UNIVERSITY OF GOTHENBURG

DEPARTMENT OF CONSERVATION

EFFECTS OF COMMERCIAL NANO-LIME PRODUCTS AS A CONSOLIDATION METHOD FOR WALL PAINTINGS

An experimental case study

Hannah Petrini

Degree project for Bachelor of Science with a major in Conservation with Specialization in Conservation of Cultural Heritage Objects
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ABSTRACT

Some of the main deterioration problems concerning wall paintings is structural degradation of the wall painting and the flaking of the painted layer. Consolidation, both in the form of reinforcement of the rendering of the wall painting and the re-adherence of a flaking paint layer to the underlying substrate, have thus been an important part of conservation efforts concerning wall paintings. Since the turn of the millenia dispersions of nanoparticles of calcium hydroxide, sometimes referred to as nano-lime, have been developed as a consolidation method for wall paintings. Research studies investigating the effects of nano-lime as a consolidation method for wall paintings are limited to wall paintings executed in the fresco technique. Current research is also limited to investigating nano-lime used in environments with generally high levels of relative humidity. In this thesis paper the effects of commercial nano-lime products Nanorestore® and Nanorestore Plus®, used on wall paintings in the secco fresco technique in climatic conditions with relatively low levels of relative humidity are investigated.

The results of a literary study and an experimental study indicate a significant influence of both the environmental conditions and the constituents of the wall painting rendering in regards to the outcome of the consolidation treatment. The results also highlight the application method as a decisive factor and implies that adjustments in application technique are necessary depending on environmental conditions and the constituents of the rendering of the wall painting. The most important conclusion of this thesis paper is the necessity of further research investigating the effects of nano-lime products in different climates and on different substrates.

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PREFACE

Firstly I would like to thank Hanna, Ingrid and Matilda at Skånes Målerikonservatorer for making it possible to perform the experimental study in Dalby church. I would also like to thank Hanna, Ingrid and Matilda for their support and guidance throughout the process of the experimental study. Furthermore I wish to extend my gratitude to my mentor Kristina Frenguelli who has supported me and encouraged me throughout the process of this research study. Lastly I would like to thank Rodorico Girogi at the Consorzio Center of Colloid and Surface Science at the University of Florence for our interesting and constructive discussions, which have been helpful in the interpretation of the results of the research study.

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1. Introduction

1.1. Introduction

Some of the more common deterioration issues concerning wall paintings is structural degradation and the flaking of the painted layer, which can result in the loss of material. Structural degradation can occur both in the rendering of the wall painting and in the pigment layer itself. Such deterioration indicates a loss of cohesion within the material due to the deterioration of the binding media. Flaking of the paint layer is a problem regarding the loss of adhesion between the pigmented layer and the underlying substrate. The loss of cohesion and the loss of adhesion is a continuing concern in regards to the preservation of wall paintings and different conservation methods are frequently being developed and examined to deal with these deterioration issues. One of these continually developing methods are nanoparticles of calcium hydroxide particles dispersed in short-chained alcohols, commonly referred to as nano-lime.

The use of nano-lime within the field of conservation of cultural heritage has been studied and developed since the end of the 20th century. Many studies (Baglioni, Carretti & Chelazzi, 2015, Baglioni et.al., 2014, Baglioni & Giorgi, 2006, Gregorio, 2010, Baglioni & Chelazzi, 2013 & D'Armada & Hirst, 2012) suggest that nano-lime can be used as a suitable conservation treatment for the consolidation of wall paintings, both in regards to reinforcement of cohesion within the material and re-adherence of flaking paint layers. However there is a need for more practical studies to be carried out, examining the effects of nano-lime in different environmental conditions and on different substrates. The research examining the use of nano-lime as a consolidation treatment for wall paintings is limited to studies performed in indoor climates with generally high levels of relative humidity and to wall paintings executed in fresco technique. Research investigating the effects of nano-lime on wall paintings in secco technique and secco fresco technique in colder and drier climates, which is found in Scandinavia, is lacking. This creates certain problems for conservators using commercial nano-lime products in climates and on substrates where the effects of the products have not yet been properly examined.

This paper will through a literary study and an experimental study investigate the effects of two commercial nano-lime products in a Scandinavian climate on wall paintings executed in the secco fresco technique. Since the presence of gypsum in the mortar is a common occurrence in medieval churches in Sweden the study will also aspire to investigate the effects of commercial nano-lime products on substrates where gypsum may be present in the mortar (Hemgren, 2001, p.10). The investigation will have an exploratory approach and experiments will be performed in Dalby church in Skåne in collaboration with Skånes Målerikonservatorer.

1.2. Purpose & aim

The purpose of this research study is to examine if commercial nano-lime products available on the market today are suitable as a consolidation material for church wall paintings in Scandinavia. Furthermore the study will aspire to initiate a discussion concerning possible adjustments that can be made in regards to application methods that can make commercial nano-lime products more suitable to be used in indoor climates with generally low levels of relative humidity.

1.3. Research questions

What are the effects of commercial nano-lime products used on wall paintings in an environment with generally low levels of relative humidity?

What are the effects of commercial nano-lime products used on wall paintings executed in the secco fresco technique with gypsum present in the mortar?

1.4. Background

1.4.1. Research object - Dalby Church

Dalby church is located in Skåne County in the south of Sweden. It was built as an episcopal church around the year 1060, making it the oldest stone church in Sweden. The building was erected in the Romanesque style and has since its construction undergone major alterations both to the exterior and interior (Ranby, 2014, p.10-11). In 1758 the church gained its current appearance after extensive renovations. Many medieval wall paintings in Swedish churches were at some point covered with an overlying lime plaster, this is usually referred to as whitewash. During the early 1900s the whitewash was removed in many churches and the original wall paintings were uncovered (Hermgren, 2001, p.10). The oldest wall paintings in Dalby church are dated to the 13th century and were uncovered during a renovation in 1936. Like most medieval church wall paintings in Sweden, the paintings were produced using the secco technique (Nisbeth, 1980, p.126). In 1936 the 13th century wall paintings were restored by conservator Hans Erlandsson and the reconstruction block painting in red and blue in the belt arch in the east vault, which will be the object of study for this investigation, was added, see figure 7-8 (Eriksson & Wedberg, Åtgärdsprogram för Dalby Kyrka, 2018, p. 10-11). The most recent conservation effort of the interior and wall paintings in the church were in 1978 (Eriksson & Wedberg, Åtgärdsprogram för Dalby Kyrka, 2018, p.5).

Figure 1: Dalby Church, Skåne, Sweden

During the renovations efforts in 1936 a central heating system, which is still used today, was installed in the church. Too efficient heating of churches can cause very low levels of relative humidity during the winter season. However, no continuous measurements of the indoor climate in the church that can provide information about the seasonal variations in temperature and relative humidity has been performed (Eriksson & Wedberg, Åtgärdsprogram för Dalby Kyrka, 2018, p.13). During three days, whilst the experiments of this research study were conducted, the temperature and relative humidity levels were monitored in the immediate vicinity of the study object, see appendix 6.1. The weather outside when the climatic measurements were recorded was clear with a temperature around 5-10°C. Since the measurements recorded are limited to the three days of the experimental study and the day time, they are not representative for the seasonal and diurnal variations that might occur in the church's indoor climate. The measurements taken do provide a small indication of the levels of relative humidity and temperature during the time of the experiments.

1.4.2. Materials and techniques of wall paintings

Generally a wall painting consists of three layers, see illustration 1. These three layers differ in their composition but they mainly consist of calcium carbonate, which was formed through the reaction between calcium hydroxide and carbon dioxide in the presence of water when the wall painting was produced (Chelazzi et.al., 2013, p.43). Originally the belt arch in the eastern vault in Dalby Church, the object of study for this research study, was constructed with these three layers. However since its construction the belt arch has been through several alterations and restorations where the old plaster have been insufficiently removed and new plaster has been added at several occasions. It is necessary to examine the stratigraphy in a wall painting in order to gain understanding about the deterioration mechanisms in the different layers. Such knowledge is vital in order to understand which consolidation measures are required and to anticipate the effects of a conservation treatment (Mecklenburg, Fuster-López & Ottolini, 2012, p.8).

The first and innermost layer, the one applied onto the wall structure of the building, is called the *arriccio*. Apart from the calcium hydroxide, the arriccio layer contains a high amount of sand, which is used as an additive to prevent the rendering shrinking and cracking upon drying. The carbonation of calcium hydroxide without the presence of an additive acting as a filler produces a non-cohesive calcium carbonate substrate (Mora, Mora & Philippot, 1984, p.51). The second layer, called the *intonaco*, contains roughly an equal amount of calcium hydroxide and sand. The third layer, which is the outer layer, is the *paint layer*. The paint layer is a thinner layer and is a mixture of pigments and calcium carbonate (Chelazzi et.al., p.43). The formulation of the rendering of a wall painting is of great importance for the wall painting's stability. If an excess of binding media is used, craquelure and detachment between the support and rendering can occur. If on the other hand an insufficient amount of binder is used loss of cohesion and powdery disintegration can occur (Mora, 1974, p.13).

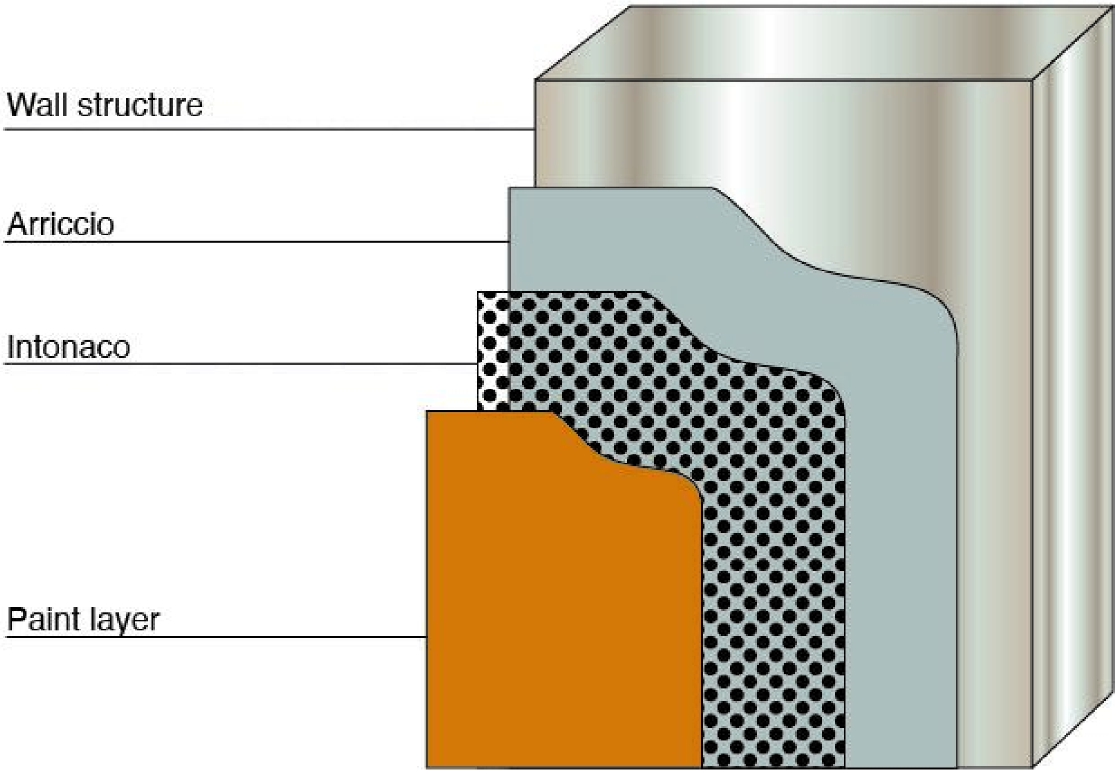


Illustration 1: Stratigraphy of a wall painting

Several different materials have historically been used for the renderings of wall paintings, the most common being lime-based, clay-based and gypsum-based. Gypsum has also historically been used as a fixative added to lime-based mortars to make the mortar more workable. Gypsum is highly soluble in water, which makes it sensitive both to direct contact with water and humidity in the atmosphere. Because of its particular properties gypsum, both as a rendering and as an additive to lime-based renderings, have been almost exclusively used in regions with climates with generally lower levels of relative humidity (Mora, Mora & Philippot, 1984, p.45-46). A rendering containing gypsum can, if exposed to high levels of relative humidity suffer from loss of cohesion in the rendering, which in turn will have detrimental effects for the painted layer (Mora, Mora & Philippot, 1984, p.186). There are several different types of gypsum, containing various amounts of crystallized water, however the common definition for gypsum is that it consists of calcium sulfate (Mora, Mora & Philippot, 1984, p.39).

The painted layer of a wall painting is applied usually with the fresco technique, secco technique or the secco fresco technique. Calcium carbonate, which is the main constituent of most wall paintings, is an alkaline substance and thus pigments used in wall paintings must not be sensitive to alkaline environments (Mora, 1974, p.12). In the secco technique the pigments are executed on the dried intonaco layer. The pigments are mixed with an organic binder that fixates the pigments onto the substrate (Mora, Mora & Philippot, 1984, p.12). This means that unlike in fresco painting, where the pigments are applied while the plaster is still wet and are fixated by the carbonation process of calcium hydroxide forming calcium carbonate, an organic binder may be present in the paint layer in wall paintings executed in the secco technique (Mora, Mora & Philippot, 1984, p. 11). Another technique, which is the one used in the belt arch in Dalby Church, is the secco fresco technique. In the secco fresco technique the pigments are mixed with an aqueous solution of calcium hydroxide, which is commonly called lime-water. They are then applied onto the dry intonaco layer. The lime-water thus acts as the binder and the painted layer is fixated on the substrate through the same carbonation process as in the fresco technique. The distinctive difference between secco fresco technique and fresco technique is that the pigments are not fixated into the plaster of the wall painting in the fresco secco technique, they only react with the lime-water that was used as the binding media ((Mora, Mora & Philippot, 1984, p. 12-13).Wall paintings executed in the secco technique are typically more sensitive to deterioration than those painted in the fresco technique, due to the presence of an organic binding media. Studies have shown that organic materials also have been used as additives to renderings of wall paintings, which means that organic materials may be present in a wall painting even if no organic binder was used for the pigments application (Casadio, Giangualano, & Piqué, 2004, p.63).

Organic materials are generally less resistant to deterioration than inorganic materials, especially in uncontrolled environmental conditions. Therefore it is important to identify any organic materials present in a wall painting before undertaking any conservation efforts. Organic materials can be difficult to detect in wall paintings. Usually a smaller amount of the material is used than in an easel painting, which requires an analytical method with a low minimum detection limit. Another aspect that can hinder the detection of organic materials in wall painting is the fact that wall paintings are exposed to uncontrolled environmental conditions, which can entail the occurrence of various forms of biodeterioration and residues from previous conservation efforts. Such an occurrencd can be misleading in the interpretation of the results of the analysis (Casadio, Giangualano, & Piqué, 2004, p.70).

1.4.3. Deterioration of wall paintings

Inorganic materials are generally more durable than organic materials, however when exposed to uncontrolled environmental conditions, as is the case with wall paintings, even the more resistant materials will gradually deteriorate (Baglioni & Giorgi, 2013, p.345). The outer paint layer of a wall painting is at the interface between the substrate and the ambient environment, which makes it particularly exposed and susceptible to deterioration (Giorgi et.al., 2010, p.9375). The main deterioration problems detected in the belt arch in Dalby Church are loss of cohesion, mainly in the intonaco layer, and loss of adhesion between the pigmented layer and the underlying substrate, see figure 2-4. There are several causes for the deterioration of wall paintings and these usually have a synergistic effect. Particularly important causes for deterioration of wall paintings is exposure to the ambient environment (including atmospheric pollutants), inherent instability of the materials, soluble salts and previous conservation efforts (Mora, 1974, p.11). Chemical processes causing deterioration in wall paintings require the presence of water, making water the universal catalyst for deterioration processes and humidity the single most important cause for the deterioration of wall paintings (Mora, 1974, p.30). Humidity can both initiate and enable many deterioration processes and secondary reactions in synergy with other deterioration causes (Mora, 1974, p.16). Humidity is introduced into wall paintings through various mechanisms, the main ones being capillary action, infiltration and condensation (Mora, 1974, p.31).

