcohol or mercury thermometer can only be judged as a relative measure. T I and T II will probably not be the same because of their different responses to incoming energy and the different losses by radiation.

At the artifact's surface, additional heat can be caused by the bombardment of ions and electrons from the plasma. Such a surface temperature may be represented by the reading of the infrared camera (T III). Consequently the optical measurement and thermocouple measurement do not necessarily have the same value. The surface region of the artifact is more like an electric insulator, while the metal core of an artifact is an electric conductor. This may cause different heating by direct radio frequency energy. Assuming that the temperature differences in the specimen are levelled out, the value of the thermocouple T II may give the artifacts' temperature. The following table shows typical temperature measurements during plasma treatment with different treatment parameters (Table 2):

Treatment parameters	T I [°C] of Pyrex glass in RF field	T II [°C] of artifact (thermo-couple)	T III [°C] of artifact surface (IR-camera)
1. 0,280 Torr, 8 in/h H ₂ , 0,8 in/h Ar, 0,9 kW, 0,80 arb. Units I-Plasma ¹⁵	110 °C	80 °C	76 °C
2. 0,330 Torr, 10 in/h H ₂ , 1 in/h Ar, 1,2 kW, 0,80 arb. Units I-Plasma ¹⁵	150 °C	125 °C	125 °C
3. 0,420 Torr, 18 in/h H ₂ , 1,8 in/h Ar, 1,25 kW, 0,84 arb. Units I-Plasma ¹⁵	165 °C	140°C	144 °C

Table 2 Typical temperature measurements during plasma treatment with different treatment parameters.

As can be seen from Table 2, the results of T II and T III are comparable while the temperature T I is different, in this case larger. It should be added that because of difficulties of calibration, the optical temperature measurement, T III, may not be accurate at low temperatures.

From our findings it seems that the artifact's actual temperature is lower than the glass tube temperature measured with a mercury or alcohol thermometer. If so, in the earlier treatments when only T I was measured, artifact temperature was probably not higher than indicated. Temperature measurements taken with a thermocouple seem to be the most accurate, provided that the disturbance of the radio frequency field can be expelled. It seems that we have reached this goal. By switching the radio frequency power off and on during test runs, we have found that the T II temperature reading does not change. Variations in the heating of the metal surface and in the isolating agglomerate layers may be, in addition to chemical treatment by reduction with hydrogen, a reason why plasma treatment facilitates mechanical cleaning.

For the time being measurements of temperature, pressure, gas, output and reflected power of the generator, as well as the plasma current, are recorded throughout every plasma treatment. These records and the general observation of the treated artifacts over long periods of time are helping to formulate the most appropriate treatment parameters for the artifacts we intend to conserve.

Acknowledgements

The author would especially like to thank Wolf-Dieter Schmidt-Ott, Martin Simnacher and Kim Travis for their support as well as the colleagues at the Swiss National Museum.

PHOTOGRAPHS

Fig. 1: Kantonsarchäologie Schaffhausen, Schaffhausen.
 Fig. 2: Kantonsarchäologie St. Gallen, St. Gallen.
 Fig. 3: Kantonsarchäologie Schaffhausen, Schaffhausen.
 Fig. 4: Kantonsarchäologie Zürich, Zürich.
 Fig. 5: Kantonsarchäologie Zürich, Zürich.

REFERENCES

- ¹ JÖRG PATSCHEIDER, *Anwendung von Wasserstoff Niederdruckentladungen zur Konservierung von Fundgegenständen aus Eisen.*, Thesis, University of Zurich, 1984.
- ² JÖRG PATSCHEIDER / STANISLAV VEPŘEK, *Application of low-pressure hydrogen plasma to the conservation of ancient iron artifacts*; in: *Studies in Conservation* 31, 1986, p. 29–37.
- ³ STANISLAV VEPŘEK / JÖRG ELMER / CHRISTIAN ECKMANN / M. JURCIK-RAJMAN, *Restoration and conservation of archaeological artifacts by means of a new plasma-chemical method*, in: *Journal of the Electrochemical society* 134, Vol 10, 1987, p. 2398–2405.
- ⁴ JÖRG ELMER / STANISLAV VEPŘEK, *Plasmachemische Eisenkonservierung*, in: *Arbeitsblätter für Restauratoren*, Heft 1, Gruppe 1, 1986, p. 213-216.
- ⁵ Installation by VACOTEC SA, 36, Av. Charles Naine, CH-2300 La Chaux-de-Fonds.
- ⁶ Personal communication of Jörg Elmer.
- ⁷ FLORENCE DUSSÈRE, *Le plasma hydrogène à basse pression. Etude critique d'une nouvelle méthode de nettoyage et de stabilisation des objets archéologiques ferreux*, Mémoire de maîtrise de Sciences et Techniques de Conservation et Restauration des Biens Culturels, Université de Paris, 1991.
- ⁸ PATRICIA ARNOULT-PERNOT / C. FORRIÈRES / B. WEBER, *Optimisation d'un traitement de déchloruration d'objets archéologiques ferreux par plasma d'hydrogène*, in: *Actes de la septième rencontre annuelle du groupe de travail ICOMcc-SFIIC section métal*, Draguignan, Conseil Général du Var, 1993, p. 93–111.
- ⁹ ANNE BEAUDOIN, *La méthode de nettoyage et de stabilisation des objets métalliques par plasma d'Hydrogène à basse pression, essai de bilan*, Mémoire de maîtrise de Sciences et Techniques de Conservation et Restauration des Biens Culturels, Université de Paris, 1994.
- ¹⁰ PATRICIA ARNOULT-PERNOT, *Traitements de déchloruration des objets archéologiques ferreux par le plasma d'hydrogène*, Thèse, Institut National Polytechnique de Lorraine, Ecole des Mines de Nancy, Laboratoire de Science et Génie des Surfaces 1994.
- ¹¹ R. F. TYLECOTE / J. W. B. BLACK: *The effect of hydrogen reduction on the properties of ferrous materials*, in: *Studies in Conservation* 25, 1980, p. 87–96.
- ¹² J. L. DOWN / M. A. MACDONALD / J. TÉTREAULT / R. S. WILLIAMS: *Adhesive testing at the Canadian Conservation Institute – an evaluation of selected poly(vinyl acetate) and acrylic adhesives*, in: *Studies in Conservation* 41, 1996, p. 19–44.
- ¹³ Covering of organic remains not to be treated by plasma with a protection paste has not proven practical. Protection pastes used for stones in the soldering of jewellery, for example, have been known to migrate into the organic features leading to loss of information. Plasma can also affect the stability of the covering material itself.
- ¹⁴ Constructed and built by Wolf-Dieter Schmidt-Ott, University of Göttingen, Germany, modified by Alex Voûte, Swiss National Museum.
- ¹⁵ Arbitrary Units I-Plasma, indicate the plasma current, the measured signal is proportional to the current flow in the gas discharge.