Artificial heating in churches through heating systems can contribute to the deterioration of wall paintings. It can cause the formation of soot and dust layers on the surface of the wall painting and it also causes changes in temperature and relative humidity, which in turn will result in the activation of damaging chemical processes (Nisbeth, 1980, p.126). As mentioned in the previous paragraph, water is the foremost cause for the deterioration of wall paintings, which means that the sudden changes in relative humidity and temperature caused by artificial heating can have detrimental effects on wall paintings (Mora, Mora & Philippot, 1984, p.209).

The loss of cohesion within the wall painting structure is a common deterioration problem This is sometimes referred to as chemical corrosion of the wall painting, which entails the deterioration of the binding media in the material, which usually is calcium carbonate (Baglioni & Giorgi, 2006, p.297). Effects of the chemical corrosion within porous structures also include the loss of adhesion between the paint layer and substrate, resulting in flaking of the paint layer (Baglioni, Giorgi & Dei, 2009, p.62). When examining the deterioration of wall paintings it is necessary to understand the difference between *loss of cohesion* and *loss of adhesion.* The term cohesion refers to a material's mechanical properties and ability to develop mechanical strength within itself. The term adhesion refers to a material’s ability to bond to other materials (Mecklenburg, Fuster-López & Ottolini, 2012, p.9). Thus, loss of cohesion in a wall painting refers to deterioration weakening the mechanical strength of the material itself, usually for wall paintings this means the deterioration of calcium carbonate. Loss of adhesion refers to deterioration concerning the weakening of the bonds between two different materials. For wall paintings in the secco technique or the secco fresco technique the loss of adhesion usually occurs between the paint layer and the substrate. In this study, due to the nature of the deterioration problems in the object of study, the forms of consolidation that will be examined are the re-adherence of a flaking paint layer, an effort dealing with the loss of adhesion, and the reinforcement of the pigment layer itself, an effort dealing with the loss of cohesion.

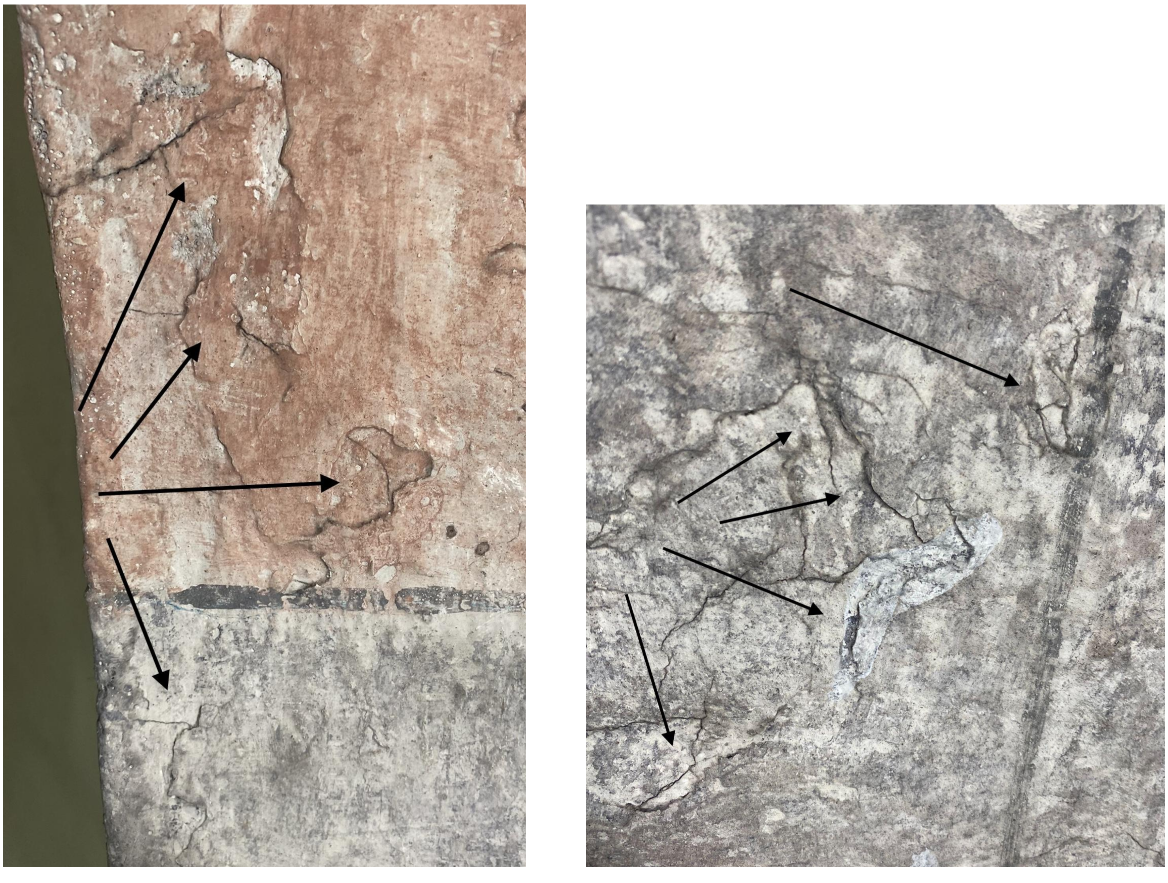


Figure 2 (left): Loss of adhesion between paint layer and substrate (flaking of painted layer) in block painting in belt arch

Figure 3 (right): Loss of adhesion between paint layer and substrate (flaking of painted layer) in block painting in belt arch

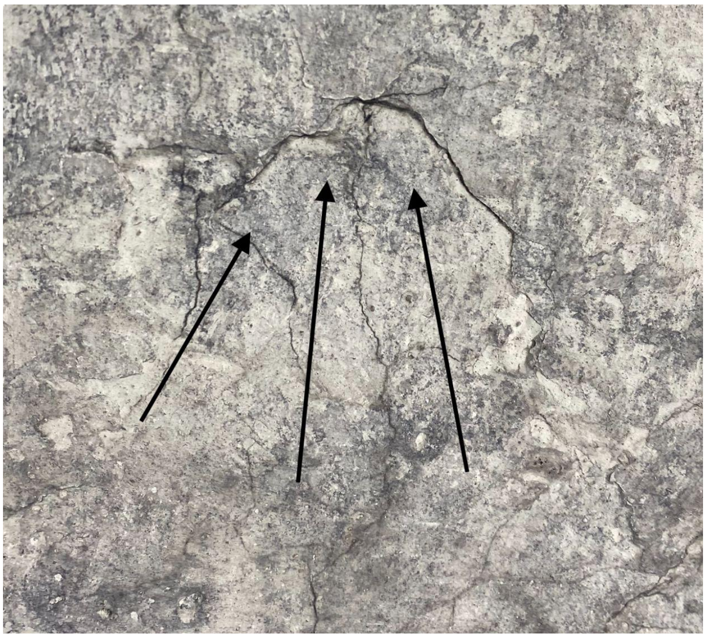


Figure 4 (right): Loss of adhesion between paint layer and substrate (flaking of painted layer) in block painting in belt arch

1.5. Theoretical considerations

The notion of reversibility has since the early 20th century been strongly advocated in the field of conservation of cultural heritage and has been considered one of the most important ethical aspects of any conservation effort. However, during the last twenty years, in connection with the emergence of contemporary conservation theories, the debate concerning the ethics of conservation decisions and treatments have become increasingly critical towards the idea of complete reversibility (Munoz-Vinas, 2005, p.185-186). It has been argued that reversibility in practicality is an unachievable ideal and cultural heritage professionals are now advocating the notion of physico-chemical compatibility with original material as a more realistic aspiration (Baglioni & Giorgi, 2013, p.349). Thus a possible shift from *reversibility* as the characterizing idea of conservation philosophy towards the more pragmatic notion of *compatibility* is arising.

1.5.1. Scientific conservation

During the second part of the 20th century a more rational scientific approach towards conservation was adopted. With the emergence of this scientific methodology, *conservation* was distinguished from *restoration*, previously the two concepts had been used more interchangeably. Conservation came to include material science and knowledge about deterioration processes to a greater extent than previously (Munoz-Vinas, 2005, p.70). The main focus in scientific conservation methodology is the preservation of the physical integrity of an object and according to Munoz-Vinas (2005, p.81) there are two basic principles defining this scientific approach. The first one being the assumption that the integrity of an object is found in its physical material properties. This assumption suggests that an object possesses objective inherent values rather than attributed and ambiguous values. The second basic principle is that conservation methods should be developed according to a scientific methodology (Munos-Vinas, 2005, p.81).

1.5.2. Contemporary Theory of Conservation

Munoz-Vinas (2005, p.78-79) suggests that the scientific conservation methodology is lacking an elaborated theoretical framework and that its emergence in some ways substituted the more theoretical and philosophical debate concerning conservation of cultural heritage. Clavir (2002, p.27) defines ethics as a means to provide a framework to guide actions. Much of the decision-making in conservation practice today is based on scientific and technical examination as well as material science and this scientific and systematic approach is a fundamental part of contemporary conservation practice. However, in the matter of ethical considerations, the scientific conservation methodology does not present any useful contribution (Clavir (2002, p.30). Clavir (2002, p.42) argues that it is equally important to make conservation decisions based upon cultural knowledge as well as scientific knowledge. Contemporary conservation theories have a more nuanced and critical approach towards conservation ethics than many of the classical conservation theories. Classical conservation theories are characterized by objectivism whereas contemporary conservation theory has a more value-based orientation (Munoz-Vinas, 2009, p.69). In contemporary conservation theories it is widely accepted that the values of an object are attributed and subjective rather than intrinsic and absolute. Munoz-Vinas (2009, p.56-57) suggests that any conservation decisions and interventions inevitably will entail a prioritizing and de-prioritizing of the values of an object. Even the decision to abstain from all interventions will result in prioritizing the historical value over the aesthetic value for instance. In the case of wall paintings that are inseparable from the substrate and the built structure to which they belong, the ethical issues become even more complex. All the dimensions of a wall painting must be considered, the painting, the substrate and the built structure (Hemgren, 2001, p.10). A holistic perspective would suggest that a wall painting cannot exist if the built construction or the substrate fails, which would indicate that the conservation of a wall painting on an unstable support would be meaningless. Thus in the case of architectural cultural heritage, including wall paintings, one could argue that the stability of the structure must always be prioritized in order to preserve historical and aesthetic values.

1.5.3. Reversibility and Compatibility

Munoz-Vinas (2005, p.185) defines reversibility as an ethical principle that requires the possibility to return an object to its state before a conservation treatment. Cesare Brandi, whose contributions to the ethical and philosophical discussion of conservation of cultural heritage are still considered to be one of the main conceptual contributions to the field, is a strong advocate for reversibility (Brandi, 2005, p.50). Many of the 19th and 20th century conservation theorists' ideas, including the scientific conservation methodology, are characterized by the basic assumption that an object possesses inherent rather than attributed values (Munoz-Vinas, 2005, p.69). According to Brandi, the ambition of any conservation effort should be the preservation of the aesthetic and historical integrity of an object (Brandi & Basile, 2005, p.43). Brandi (2005, p. 56) is an advocate for reversibility and has expressed criticism towards inorganic consolidation materials. The aspects of inorganic consolidation materials that he is particularly critical towards is the irreversibility and uncontrollability of the consolidation process. Munoz-Vinas (2005, p.185) have suggested that the reversibility of a conservation intervention entails a possible lack of responsibility for the cultural heritage professional performing the conservation treatment. In other words, Munoz-Vinas considers the possibility that relying completely on the reversibility of a conservation treatment can result in a lack of precautionary considerations by the cultural heritage professional. It can be suggested that the advocacy of reversibility within aesthetic conservation theories is a way to ethically justify somewhat invasive restoration efforts enforced to preserve what is considered to be the aesthetic integrity of works of art.

As mentioned, the notion of reversibility has shaped the conservation discourse since the second part of the 20th century. One of the reasons for this strong advocacy for reversibility is the fact that it is impossible to predict the long-term effect of a conservation material. Using conservation materials that have not been tested by real time aging will always imply a risk and it is impossible to guarantee its durability (Munoz-Vinas, 2005, p.184-185). In contemporary conservation theories the idea of reversibility has been criticized for being an impossible ideal. Chemical processes are constantly occurring within materials, which inevitably will entail changes in the material properties of an object and of the conservation material used (Munoz-Vinas, 2005, p.186). One might argue that this fact makes it as impossible to predict the reversibility of a conservation material as it is to predict the real-time aging of conservation materials, which is one of the main arguments in favor of reversibility. In contemporary conservation theories the idea of reversibility is being replaced by the more realistic notions of removability and retreatability (Munoz-Vinas, 2005, p.187).

Scientists Baglioni, Dei and Giorgi, who have conducted a great deal of research in the area of how inorganic nano-materials can be used for the conservation of cultural heritage, stress that complete reversibility does not exist (Baglioni, Dei & Giorgi, 2009, p.63). They advocate that the aim of a conservation treatment should be to use materials that largely have the same physical and chemical behavior as the original material. Physico-chemical compatibility has been suggested as an alternative ethical principle to reversibility (Baglioni & Giorgi, 2013, p.349). A high degree of physico-chemical compatibility with the original material will allow the conservation material to deteriorate through similar processes as the original material. Since it can be considered impossible to predict the aging of conservation materials, the idea of compatibility might be a favorable alternative. If a conservation material has a high physico-chemical compatibility with the original material, the prediction of its possible alterations is not as important since any alterations will occur harmoniously with the original material. Compatibility might be especially advantageous for architectural cultural heritage and in-situ objects where preventative conservation is difficult and artificial aging often unreliable. For cultural heritage situated in uncontrollable environmental conditions it is especially important to ensure that materials introduced to an object during conservation will deteriorate in a manner not harmful to the object. Thus a major argument for the use of physico-chemical compatible conservation materials is that it reduces the risk of unforeseen detrimental long-term effects (Baglioni & Giorgi, 2013, p.351).

1.6. Method

The research questions were investigated theoretically through a literary study and practically through an experimental study. The study will have an exploratory systematic approach in which deductive reasoning based on scientific evidence will be applied (Clavir, 2002, p.40). The analytical methods used in the experimental study were visual examination, tapping-sound testing, optical microscopy, X-ray fluorescence and Fourier Transform Infrared Spectroscopy. Tapping-sound testing was used in order to investigate the consolidation effects after treatment that could not be examined through surface examination. Optical microscopy was used as a complement to visual examination to examine the effects of the consolidation treatment and detect any alterations to the surface. Fourier Transform Infrared Spectroscopy is used to identify elements and was used in this research study for the detection of possible organic materials present in the wall painting. The possible occurrence of an organic binder present in the block painting in the belt arch would be useful in determining if the wall painting were executed in the secco technique, in which case an organic binder would be present, or if it was executed in the fresco secco technique, in which case no organic material should be detected. X-ray fluorescence provides both a quantitative and qualitative indication of elements present in the sample and was used mainly for identification of pigments.

1.6.1. Optical microscopy

The surface areas of the wall painting that was to be treated was examined through optical microscopy before and after the treatment with the commercial nano-lime products as well as in between the three applications. The optical microscopy used was the Dino-Lite EDGE with a resolution of 5 megapixels.

1.6.2. X-ray fluorescence

X-ray fluorescence (XRF) is an analytical investigative technique that can be used to obtain information about the elemental composition of a material. It is a qualitative and quantitative method, which means that it is possible to gain information both about the elements present in a material and in which quantity (Stuart, 2007, p.234). The analytical instrument can be used for a wide range of materials including wall paintings. XRF is frequently used for the identification of inorganic pigments in paintings, many pigments are possible to identify through the presence of one or two elements that are detectable with the XRF (Stuart, 2007, p.240). The XRF cannot detect elements lighter than sodium, this is because the fluorescent signal emitted from lighter elements is not strong enough to be detected by the instrument (Stuart, 2007, p.236). The principle of X-ray fluorescence is that the sample is placed in a high energy beam of photons, which are produced by an X-ray tube. The atoms in the sample absorb the radiation and become excited, meaning that their electrons are in a higher energy state than in the ground state. An excited atom is unstable and as the atom returns its more stable state it releases energy, which is emitted in the form of radiation. Since each element has a particular set of energy levels, the emitted radiation will have unique characteristics (Stuart, 2007, p.234). There are two main types of XRF spectrometers. There is the wavelength dispersive spectrometer (WDXRF), which measures the wavelengths of the fluorescence radiation emitted, and there is the energy dispersive spectrometer (EDXRF), which measures the energy of the fluorescence radiation emitted (Stuart, 2007, p.236). In this study an energy dispersive spectrometer will be used. Usually XRF is used as a non-destructive analytical method since sampling is not required. However in this paper, the samples that were acquired for the FTIR-analysis, which is a destructive analytical method that requires sampling, were used for the XRF-analysis. The instrument used in this study is the Bruker ELIO Portable Micro X-ray Fluorescence Spectrometer.

1.6.3. Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is a commonly used infrared spectroscopy analytical technique. FTIR is primarily a qualitative analytical method that is used to understand the molecular composition of materials (Stuart, 2007, p.117). An advantage of the FTIR is that it detects both organic and inorganic materials. When examining a wall painting, pigments, binders and other additives may all be identified. However, all inorganic pigments can not be detected in the mid-infrared radiation region, which is used in FTIR-analysis, this includes metal oxides and sulfides (Stuart, 2007, p.126). The basic principle of infrared spectroscopy is the measurement of vibrations of atoms within a molecule. Since the different bonds in a molecule vibrate at different energies they will absorb different wavelengths of the infrared radiation. The specific frequencies at which the radiation is absorbed by the sample is correlated to the vibrational bond energies between the atoms within a molecule (Stuart, 2007, p.110). The infrared radiation passes through the sample and is absorbed by the sample. The energy from the radiation causes vibrations to occur of specific atomic bonds in the molecule. Some of the radiation is reflected back but most is absorbed and transmitted through the sample. The absorbed energy carries the molecular information and is transmitted to a detector. In FTIR the radiation is passed through an interferometer before passing through the sample and then reaching the detector (Stuart, 2007, p.110-111). The frequency and intensity of the vibrations transmitted to the detector is convertible through the mathematical method of Fourier Transformation, which creates a spectra characteristic to each molecule (Stuart, 2007, p.111). The spectra produced from an analysis can then be compared to spectras in a database with FTIR-spectrums to find a match and thus identify the elements of the analyzed sample. The instrument used in this study was Bruker ALPHA-R med Platinum-ATR and triclyceringsulfate-detector settings that measured the emitted radiation in the range 4000-400 cm-1.

1.7. Research overview

There is a substantial amount of literature that discusses the use of nanotechnology in the conservation of cultural heritage. Since the emergence of nanotechnology into the field of cultural heritage around the turn of the millenia there has been great development within the research field and several case studies examining nanoparticles of alkaline earth-metals dispersed in short-chained alcohols and their consolidation effects on wall paintings have been published. However a considerable amount of the research published is authored by mostly the same scientists. Moreover most of the case studies have been performed in either climates with generally high levels of relative humidity and temperature, research investigating the effects of nano-lime in a Scandinavian climate have not been found.

1.7.1. Inorganic nanomaterials for the consolidation of wall paintings

A large portion of the research of inorganic nanomaterials as conservation materials for cultural heritage published in the last twenty years have been contributed by italian chemists Piero Baglioni and Rodorico Giorgi at the University of Florence at the Department of Chemistry and Center for Colloids and Surface Science. (Baglioni & Giorgi, 2006). In the article "Nanomaterials in art conservation", an overview report of the use of nanotechnology for conservation of cultural heritage is presented. The article accounts briefly for different types of nanomaterials and their potential use as conservation treatments for different materials, including wall paintings (Baglioni, Carretti & Chelazzi, 2015). Nanomaterials are presented as an environmentally sustainable material for conservation with a high physico-chemical compatibility with the original materials (Baglioni, Carretti & Chelazzi, 2015, p.287). Nanomaterials are showing great potential within the field of conservation of cultural heritage and have demonstrated successful results as conservation treatments for different materials.

As well as the publication of many scientific articles and case studies, Baglioni and Giorgi authored and edited the book "Nanoscience for the conservation of works of art" (2013), which have become one of the most influential publications for the use of nanotechnologies in conservation of cultural heritage. The reduction in particle size in one or several dimensions gives nanomaterials their particular properties (Bonnini, Baglioni & Chelazzi, 2013, p.316-318). These alterations in the chemical properties are fundamental for the possibility to use nanomaterials for conservation purposes. In some regards calcium hydroxide is an ideal material for the consolidation of wall paintings since it has a high physico-chemical compatibility with the original material (calcium hydroxide is the original binding media in many wall paintings). High compatibility between conservation and original material favor homogeneous degradation, avoiding causing localized mechanical stress in the material as well as reducing the risks of unforeseen harmful long-term effects. It has however been ineffective to use calcium hydroxide as a consolidant for wall paintings due to the low solubility of calcium hydroxide in water (Baglioni & Giorgi, 2013, p.350). Baglioni, Dei & Giorgi first addressed this problem in an article published in 2000. The problem with calciumhydroxide particles dispersed in water as a consolidation treatment for wall paintings is the low solubility of calcium hydroxide in water, which means that the concentration of the active substance calciumhydroxide will be too low for it to be effective as a consolidant. The other main issue is that suspensions of calciumhydroxide in water is kinetically unstable and forms aggregates, which makes it unable to be applied to a wall painting (Giorgi, Dei & Baglioni, 2000, p.154). The reduction of calcium hydroxide particles to nano-size increases the solubility making it possible to retain a concentration sufficient enough for consolidation purposes. Moreover, instead of using water as the carrier media for the calciumhydroxide nanoparticles it was shown that suspended in short-chained alcohols a kinetically stable dispersion was created (Baglioni & Giorgi, 2013, p.354).

The article “A new method for consolidation of wall paintings based on dispersions of lime in alcohol” (Giorgi, Dei & Baglioni) published in 2000 is an important predecessor for the development of dispersions of calcium hydroxide nanoparticles used for the consolidation of wall paintings. It is one of the research studies that the effects of a reduction in particle size for calcium hydroxide was recorded, which became an important step in the development towards dispersions of calcium hydroxide nanoparticles in short-chained alcohols that could be used for the consolidation of wall paintings. Dispersions of calcium hydroxide in short-chained alcohols are examined as a potential new consolidation treatment för wall paintings. The high physico-chemical compatibility of calcium hydroxide is highlighted as a major advantage of dispersions of calcium hydroxide particles as a consolidation material (Giorgi, Dei & Baglioni, 2000, p.155). This high physico-chemical compatibility with the original material is also stated as one of the most important aspects of dispersions of calcium hydroxide particles by other authors Chelazzi et.al (2013), Di Gregorio (2012) and Girginova et.al. (2018). The first part of the study examines the stability of calciumhydroxide particles in a dispersion of propanol and the second part of the study examines and evaluates the effectiveness of the dispersion as a consolidation treatment for wall paintings. The results demonstrate that the dispersion of calciumhydroxide in propanol is stable and therefore applicable to the wall painting. The results also show good consolidation effects from the treatment with an increased cohesion and compactness in the wall painting (Giorgi, Dei & Baglioni, 2000, p.156-158).

1.7.2. Commercial nanolime-based consolidants

In 2017, Pondelak et.al. performed an in-situ comparative study that examined the consolidations effects of three different commercial conservation products used for consolidation of wall paintings. Two of these three were nano-lime products Nanorestore® and CaLoSiL, the third product examined in the study was not a nanomaterial. The wall paintings being investigated in the study are executed in the fresco technique and dated to the 1930s (Pondelak, et.al., 2017, p.1). The authors argue that there is a lack of research studies investigating the effects of nano-lime consolidation products in-situ using methods other than visual examination. A distinguishing feature of this study is the use of technical analysis methods in-situ. Possible alterations in the aesthetic appearance were measured through spectrophotometry and visual examination. Consolidation effects were examined through ultrasound velocity, surface hardness and DRMS (drilling resistance measurements) (Pondelak et.al., 2017, p.1-2). Both of the nano-lime products showed inferior results both in regards to consolidation effects and aesthetic alterations compared to the third product, which was a calcium acetoacetate-based product dispersed in water (CFW) (Pondelak et.al., 2017, p.1).

1.7.3. The influence of environmental conditions on consolidations treatments using nanolime-based consolidation treatments

A majority of the research studies examining the effects on nanolime on wall paintings are performed in-situ, which makes it very difficult to achieve control over climatic conditions. Di Gregorio (2010) performed a laboratory study where the effects of the commercial nanolime product, Nanorestore®, was examined in controlled climatic conditions. The results of the study shows that a higher level of relative humidity decelerate the carbonation process, which favorably affects the consolidation treatment by allowing the calcium hydroxide nanoparticles sufficient time to penetrate the substrate, which prevents the formation of a white haze on the painted surface (Di Gregorio, 2012, p.3). Chelazzi et.al. (2013) and Girginova et.al. (2018) gives prominence to the ambient climatic conditions as a major influencing factor for the consolidation effects of nano-lime. Suggested as the most influential environmental factors by Giorgi et.al. (2010, p.9377) are relative humidity levels, the carbon dioxide concentration and the permeability of the wall painting. Baglioni et.al. (2014, p.724-725) examines the consolidation effects of Nanorestore® in different levels of relative humidity in which the results indicate a significant influence of different relative humidity conditions. Higher levels of relative humidity (75-90%) generate a faster carbonation process, creating larger particles of calcium carbonate and a higher crystallinity whereas lower levels of relative humidity (33-54%) results in a slower carbonation process and a smaller particle size and lower crystallinity (Baglioni et.al., 2014, p.725).

1.8. Limitations

The study will be limited to investigating the effects of commercial nano-lime products Nanorestore® and Nanorestore Plus® used in a Scandinavian climate with generally low temperatures and levels of relative humidity. The results of this study will not be applicable for wall paintings in different climates. As mentioned by Mora et.al. in *Conservation of Wall paintings* (1984, p.39) different materials and different compositions of materials have been used historically for the renderings of wall paintings. The different materials used for the renderings have often been correlated to the environmental conditions. The properties of the material and the chemical composition of the object of study will shape the orientation of the investigation. The study will be limited to examining wall paintings with a lime-based rendering where gypsum has been used as an additive. The study will also be limited to investigating the effects of the commercial nano-lime products on wall paintings executed in the secco fresco technique.

A common deterioration problem for wall paintings is the presence of soluble salts. In wall paintings with high amounts of salts the use of calcium hydroxide as a consolidation material can be problematic. The calcium hydroxide can react with the salts present and form other compounds with poor consolidating abilities, weakening the wall painting. For wall paintings contaminated with sulfates the Ferroni-Dini-Method may be a more suitable choice for consolidation and desalination (Baglioni & Giorgi, 2013, p.359). In the wall paintings in Dalby Church high amounts of salts have not been encountered. Thus the effects of nano–lime on wall paintings with high amounts of salts present will not be examined in this study.

There are several other inorganic nano-products used for the consolidation of wall paintings, such as other hydroxides of alkaline earth-metals and silica-based inorganic nanocomposites

(Girginova et.al., 2018). These will not be considered in this investigation. The study will also be limited to the commercial nano-lime products Nanorestore Plus® and Nanorestore®, other commercial nano-lime products available on the market will not be considered.

Depending on the deterioration in a wall painting there are different types of consolidation that may be required. In the case of degradation of the rendering more in-depth consolidation is desirable and a consolidation method with sufficient penetration ability is necessary (Giorgi, Dei & Baglioni, 2000, p.154). Due to the character of the deterioration problems in the object of study a more superficial consolidation is what will be dealt with in this paper. Examination of the effects regarding more in-depth consolidation with the use of nano-lime will not be included.

There are several different application methods commonly used when applying dispersions of nano-lime including brushing, spraying and injection. Which application method that is suitable depends on the properties of the material being treated as well as the character of the deterioration. Since the aim of the experimental study is a superficial consolidation the application technique used will be brushing. Thus the results and conclusions of this paper will be representative only for this application method.

2. Theoretical study

2.1. Requirements for consolidation materials

Wall paintings have several characteristics that distinguish them from other forms of painting. Wall paintings are inescapably linked with the architecture on which they exist, which entails that the whole built structure and the indoor environment of the building must be taken into consideration when undertaking any form of conservation effort. (Mora, Mora & Philippot, 1984,, p.7). General demands for a conservation treatment is that the conservation material used is durable, chemically inert, compatible with the original material and reversible (Baglioni, Giorgi & Dei, 2009, p.63). A high physico-chemical compatibility with the original material implies that the conservation material used will not alter structural or aesthetic properties of the original material significantly (Giorgi, Dei & Baglioni, 2000, p.154). There are different forms of consolidation and different consolidation materials may be more or less suitable depending on specific deterioration problems (Mora, Mora & Philippot, 1984, p.216). A flaking paint layer is an indication of a loss of adhesion between the paint layer and substrate, which requires a consolidation material with sufficient adhesive properties and the ability to re-adhere the paint layer to the substrate. A powdering paint layer indicates a loss of binder and an internal de-cohesion of the paint layer itself and is thus a problem of loss of cohesion. When dealing with the loss of cohesion consolidation materials with sufficient cohesive and penetration abilities are necessary. (Giorgi, Dei & Baglioni, 2000, p.154). Requirements for an efficient and suitable consolidation material used in the conservation of wall paintings is a high degree of compatibility with the original material, reinforcement of mechanical and physical properties of the wall painting, sufficient penetration ability and that it does not cause alterations in the aesthetic appearance of the wall painting (Girginova, 2018, p.4169). Insufficient penetration of a consolidation material will diminish the consolidation effects and it is possible that a film forms on the surface, changing the aesthetic appearance of the wall painting (Mora, Mora & Philippot, 1984, et.al., p.218). Physico-chemical penetration parameters that should be considered when examining a consolidation material for wall paintings is the particle size, smaller particles generally penetrate deeper into porous materials, and the evaporation rate of the carrier medium (Mora, Mora & Philippot, 1984, p.219). Other factors to consider are the durability of a consolidation material, it is vital that the material used can withstand environmental changes (Chelazzi et.al., 2013, p.42). This is especially important regarding materials used for in-situ conservation, which must be resistant to lengthy periods of exposure to the ambient environment and atmospheric pollutants (Mora, Mora, Philippot, 1984, p.221).

2.2. Properties of nanomaterials

The definition of a nanomaterial is a material that has one or more structures within the dimension of the nanometre scale, which is one billionth of a meter. Unlike materials with dimensions in the micrometer scale, which generally have the same properties as in bulk form, the properties of nanomaterials are different from the same material in bulk form (Cao & Wang, 2011, p.1-3). Nanomaterials gain these properties due to their nanosize structure. The reduction in particle size gives an increased proportion of surface atoms to the structure, which alters the chemical properties of the material, significantly enhancing the chemical reactivity of the material (Baglioni & Giorgi, 2013, p.316-318). Other properties of nanomaterials are a lower melting point, increased solubility and change in thermal stability (greater stability at lower temperatures) (Cao & Wang, 2011, p.2).

Since around the turn of the millenia nanostructured calcium hydroxide, also referred to as nano-lime, have been used for the consolidation of wall paintings. The nanoparticles penetrate the porous material and react with the atmospheric carbon dioxide in the presence of water and form calcium carbonate. The formed calcium carbonate reinforces the carbonatic matrix of the original material and stabilizes the wall painting (Baglioni, Caretti & Chelazzi, 2015, p.289). Historically, conservators in Sweden, unlike in countries in southern Europe where they commonly used oil or wax, used lime-water for the stabilization of wall paintings (Nisbeth, 2001, p.126). Although lime water has a high compatibility with the original material there are several factors limiting the effectiveness of lime-water as a consolidation material for wall paintings. The two main problems being the low solubility of calcium hydroxide in water and its instability suspended in water. Due to the low solubility, saturated solutions of calcium hydroxide suspended in water are too weak to effectively consolidate a wall painting. The instability of suspensions of calcium hydroxide in water makes it very difficult to apply to painted surfaces (Giorgi, Dei & Baglioni, 2000, p.154). The issue of unstable dispersions of calcium hydroxide in water have been resolved by instead using short-chained alcohols as dispersing agents, which have shown to be suitable for alkaline earth-metals hydroxide nanoparticles. Commonly used are ethanol, propanol and isopropanol (Chelazzi et.al., 2013, p.45). The short-chained alcohols prevent the nanoparticles from forming aggregates in aqueous solution, allowing them to form kinetically stable dispersions (Baglioni & Giorgi, 2013, p.354). It has also been shown that dispersions of calcium hydroxide in propanol with a smaller particle size has an increased stability compared to dispersions of calcium hydroxide in propanol with a larger particle size. (Giorgi, Dei & Baglioni, 2000, p.156-158). The alcohol used as a carrier medium must not be too volatile since a too fast evaporation will prevent the nanoparticles from penetrating the porous material, which can cause the formation of a white haze on the surface (Chelazzi et.al., 2013, p.45).

The reduction in particle size is fundamental in making it possible to effectively use dispersions of calcium hydroxide as a consolidation material for wall paintings. The reduced particle size increases the solubility of calcium hydroxide making it possible to create a more concentrated solution. The reduced particle size also increases the reactivity of the material generating greater penetration into the porous material of the wall painting (Chelazzi et.al., 2013, p.43). Thus the combination of using a short-chained alcohol as the dispersing agent and the reduction of particle size gives calcium hydroxide favorable properties to be used as a consolidation material for wall paintings.

2.3. Compatibility with original material

During the 20th century synthetic polymers were commonly used as a consolidation material for wall paintings in Europe. There have been cases where the use of synthetic polymers have shown to have damaging long-term effects for the original material of the wall painting. These synthetic materials are organic, which entails a poor physico-chemical compatibility between the conservation material and original material, which has proven to have detrimental effects for wall paintings in some cases (Chelazzi et.al., 2013, p.43). In a controlled environment synthetic polymers have been used with successful results, however in an uncontrolled environment they have shown to have a low durability making them an unsuitable conservation material for wall paintings. On an historical site in Mexico some of the wall paintings had been treated with the synthetic polymer Paraloid B72 in previous restoration efforts and others with inorganic consolidation materials. The wall paintings that had been treated with synthetic polymers showed a significantly more severe degradation than those treated with inorganic conservation materials (Baglioni, Giorgi & Dei, 2009, p.65-66). Some of the more important negative effects that have been reported for traditional organic consolidation materials, such as synthetic polymers, are their low durability. With time they undergo chemical alterations, which makes them insoluble and very difficult to remove. Furthermore some synthetic polymers have been prone to change appearance upon aging, affecting the aesthetic appearance of the wall painting (Baglioni, Giorgi & Dei, 2009, p.69).

Inorganic consolidation materials have a higher physico-chemical compatibility with the original material of wall paintings as well as being more durable and resistant to chemical alterations upon aging (Mora, Mora & Philippot, 1984, p.224-226). Since calcium hydroxide is the original binding media used in the production of many wall paintings nano-lime has a high physico-chemical compatibility with the original material. In the book *Conservation of Wall Paintings* by Mora et.al. the following quote is found commentating the importance of a high degree of physico-chemical compatibility between the consolidation material and original material:

> Because the permanent fixative must remain in contact with the original materials of which the work is composed, there must be the strongest guarantees of its durability and it must be easily removable if desired or else age in a way that it disintegrates without causing alterations in the paint layer. (Mora, Mora & Philippot, 1984, p.216-217).

One of the most important advantages of using a consolidation material with a high physico-chemical compatibility is that the conservation material will deteriorate through similar processes as the original material. This entails a homogeneous deterioration throughout the material and avoids localized stress in the structure (Giorgi et.al, 2010, p.9381). A significant disadvantage with inorganic consolidation materials, including nano-lime, is the difficulty in controlling the consolidation process, which can be an argument for nano-lime being an unreliable conservation material. Other negative aspects of inorganic consolidation materials is that they can be time-consuming, requiring many applications, and that they are very difficult to remove, which practically makes them irreversible. In some cases the consolidation process has been reported to form unwanted residual products, this should however not be a concern when using dispersions of nanoparticles of calcium hydroxide on wall paintings that do not contain high concentrations of salts (Mora, Mora & Philippot, 1984, p.226).

2.4. Influence of environmental conditions and application technique

The ambient environment is always an important aspect of any conservation effort, it is however an even more decisive factor when working with in-situ conservation as with wall paintings. The basic principle of using dispersions of nanoparticles of calcium hydroxide is the formation of calcium carbonate, which is the main constituent of many wall paintings. This is referred to as the carbonation process, which is the same process through which the original material was formed. Through this carbonation process a crystalline network of calcium carbonate is formed, which increases the cohesion and reproduces the mechanical properties of the original material (Baglioni & Giorgi, 2013, p.354). Water and carbon dioxide are necessary components for the carbonation process to occur. Atmospheric carbon dioxide reacts with the calcium hydroxide in the presence of water, the carbon dioxide can only react with the calcium hydroxide dissolved in water as carbonic acid (D'Armada & Hirst, 2012, p.76). After the application of the dispersion of nanoparticles of calcium hydroxide the carrier medium (short-chained alcohol) evaporates as the nanoparticles penetrate the substrate. The calcium hydroxide then reacts with the atmospheric carbon dioxide, which has formed carbonic acid through a reaction with the water present in the wall painting. The reaction between the calcium hydroxide particles and the carbonic acid forms calcium carbonate and water vapor, see reaction formula below (Girginova et.al., 2018, p.4171). Thus the consolidating ability of nano-lime is highly dependent upon the climatic conditions in which the carbonation process takes place. The amount of carbon dioxide present in the ambient environment as well as the levels of relative humidity will have a significant impact on the carbonation process. (Baglioni, Caretti & Chelazzi, 2015, p.289).

Calcium hydroxide + (Water + Carbon dioxide) (forming carbonic acid) → Calcium carbonate + Water

$$Ca(OH)_2 + H_2O + CO_2\ (g)\ \text{--------->}\ CaCO_3 + H_2O\ (g)$$

The carbonation process is influenced by several different factors; climatic conditions, particle size, carrier medium characteristics (Baglioni et.al., 2014, p.726), carbon dioxide concentration and permeability of the mortar. The environmental conditions thus have a great influence in regards to the carbonation process, the most important influencing factor being the relative humidity levels (Giorgi et.al., 2010, p.9377). Research studies that have examined the use of commercial nano-lime product Nanorestore® suggests that higher levels of relative humidity (75-90%) results in an increase in carbonation of the calcium hydroxide particles and that lower levels of relative humidity (33-54%) results in a lower degree of carbonation (Baglioni et.al., 2014, p.724-725). This suggests that nano-lime as a consolidation material may be less effective in a Scandinavian climate with generally lower levels of relative humidity. This indication makes it necessary to adjust the guidelines for the use of nano-lime in drier climates compared to environments with higher levels of relative humidity. It is probable, due to the generally lower levels of relative humidity commonly encountered in churches in Scandinavia, that different requirements in regards to the application method of nano-lime are necessary.

Aspects of the application that affect the carbonation process and thus the consolidation effect include the concentration of the dispersion of nanoparticles, number of applications, time intervals between the applications and the amount of nano-lime applied as well as application technique used (Girginova et.al., 2018, p.4172). Research studies indicate that several applications are required to achieve the desired consolidating effect and that several applications with a lower particle concentration are more effective than a single application with a higher particle concentration (Baglioni & Giorgi, 2013, p.361). The most commonly used application techniques for nano-lime are injection, brushing and spraying. Which of these application techniques are appropriate depends on the condition of the substrate, the constituents of the rendering, what type of consolidation that is required as well as on the environmental conditions. The application technique used in the experimental study of this research paper will be brushing. The dispersion of nano-lime is applied using a brush onto the area that is to be treated through a veil of Japanese paper, which protects the surface of the wall painting and allows a homogeneous distribution of the nanoparticles into the surface layers (Baglioni & Giorgi, 2013, p.361). Since the relative humidity levels in Dalby Church, where the experiments are performed, are quite low a cotton compress hydrated with deionized water was applied onto the Japanese paper saturated with nano-lime. The hydrated compress should slow down the evaporation process of the carrier medium, allowing the nanoparticles to sufficiently penetrate the substrate before carbonating (Baglioni & Giorgi, 2013, p.725).

2.5. Commercial nanolime products

Two of the commercial nano-lime products available on the market today is Nanorestore® and Nanorestore Plus®. Both products are developed and patented by the Consorzio Center of Colloid and Surface Science at the University of Florence, Italy. These products, which are commonly referred to as nano-limes, are formulations composed of calcium hydroxide nanoparticles dispersed in short-chain alcohols. The average diameter particle size in nano-limes is between 50-300 nm, calcium hydroxide particles in bulk form have an average particle diameter of 8000 nm (D'armada & Hirst, 2012, p.321). Nanorestore® was developed in the end of the 1900s and was one of the early nano-lime products available on the market (Baglioni & Girogi, 2013, p.354). Nanorestore® is dispersed in isopropanol and the calcium hydroxide particles have an average particle size of 250 nm (Baglioni et.al., 2014, p.725). Nanorestore Plus® was developed later and is available in a range of formulations with different dispersing media at different concentrations. The formulation used in this study was the Nanorestore Plus® Ethanol 10. R. Giorgi (personal communication, 21st of april 2023), MD in Chemistry and PhD in Conservation Science at the University of Florence, states that the main difference between Nanorestore® and Nanorestore Plus® is the average particle size, which in Nanorestore Plus® is around 30% smaller than in the nanoparticles in Nanorestore®. Another difference is the particle size distribution, which is narrower for Nanorestore Plus®.

3. Experimental study

3.1. Object of study

The experimental study is centered around a wall painting in Dalby church. The object of study is specifically the pointed belt arch in the eastern vault, see figure 5-8. The reconstructed block painting in the belt arch was added in conjunction with the restoration carried out in 1936. When medieval wall paintings were restored during the 20th century it often included extensive retouching and reconstructive painting (Nisbeth, 2001, p.16). The red and blue block painting is executed in the secco fresco technique, which is a common technique used in medieval wall paintings in Swedish churches. It is probable that the conservator performing the reconstruction painting aspired to use traditional techniques and materials for the reconstruction painting. Additional layers of plasters have been applied onto the original plaster without the complete removal of the older plaster, thus the substrate consists of several different plasters applied at different instances.

The overall and most prominent deterioration problems in the 1930s block painting is loss of cohesion within the material, probably in the intonaco layer, and loss of adhesion between substrate and painted layer, see illustration 2 & 3. A possible cause for this type of deterioration are generally low levels of relative humidity at the time of production of the wall painting. In dryer climates adsorption is the active mechanism and only a few separate layers can be bound. However in climates with generally higher relative humidity capillary action mechanisms are active making it possible for more of the layers to bind together, which provides a stronger adhesion between substrate and painted layer (Skånes Målerikonservatorer, 2018, p.14). Overall on the surface craquelure occurs, however some of these cracks appear stable, which indicate that they occurred in correlation with the drying process when the wall painting was produced. Such craquelure does not necessarily indicate poor cohesion within the material (Skånes Målerikonservatorer, 2018, p.15)

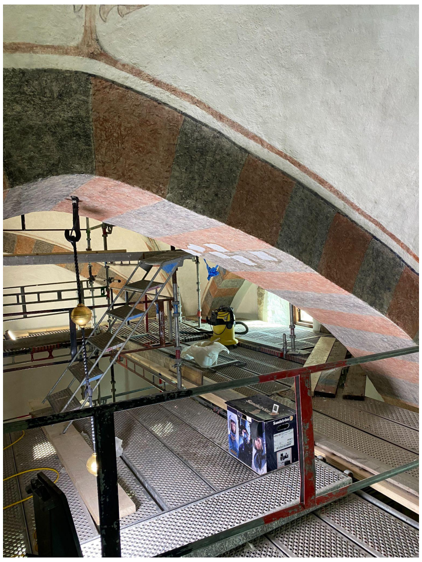


Figure 5 (left): Pointed belt arch Figure 6 (right): Pointed belt arch

Figure 7 (left): Research object: Red wall painting in belt arch
Figure 8 (right): Research object: Blue wall painting in belt arch

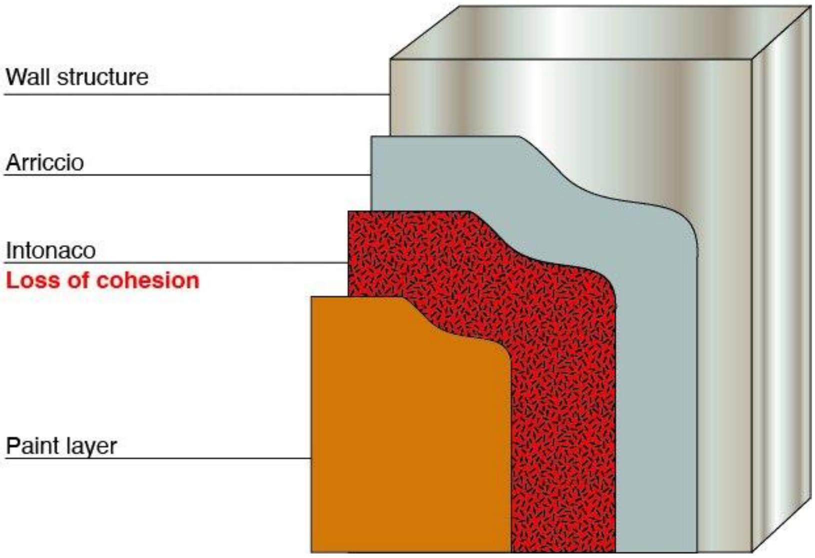


Illustration 2: Loss of cohesion in the intonaco layer of wall painting.

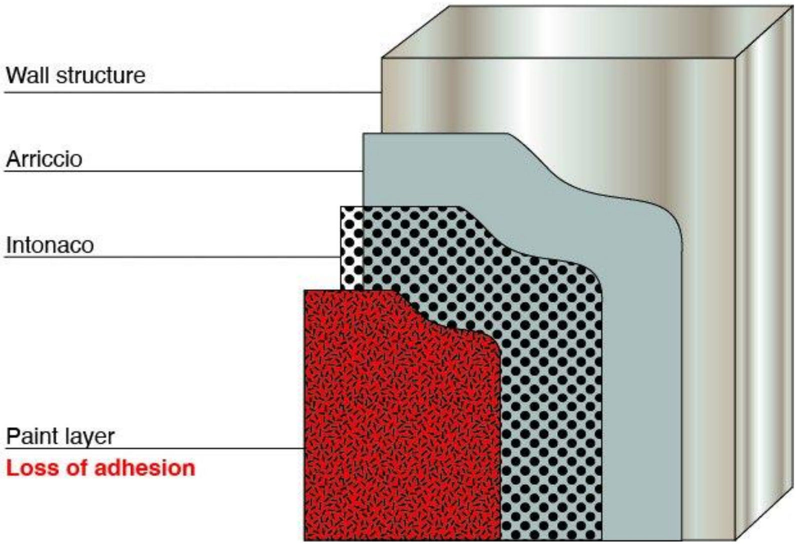


Illustration 3: Loss of adhesion in the paint layer of wall painting

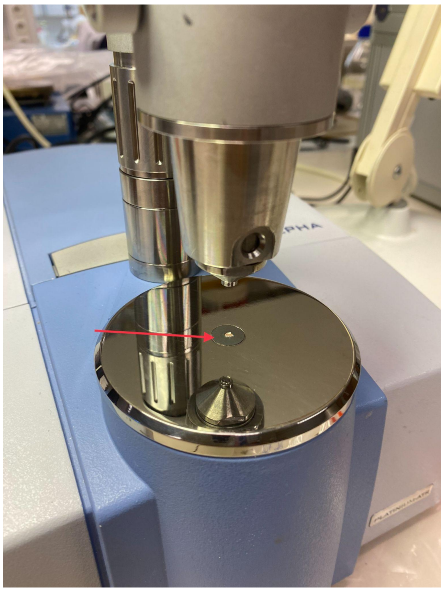
3.2. Analytical investigations

3.2.1. Fourier Transform Infrared Spectroscopy

Analysis were performed on samples taken from the blue respectively the red wall painting in the belt arch. Analysis was carried out on both the front side (the pigmented side) and the backside of the samples. Before the sample is placed in the FTIR-instrument, all equipment and the instrument is cleaned with ethanol. The sample is then placed in the instrument, see figure 9, and then the handle is folded down, see figure 10, and the analysis can be performed. To avoid detecting atmospheric substances in the analysis an initial measurement is performed without a sample present, which will create a single channel reference spectra. The next spectra will be with the sample and will be a single channel spectra. The sample spectrum is then divided by the reference spectrum, which creates the transmission spectra (Stuart, 2007, p.110).

Three analyzes were performed on two samples taken from the blue wall painting in the belt arch, named in this research study as *Sample Blue 1* and *Sample Blue 2.* An initial analysis was made on the front side of *Sample Blue 1* and another analysis was performed on the front side of *Sample Blue 2* to be used as a reference. The third analysis was performed on the backside of *Sample Blue 2.*

For analysis of the red wall painting four analyzes were performed on three different samples, named in this research study *Sample Red 1, Sample Red 2* and *Sample Red 3.* Analysis of the front side of *Sample Red 1* and *Sample Red 2* were performed and as with the blue samples, two analyses were performed on two different samples so one could be used as a reference. Two more analyses were performed, one on the backside of *Sample Red 2* and one on the backside of *Sample Red 3* The reason for two analyses being performed on the backside of different samples was that the backside of the two samples had different appearances, one being more gray in colour and the other more white.



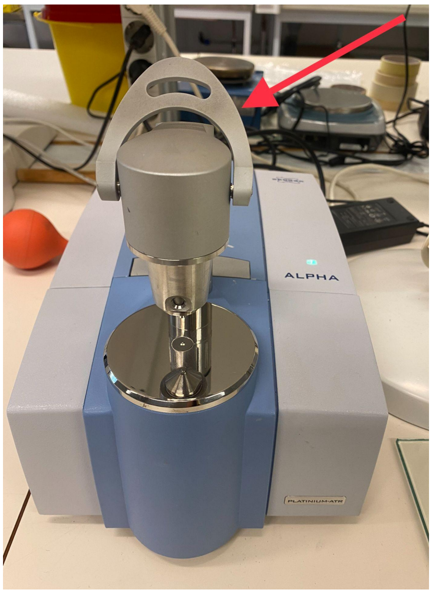


Figure 9 (left): FTIR-instrument: sampling area
Figure 10 (right): FTIR-instrument

3.2.2. X-ray fluorescence

In total four analyzes were performed with the XRF, two analyzes on the sample from the red wall painting and two analyzes on the sample from the blue wall painting. Two analyzes of the same sample were performed so that one could be used as a reference. The analysis for all four samples was performed on the front side of the samples (the side with the pigments). Analysis was not carried out on the backside of the samples since the purpose of the analysis was to identify the pigments used in the wall painting. To avoid the detection of commonly detected elements occurring in the atmosphere the instrument was set to exclude elements Argon (Ar), Rh (Rhodium) and Krypton (Kr) from the analysis.

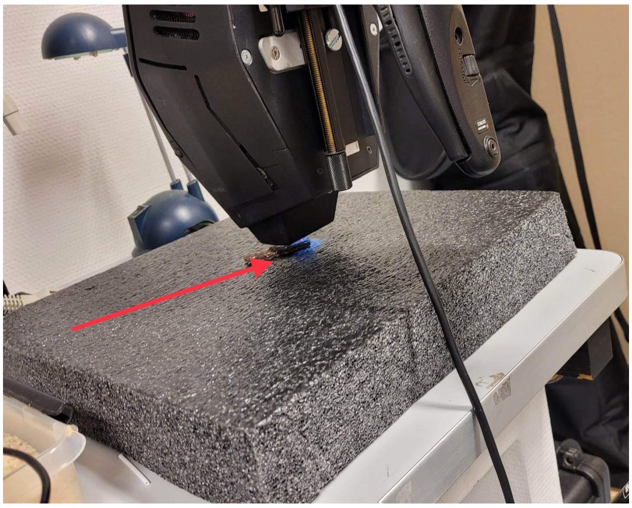


Figure 11 (left): XRF-instrument: sampling area
Figure 12 (right): XRF-instrument

3.3. Conducting experiments

3.3.1. Framework for experiments

For the experiments two areas of the red and blue wall painting respectively, in total four areas, were selected for the application of the nano-lime products. Due to the sensitivity of the surface of the wall painting no marking could be made on the wall painting, marking was done on documentation photographs, see figure 13-18. When the treatment areas had been established and marked they were documented through microscopic photography. The two nano-lime products, Nanorestore® (marked in blue colour) and Nanorestore Plus® (marked in green colour) were applied to one area on the red wall painting and one area on the blue wall painting respectively.

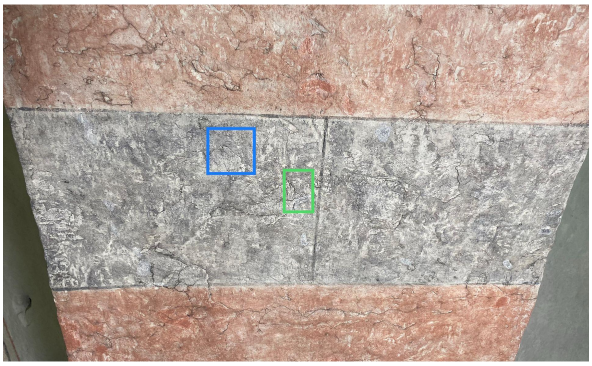


Figure 13 (left): Red wall painting: areas to be treated
Figure 14 (right): Blue wall painting: areas to be treated.

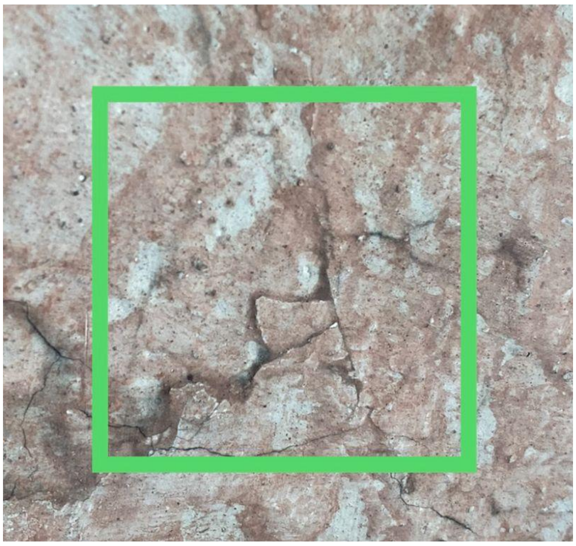


Figure 15 (left): Red wall painting: area R1
Figure 16 (right): Red wall painting: area R2

Figure 17 (left): Blue wall painting: area B1
Figure 18 (right): Blue wall painting: area B2

3.3.2. Application

Before the nano-lime products were applied a dry mechanical cleaning, using a soft brush, of the areas to be treated was performed. A clean surface is important to avoid contaminations to be consolidated along with the material. Sheets of Japanese paper and compresses of cotton were cut into a suitable size for the area that were to be treated. Before application the dispersion was shaken for 1-2 minutes. The dispersion of nano-lime was applied with a brush through a sheet of Japanese paper, see figure 19. The sheet of Japanese paper should be saturated, however dispersion leaking outside the sheet of Japanese paper should be avoided. A compress of cotton soaked in deionized water is applied on top of the saturated sheet of

Japanese paper, see figure 20. Pressure is applied to the cotton compress for enhanced consolidation effect through mechanical action. The compresses are then left to dehydrate until the next day. After about 24h the compresses are removed and the treated areas are documented through visual examination, tapping-sound test and optical microscopy. The application process is repeated two more times.

For those areas where a white haze had formed on the surface, carbonated water was applied with a cotton swab in an attempt to remove the white haze. This method was successful in reducing the white haze, it did not however remove it completely, see figure 22 & 23. This procedure, although successful in reducing the white haze on the surface, should not be repeated more than one or two times since the painted surface is sensitive to mechanical action and there is a risk for unwanted removal of fragments.

Figure 19 (left): Area R1: sheet of Japanese paper saturated with Nanorestore
Figure 20 (right): Area R1: hydrated cotton compress applied to sheet of Japanese paper

Figure 21: Application of nano-lime products with Japanese paper and cotton compresses

Figure 22 (left): Area B1: formation of white haze after treatment with Nanorestore®
Figure 23 (right): Area B1: after removal of white haze with carbonized water

4. Results and discussion

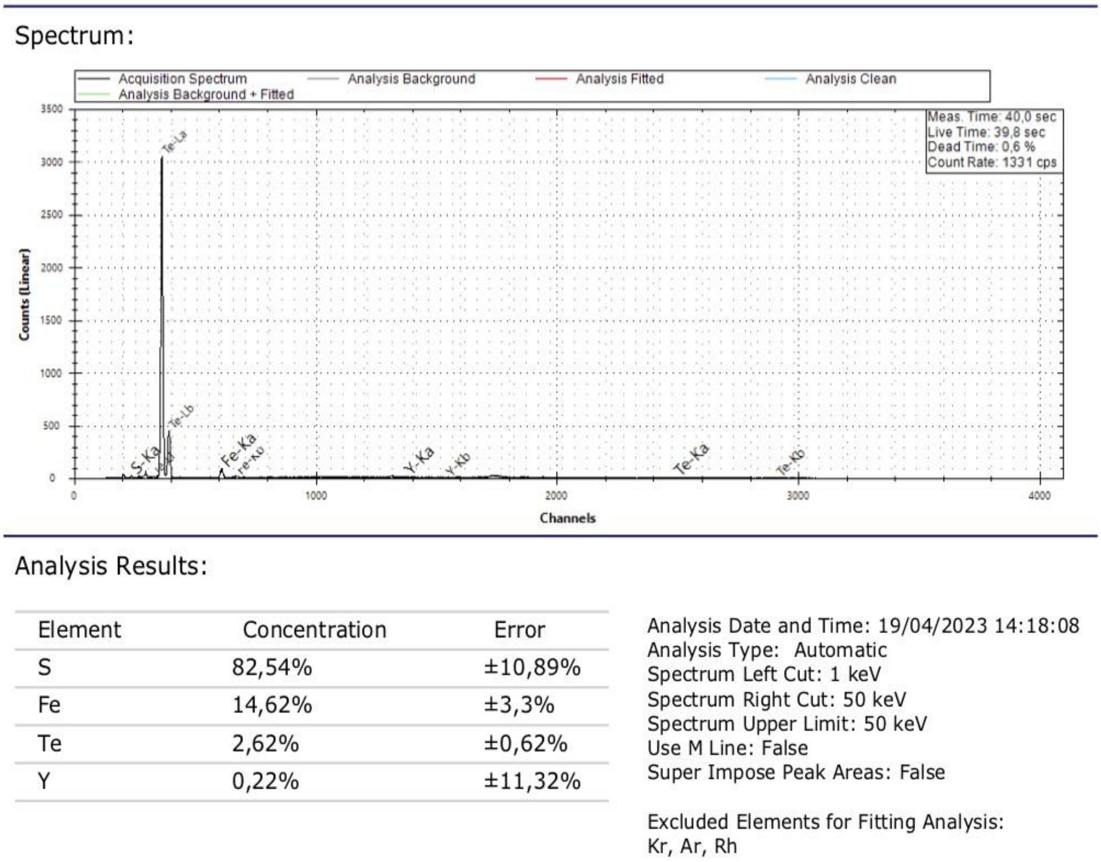
In this section the results of the analytical methods, X-ray fluorescence and Fourier Transform Infrared Spectroscopy, used in the experimental study will be presented. The results of the experiments performed with Nanorestore® and Nanorestore Plus® will also be presented.

4.1. Results

4.1.1. X-ray fluorescence

The XRF-results of the samples taken from the red wall painting shows presence of iron, see figure 24, which likely is to be a red iron oxide pigment. The XRF-results from the sample taken from the blue wall painting showed no detection of any elements that could indicate a blue pigment being present in the sample. Many elements characteristic for blue pigments are detectable through XRF-analysis (Stuart, 2007, p.242). Such a result suggests that a black, probably coal-based, pigment was used for the blue/gray colour of the wall painting.

The results show a high percentage of sulfur in both the red and blue sample, see figure 24 & 25, which can be due to several different reasons. Sulfur is a component in a number of red pigments (Rutherford et.al., 1993, p.166) as well as being an atmospheric pollutant. However, the most probable cause, due to the high percentage of sulfur detected in the sample, is that gypsum (calcium sulfate) is present in the rendering of the wall painting. The presence of gypsum in the plaster is not uncommon in wall paintings in churches in Sweden (Hemgren, 2001, p.10).



Spectrum:

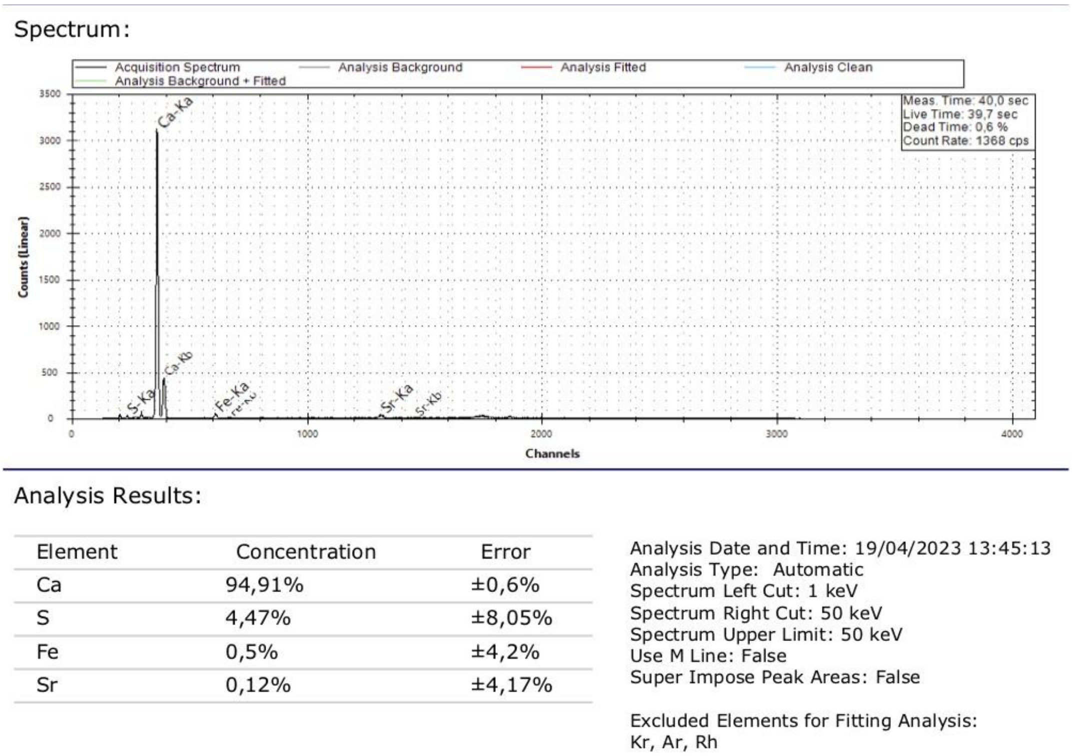
Analysis Results:

Element	Concentration	Error
S	82,54%	±10,89%
Fe	14,62%	±3,3%
Te	2,62%	±0,62%
Y	0,22%	±11,32%

Analysis Date and Time: 19/04/2023 14:18:08
Analysis Type: Automatic
Spectrum Left Cut: 1 keV
Spectrum Right Cut: 50 keV
Spectrum Upper Limit: 50 keV
Use M Line: False
Super Impose Peak Areas: False

Excluded Elements for Fitting Analysis:
Kr, Ar, Rh

Figure 24: Red wall painting: Results from XRF-analysis



Spectrum:

Analysis Results:

Element	Concentration	Error
Ca	94,91%	±0,6%
S	4,47%	±8,05%
Fe	0,5%	±4,2%
Sr	0,12%	±4,17%

Analysis Date and Time: 19/04/2023 13:45:13
Analysis Type: Automatic
Spectrum Left Cut: 1 keV
Spectrum Right Cut: 50 keV
Spectrum Upper Limit: 50 keV
Use M Line: False
Super Impose Peak Areas: False

Excluded Elements for Fitting Analysis:
Kr, Ar, Rh

Figure 25: Blue wall painting: Results from XRF-analysis

4.1.2. Fourier Transform Infrared Spectroscopy

FTIR-analysis showed no indication of any organic substance being present in any of the samples from either the blue or red wall painting. Transmission spectras containing organic materials have energy peaks within the wavelengths of 4000-2000 (Stuart, 2007, p.118-119), which was not present in any of the transmission spectrums produced by either the red or blue wall painting samples analyzed, see figure 26 & table 1.

The analysis of the backside and front side of the *Sample Blue 1* and *Sample Blue 2* show the same results. The results of the analysis of the front- and backside of *Sample Red 2* and *Sample Red 3* show some differences. The transmission spectra for the front-side of *Sample Red 2* and *Sample Red 3* show energy peaks within the wavelengths of 1394-1397, 871-872 and 712-712, see figure 28 & table 1, which are the same as for the transmission spectras of the blue wall painting samples. Analysis from the backside of *Sample Red 2* and *Sample Red 3* have energy peaks in the same wavelengths as the front-side of *Sample Red 2* and *Sample Red 3*, however they have some additional energy peaks, see figure 29-30 & table 1.

Table 1: Results of FTIR-analysis

Sample	**Wavelengths range (front-side)**
Blue 1 (front-side)	1397-1400, 871-872, 712-712
Blue 2 (front-side)	1397-1400, 871-872, 712-712
Blue 2 (backside)	1397-1400, 871-872, 712-712
Red 1 (front-side)	1394-1397, 871-872, 712-712
Red 2 (front-side)	1394-1397, 871-872, 712-712
Red 3 (front-side)	1394-1397, 871-872, 712-712
Red 2 (backside)	1400-1402, 1032-1032, 871-872, 712-712, 537, 469-470.
Red 3 (backside)	1400-1402, 1032-1032, 871-872, 712-712, 537, 469-470.

The transmissions spectrums produced from the analyzes were compared to transmissions spectrums found in a FTIR-database, see figure 31 & 32. The transmission spectrum collected from the database can be interpreted in the same way as the transmission spectras from the analysis of the research study; it is the wavelength ranges of the energy peaks that provide the information. Samples containing calcite have been reported to produce energy peaks within the wavelengths ranges 1429-1492, 879 and 706 (Stuart, 2007, p.127), which can be seen in the transmission spectrum of calcium carbonate found in the database, see figure 31. As expected the transmission spectrums of the samples from the wall painting had energy peaks around the same wavelength ranges. The energy peaks produced by the samples from the red and blue wall painting do not match the energy peaks presented in the transmission spectra for gypsum found in the database, see figure 32. Only one of the energy peaks found in the results of the FTIR-analyzes is found in the wavelength range that is reported to be the wavelength ranges for gypsum (Stuart, 2007, p.130). These results should be interpreted as an indication rather than a complete confirmation in regards to organic material present in the wall painting. The presence of organic materials or an additive such as gypsum can be very difficult to detect using analytical techniques. The reason for this is that the amount of additive or binder used in wall paintings is usually very small. Thus it requires an analytical instrument with a very low minimum detection limit in order to detect these elements (Casadio, Giangualano & Piqué, 2004, p.63). The reason that a high percentage of sulfur can be detected in the XRF-analysis, even though gypsum is not detected in FTIR-analysis due to its low quantity, is that gypsum is highly soluble in water and probably have migrated towards the surface with the moisture moving within the wall painting. Such mechanisms entail a high concentration of sulfur present on the surface of the wall painting even if the overall amount of gypsum in the material is relatively low.

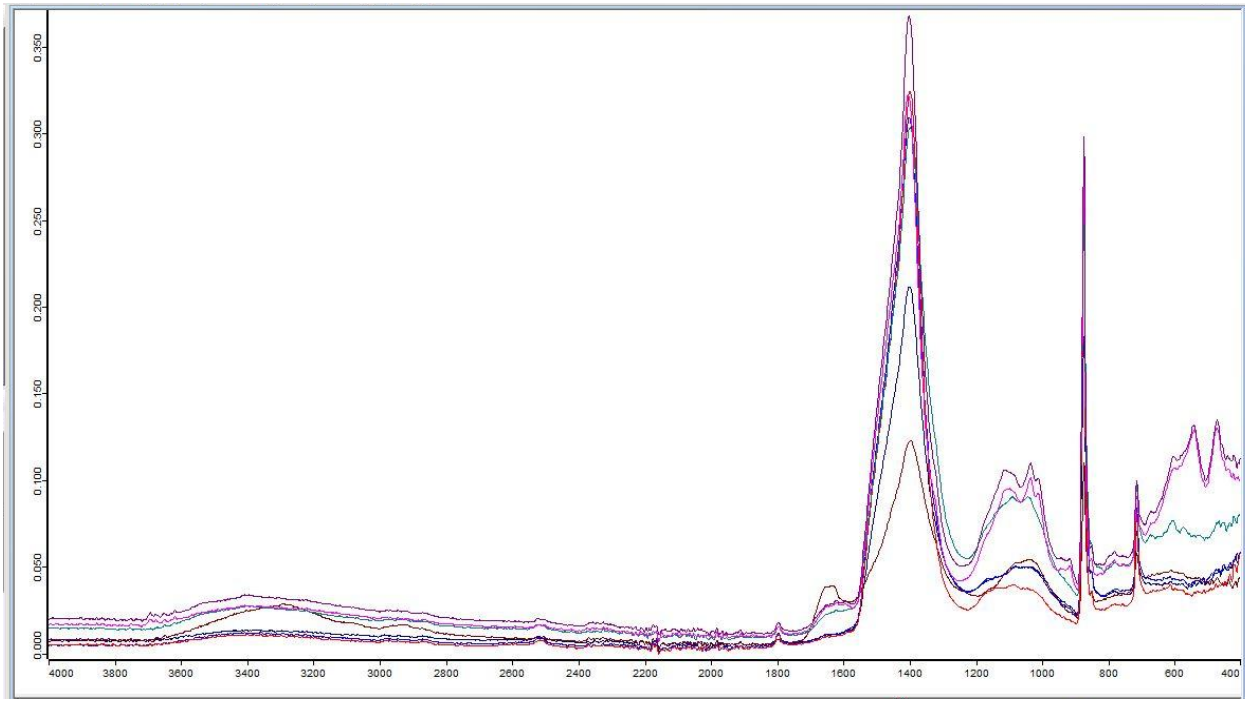


Figure 26: FTIR-spectrum: results from all 7 samples that were analyzed.

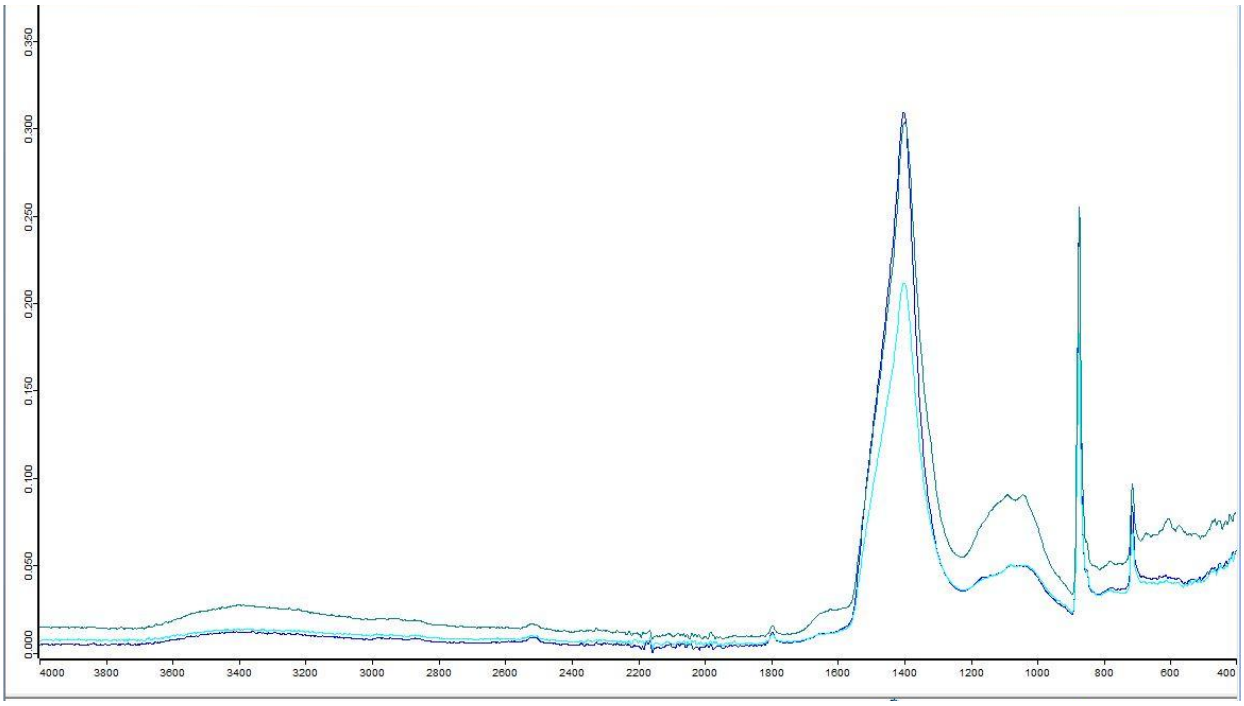


Figure 27: FTIR-spectrum: Sample Blue 1 (front-side), Sample Blue 2 (front-side) & Sample Blue 2 (backside)

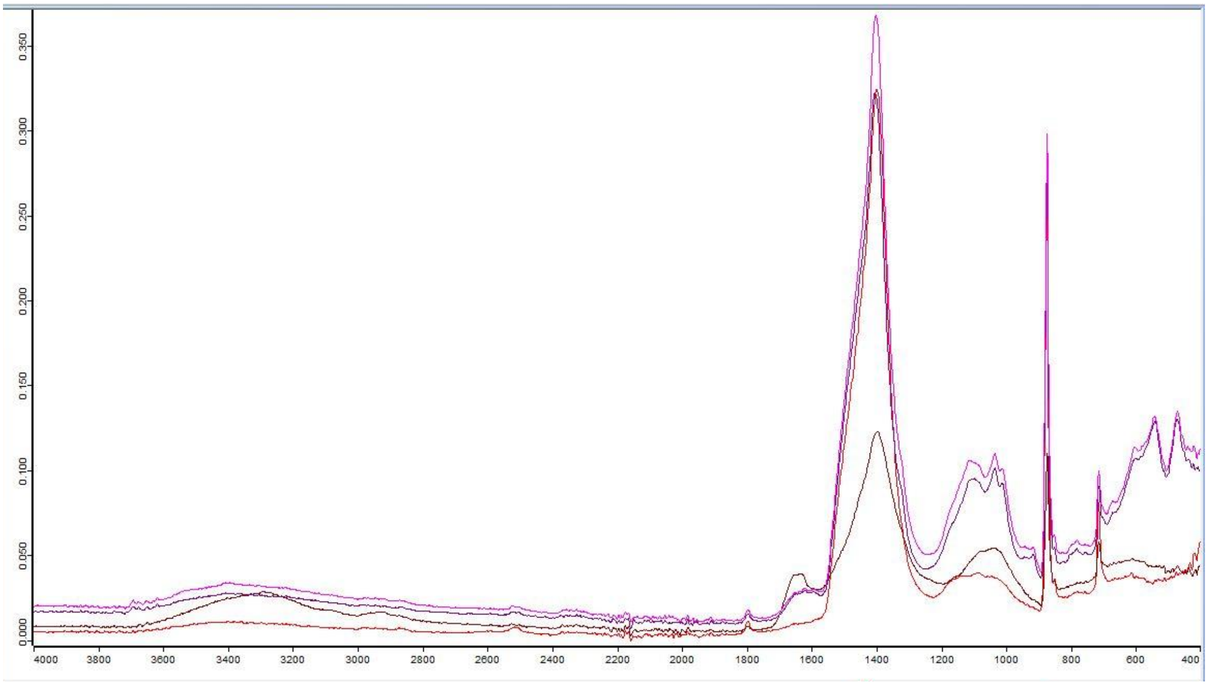


Figure 28: FTIR-spectrum: Sample Red 1 (front-side), Sample Red 2 (front-side), Sample Red 2 (backside), Sample Red 3 (front-side) & Sample Red 3 (backside)

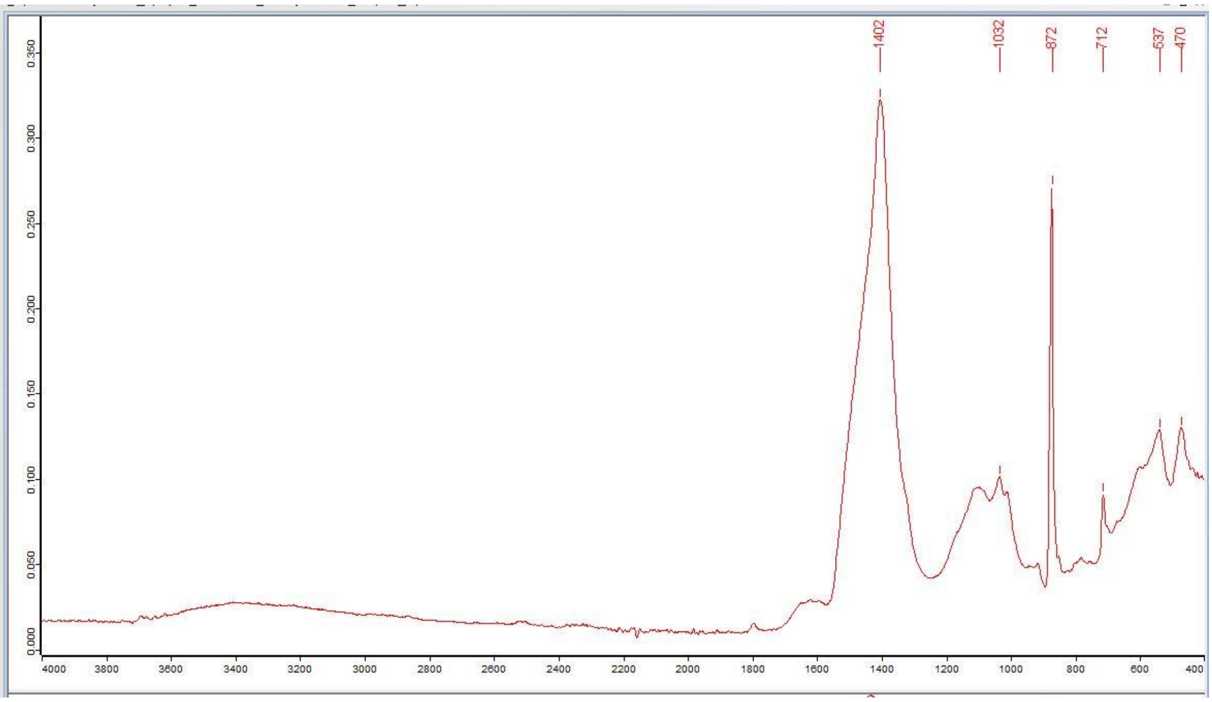


Figure 29: FTIR-spectrum: Sample Red 2 (backside)

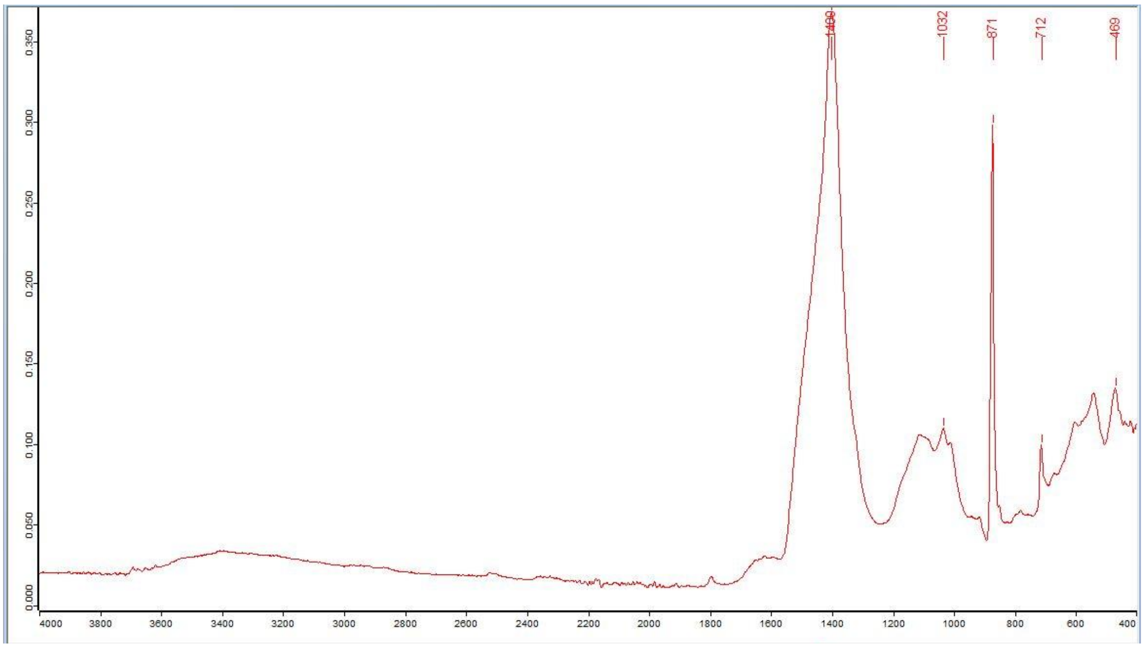


Figure 30: FTIR-spectrum: Sample Red 3 (backside)

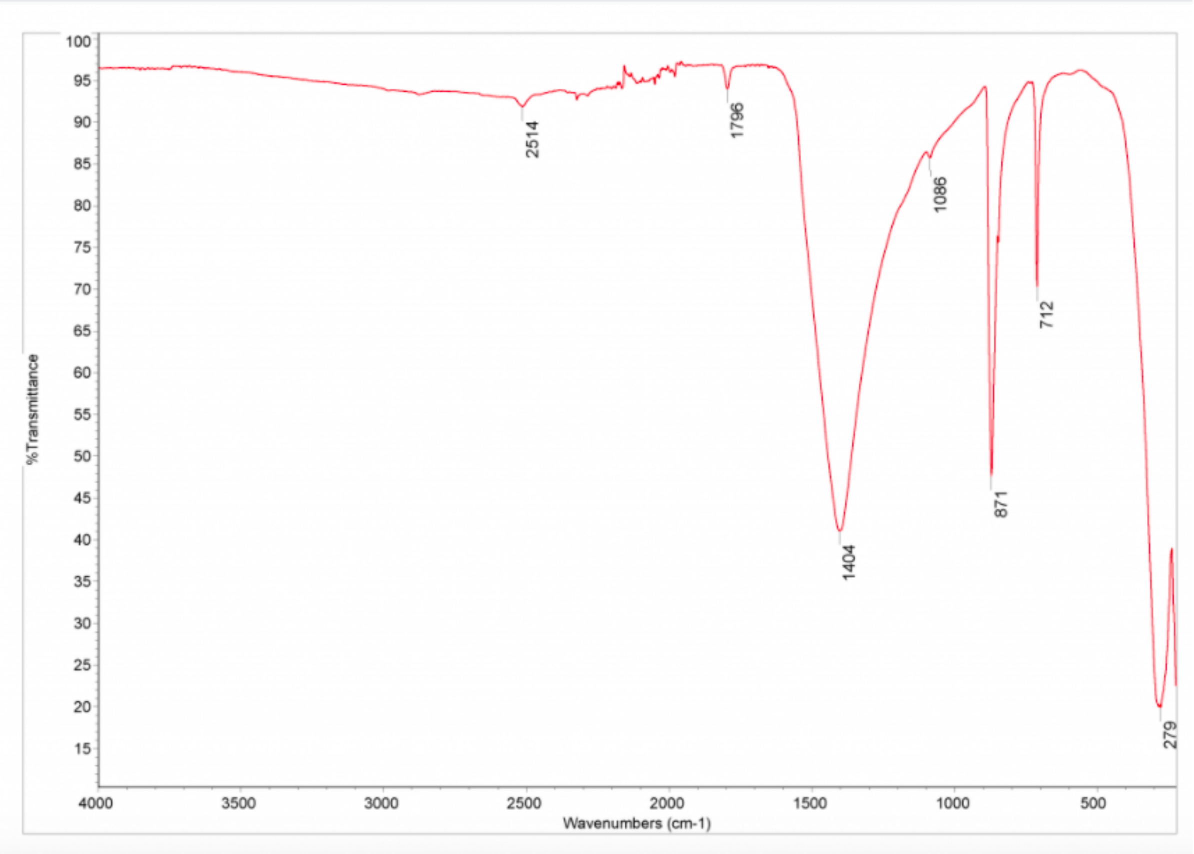


Figure 31: FTIR- spectrum from Database: Calcium carbonate.

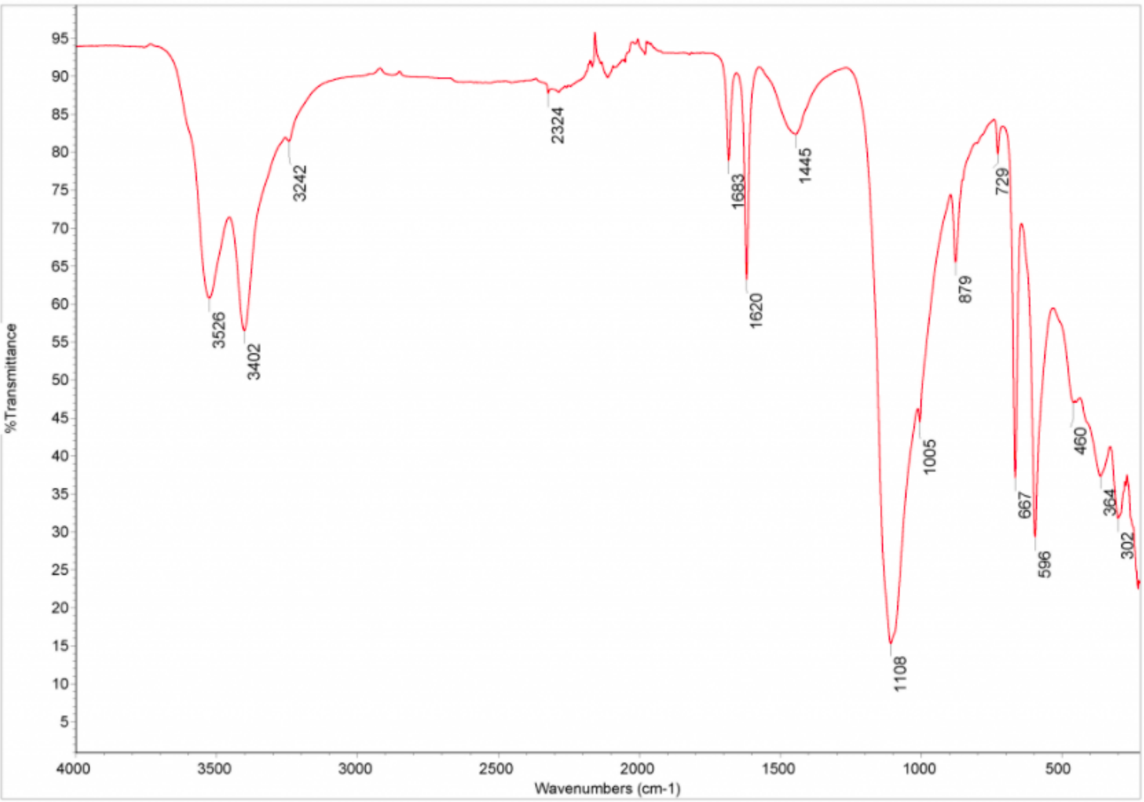


Figure 32: FTIR-spectrum from Database: Gypsum (construction Gypsum, $CaSO_4 \cdot 2H_2O$)

4.1.2. Evaluation of treatments with nano-lime products

The results of the treatment were evaluated based on the following three parameters; consolidation ability, formation of a white haze upon surface and loss of material. No systematic differences in the results between the red and the blue wall painting was recorded. However the consolidation and visual effects differ significantly between the two commercial nano-lime products. The loss of painted fragments was evident after the first application on all treated areas, see figures 64, 70 & 82. Loss of painted fragments appears to be most severe from the first and the second application, which might suggest that the surface has been successfully consolidated with the nano-lime products. Although the reason for this can also be that the most sensitive fragments of the surface were lost in the first or second application. The areas treated with Nanorestore® show an increase in mechanical strength with each application, the greatest consolidation effects are found after the third application. The hollow sound produced upon tapping the surface before treatment has significantly decreased and crevices and cracks on the surface have been reinforced. The newly formed calcium carbonate bonds in the crevices can be seen through optical microscopy, see figure 40, 41, 46, 55, 58, 59, 70 & 71.

Results indicate that Nanoresore Plus® has a lesser consolidation ability than Nanorestore®. Areas treated with Nanorestore Plus® do not show the same reinforcement of crevices and a much slighter decrease of the hollow sound upon the tapping-sound test than the areas treated with Nanorestore®. All treated areas showed a formation of a white haze on the surface, see figures 53, 61 & 67. However the extent of the white haze was substantially more severe for the areas treated with Nanorestore Plus®. The most severe formation of the white haze on areas R2 and B2 occurred during the second application for Area B2 and during the third application for Area R2. The results of the areas treated with Nanorestore® are favorable compared to those of the areas treated with Nanorestore Plus® in terms of consolidation ability and formation of white haze on the surface. The more severe formation of a white haze after the first application of Nanorestore® on the blue wall painting (Area B1), see figure 53 & 67, was probably caused by faulty application of the cotton compress, causing a too speedy evaporation process of the dispersing media, which in turned resulted in insufficient penetration of the nano-lime particles and carbonation of the calcium hydroxide occurring on the surface. In terms of material loss all the treated areas suffered a similar degree of loss of fragments of the painted layer. This suggests that the loss of material correlates primarily to the sensitivity of the surface of the wall painting and application technique rather than the nano-lime products.

Figure 33 (left): Red wall painting: before conservation treatment
Figure 34 (right): Red wall painting: after conservation treatment and retouching[1]

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[1] Retouching performed with conservation product Rollovit®


Figure 35 (left): Blue wall painting: before conservation treatment
Figure 36 (right): Blue wall painting: after conservation treatment and retouching[2]

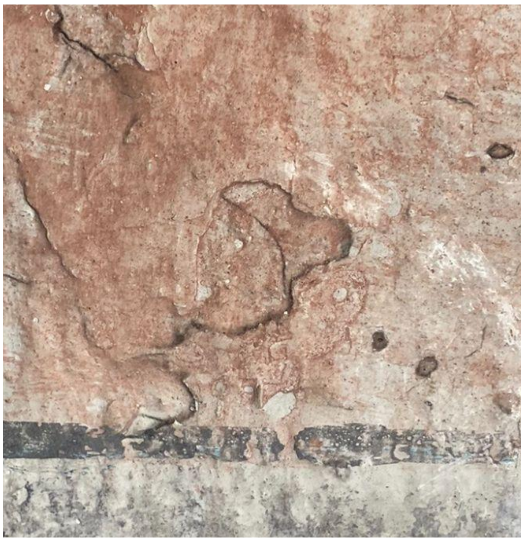


Figure 37 (left): Area R1: before treatment with Nanorestore®
Figure 38 (right): Area R1: after treatment with Nanorestore® and retouching[3]



Figure 39 (left): Area R1: Optical microscopy before treatment with Nanorestore®
Figure 40 (middle): Area R1: Optical microscopy after treatment with Nanorestore®
Figure 41 (right): Area R1: Optical microscopy after treatment with Nanorestore®

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[2] Retouching performed with conservation product Rollovit®
[3] Retouching performed with conservation product Rollovit®


Figure 42 (left): Area R2: before treatment with Nanorestore Plus®
Figure 43 (right): Area R2: after treatment with Nanorestore Plus® and retouching[4]



Figure 44 (left): Area R2: Optical microscopy before treatment with Nanorestore Plus®
Figure 45 (middle): Area R2: Optical microscopy after treatment with Nanorestore Plus®
Figure 46 (right): Area R2: Optical microscopy after treatment with Nanorestore Plus®

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[4] Retouching performed with conservation product Rollovit®



Figure 47 (left): Area B1: Before treatment with Nanorestore®
Figure 48 (right): Area B1: After treatment with Nanorestore® and retouching[5]




Figure 49 (left): Area B1: Optical microscopy before treatment with Nanorestore®
Figure 50 (middle): Area B1: Optical microscopy after treatment with Nanorestore®
Figure 51 (right): Area B1: Optical microscopy after treatment with Nanorestore®

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[5] Retouching performed with conservation product Rollovit®


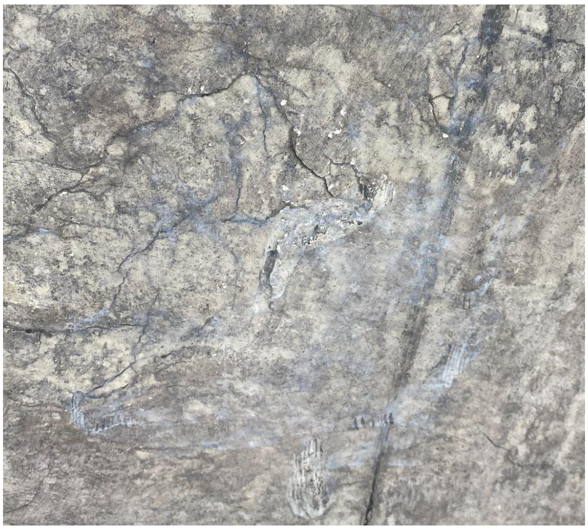

Figure 52 (left): Area B2: Before treatment with Nanorestore Plus®
Figure 53 (right): Area B2: After treatment with Nanorestore Plus® and retouching[6]



Figure 54 (left): Area B2: Optical microscopy before treatment with Nanorestore Plus®
Figure 55 (middle): Area B2: Optical microscopy after treatment with Nanorestore Plus®
Figure 56 (right): Area B2: Optical microscopy after treatment with Nanorestore Plus®

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[6] Retouching performed with conservation product Rollovit®

Table 2: Application 1: Red wall painting

Red wall painting	**Consolidation ability**	**Formation of white haze**	**Loss of sensitive surface fragments**	**Comments**
R1:Nanorestore (dispersed in isopropanol)	Cracks appear to have been consolidated, new bindings of calcium carbonate are visible through microscopy. Still a hollow sound upon tapping but noticeably more mute than before treatment.	A slight formation of white haze is detectable, the white haze has a slight purple colour tone.	Some loss of surface fragments when compress is removed. Detectable both with visible inspection and microscopy.	It is plausible that some superficial cleaning has been performed in connection with the treatment.
R2:Nanorestore Plus (dispersed in ethanol)	Cracks appear to have been consolidated, new bindings of calcium carbonate are visible through microscopy. Still a hollow sound upon tapping but noticeably more mute than before treatment.	A slight formation of white haze is detectable, the white haze has a slight purple colour tone.	Some loss of surface fragments when compress is removed. Detectable both with visible inspection and microscopy.	It is plausible that some superficial cleaning has been performed in connection with the treatment.

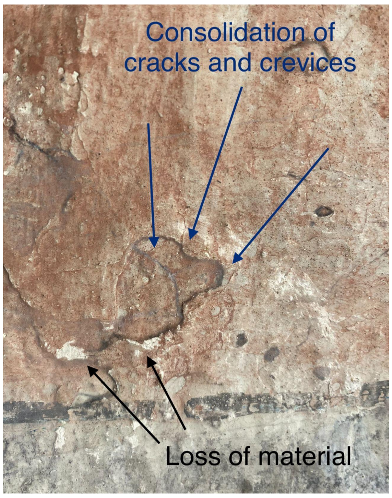

Figure 57 (left): Area R1: after 1st application with Nanorestore ®
Figure 58 (middle): Microscopic image, Area R1: Consolidation of crack after 1st application with Nanorestore®
Figure 59 (right): Microscopic image, Area R1: Consolidation of crack after 1st application with Nanorestore ®

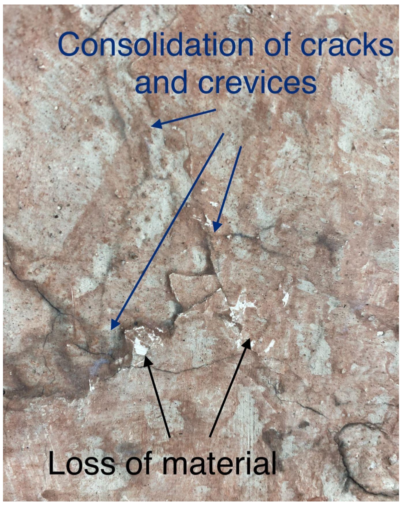

Figure 60 (left): Area R2: after 1st application with Nanorestore Plus®
Figure 61 (middle): Microscopic image, Area R2: Formation of white haze after 1st application with Nanorestore Plus®
Figure 62 (right): Microscopic image, Area R2: Consolidation of crack after 1st application with Nanorestore Plus®

Table 3: Application 1: Blue wall painting

Blue wall painting	**Consolidation ability**	**Formation of a white haze**	**Loss of sensitive surface fragments**	**Comments**
B1:Nanorestore (dispersed in isopropanol)	Cracks appear to have been consolidated, new bindings of calcium carbonate are visible through microscopy. Still a hollow sound upon tapping but noticeably more mute than before treatment.	A slight formation of white haze is detectable, the white haze has a slight purple colour tone.	Some loss of surface fragments when compress is removed. Detectable both with visible inspection and microscopy.	Discoloration due to faulty application: too small compress. Discoloration due to uneven surface. A larger amount of moisture is required.
B2:Nanorestore Plus (dispersed in ethanol)	Cracks appear to have been consolidated, new bindings of calcium carbonate are visible through microscopy. Still a hollow sound upon tapping but noticeably more mute than before treatment.	A slight formation of white haze is detectable, the white haze has a slight purple colour tone.	Slight loss of surface fragments when compress is removed. Detectable both with visible inspection and microscopy.	Discoloration due to faulty application: too small compress. Discoloration due to uneven surface. A larger amount of moisture is required.

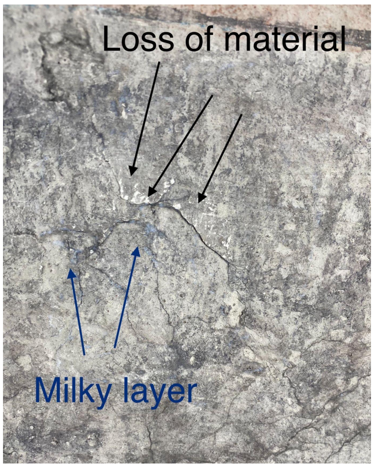

Figure 63 (left): Area B1: after 1st application with Nanorestore®
Figure 64 (middle): Microscopic image, Area B1: Loss of material after 1st application with Nanorestore®
Figure 65 (right): Microscopic image, Area B1: Consolidation of crack after 1st application with Nanorestore®

Figure 66 (left): Area B2: Formation of white haze after 1st application with Nanorestore Plus®
Figure 67 (middle): Microscopic image, Area B2: Formation of white haze after 1st application with Nanorestore Plus®
Figure 68 (right): Microscopic image, Area B2: Crevice after 1st application with Nanorestore Plus®

Table 4: Application 2: Red wall painting

Red wall painting	**Consolidation ability**	**Formation of a white haze**	**Loss of sensitive surface fragments**	**Comments**
R1:Nanorestore (dispersed in isopropanol)	Area is not completely mute upon tapping, it is however significantly less hollow than before treatment and after 1st application. Cracks have been consolidated and "filled in" and brightened by the formation of new calcium carbonate. Edges have been significantly reinforced.	A slight formation of white haze is detectable, the white haze has a slight purple colour tone.	Severe loss of surface fragments when compress is removed. Detectable both with visible inspection and microscopy.	Significantly better consolidation effects from the 1st application. Difficult to determine loss of fragments is from the first or second application.
R2:Nanorestore Plus (dispersed in ethanol)	Area is not completely mute upon tapping, it is however significantly less hollow than before treatment and after 1st application. Cracks have been consolidated and "filled in" and brightened by the formation of new calcium carbonate. Edges have been significantly reinforced.	A slight formation of white haze is detectable, the white haze has a slight purple colour tone.	Some loss of surface fragments when compress is removed. Detectable both with visible inspection and microscopy.	Significantly better consolidation effects from the 1st application. Difficult to determine loss of fragments is from the first or second application.

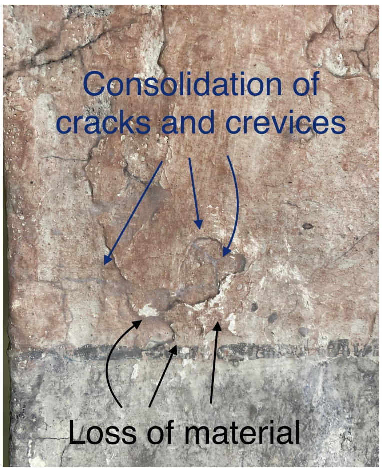

Figure 69 (left): Area R1: after 2nd application with Nanorestore®
Figure 70 (middle): Microscopic image, Area R1: Loss of material after 2nd application with Nanorestore®
Figure 71 (right): Microscopic image, Area R1: Consolidation of crack after 2nd application with Nanorestore®

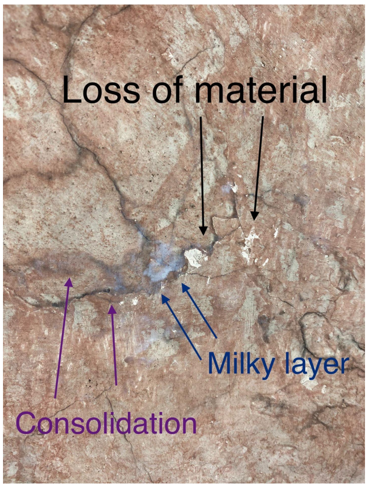

Figure 72 (left): Area R2: after 2nd application with Nanorestore Plus®
Figure 73 (middle): Microscopic image, Area R2: Formation of white haze after 2nd application with Nanorestore Plus®
Figure 74 (right): Microscopic image, Area R2: Consolidation of crevice after 2nd application with Nanorestore Plus®

Table 5: Application 2: Blue wall painting

Blue wall painting	**Consolidation ability**	**Formation of a white haze**	**Loss of sensitive surface fragments**	**Comments**
B1:Nanorestore (dispersed in isopropanol)	Area is not completely mute upon tapping, it is however significantly less hollow than before treatment and after 1st application. Cracks have been consolidated and “filled in” and brightened by the formation of new calcium carbonate. Edges have been significantly reinforced	A slight formation of white haze is detectable, the white haze has a slight purple colour tone.	Some loss of surface fragments when compress is removed. Detectable both with visible inspection and microscopy.	Difficult to determine loss of fragments is from the first or second application.
B2:Nanorestore Plus (dispersed in ethanol)	Treated area still gives a hollow sound upon tapping. Very slight reinforcements of edges.	Severe formation of white haze detectable, more severe compared than from the 1st application. Discoloration appears both around edges of compress and in the middle of the compress.	Some loss of surface fragments when compress is removed. Detectable both with visible inspection and microscopy.	Difficult to determine loss of fragments is from the first or second application.

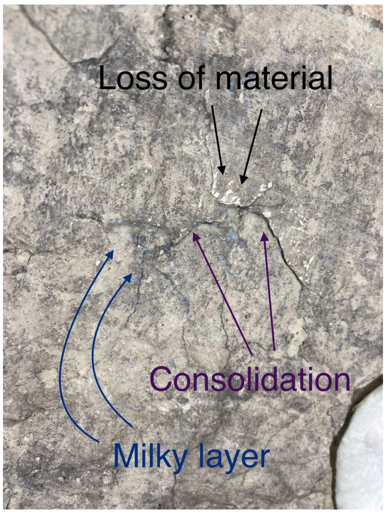

Figure 75 (right): Area B1: after 2nd application with Nanorestore®
Figure 76 (middle): Microscopic image, Area B1: Consolidation of crevice after 2nd application with Nanorestore®
Figure 77 (left): Microscopic image, Area B1: Consolidation of crevice and loss of material after 2nd application with Nanorestore®

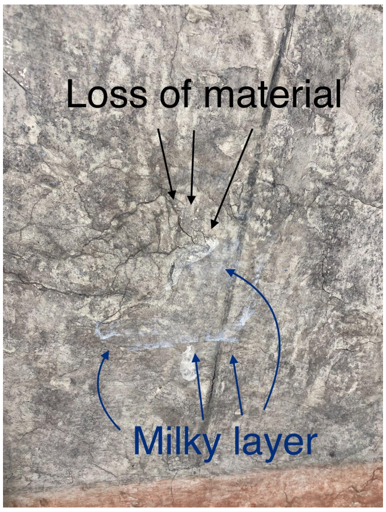

Figure 78 (left): Area B2: after 2nd application with Nanorestore Plus®
Figure 79 (middle): Microscopic image, Area B2: Consolidation of crevice after 2nd application with Nanorestore Plus®
Figure 80 (right): Microscopic image, Area B2: Formation of white haze after 2nd application with Nanorestore Plus®

Table 6: Application 3: Red wall painting

Red wall painting	**Consolidation ability**	**Formation of a white haze**	**Loss of sensitive surface fragments**	**Comments**
R1:Nanorestore (dispersed in isopropanol)	Good consolidation effect, treated area is almost completely mute upon tapping. Cracks have been consolidated and “filled in" and brightened by the formation of new calcium carbonate. Edges have been significantly reinforced.	A slight formation of white haze is detectable, the white haze has a slight purple colour tone.	Loss of painted layer when compress is removed. Detectable both with visible inspection and microscopy.	
R2:Nanorestore Plus (dispersed in ethanol)	Treated area still gives a hollow sound upon tapping. Very slight reinforcements of edges.	Severe formation of white haze is detectable, the white haze has a slight purple colour tone.	Loss of painted layer when compress is removed. Detectable both with visible inspection and microscopy.	

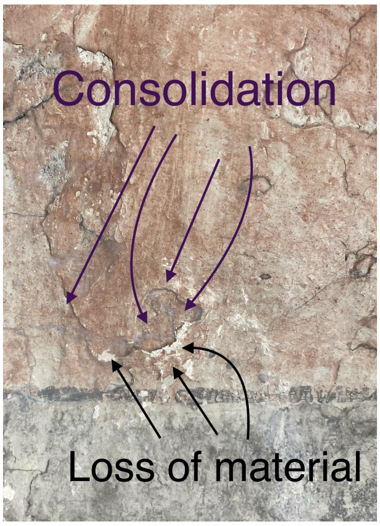

Figure 80 (left): Area R1: after 3rd application with Nanorestore®
Figure 81 (middle): Microscopic image, Area R1: Consolidation of crevice and loss of material after 3d application with Nanorestore ®
Figure 82 (right): Microscopic image, Area R1: Consolidation of crevice and loss of material after 3rd application with Nanorestore®

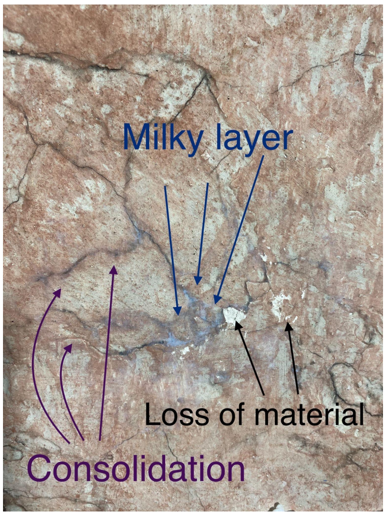

Figure 83 (left): Area R2: after 3rd application with Nanorestore Plus®
Figure 84 (middle): Microscopic image, Area R2: Formation of white haze after 3rd application with Nanorestore Plus®
Figure 85 (right): Microscopic image, Area R2: Loss of material after 3rd application with Nanorestore Plus®

Table 7: Application 3: Blue wall painting

Blue wall painting	**Consolidation ability**	**Formation of a white haze**	**Loss of sensitive surface fragments**	**Comments**
B1:Nanorestore (dispersed in isopropanol)	Good consolidation effect. Treated area is almost completely mute upon tapping. Edges have been significantly reinforced. One severe crevice has not been reinforced.	Very slight formation of white haze in the cracks.	Loss of painted layer when compress is removed. Detectable both with visible inspection and microscopy.	
B2:Nanorestore Plus (dispersed in ethanol)	Treated area still gives a hollow sound upon tapping. Very slight reinforcements of edges.	Severe formation of white haze both around the edges of where the compress was located and in the middle of the compress.	Loss of painted layer when compress is removed. Detectable both with visible inspection and microscopy.	

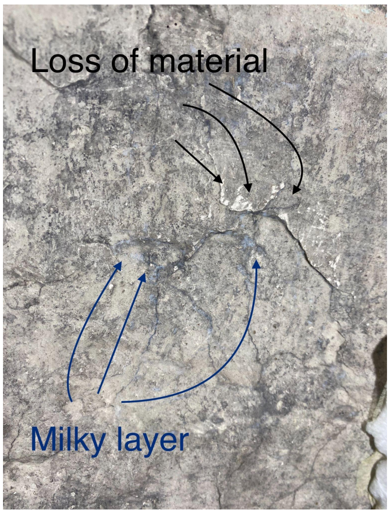

Figure 86 (left): Microscopic image, Area B1: Consolidation of crevice and loss of material after 3rd application with Nanorestore®

Figure 87 (middle): Microscopic image, Area B1: Consolidation of crevice and loss of material after 3rd application with Nanorestore ®

Figure 88 (right): Area B1: after 3rd application with Nanorestore®

Figure 89 (left): Area B2: after 3rd application with Nanorestore Plus®

Figure 90 (middle): Microscopic image, Area B2: Formation of white haze and loss of material after 3rd application with Nanorestore Plus®

Figure 91 (right): Microscopic image, Area B2: Consolidation of crevice after 3rd application with Nanorestore Plus®



Figure 92 (left): Microscopic image, Area B2: formation of white haze after treatment with Nanorestore Plus®
Figure 93 (middle): Microscopic image, Area B2: formation of white haze after treatment with Nanorestore Plus®
Figure 94 (right): Microscopic image, Area R2: formation of white haze after treatment with Nanorestore Plus®

4.2. Discussion

One of the negative aspects of nano-lime is the low controllability of the consolidation process. It is important that the nanoparticles of calcium hydroxide are allowed sufficient penetration into the material, insufficient penetration can result in the formation of a white haze on the surface of the wall painting. The formation of a white haze on the surface appears when the carbonation process occurs on the surface of the wall painting rather than internally in the material, see figure 92-94. Not only will this cause an aesthetic alteration of the object, but it will also undermine the sought for consolidation effects. Insufficient penetration of the calcium hydroxide nanoparticles can be caused by several different reasons, which often correlates to one another creating a synergistic effect.

Based on an interpretation of the results from the experimental study one of the the main influencing factors appears to be the application method. Formation of a white haze on the surface can be traced to the fact that the hydrated compress did not sufficiently cover the sheet of Japanese paper to which the nano-lime was applied, see figure 91 & 92. This resulted in accelerated evaporation of the dispersion agent, not providing sufficient time for the nanoparticles of calcium hydroxide to penetrate the material. Thus the carbonation process occurs on the surface of the wall painting, creating the white haze, rather than internally in the material on the areas not sufficiently covered by the hydrated compress. However, the results from the experimental study also show the formation of a white haze on areas completely covered by the hydrated compress, the reason for this is likely to be the unevenness of the surface of the wall painting. It is possible that the hydrated compress might not have reached sufficiently into cavities and crevices on the uneven surface, which resulted in a speedy evaporation of the alcohol, not giving the nanoparticles of calcium hydroxide sufficient time to penetrate the substrate, which in turn causes the carbonation process to occur on the surface, creating a white haze.

The results of the experimental study indicate the application method as a likely cause for the insufficient penetration of the calcium hydroxide nanoparticles. The results suggest that an adjustment in the application method should be examined in order to allow sufficient penetration of the nano-lime products used in environments with generally lower levels of relative humidity. One possibility that could be considered is the wetting of the surface that is to be treated with nano-lime with alcohol before application. This could increase the penetration ability of the calcium hydroxide particles into the porous material of the wall painting.

The results of the treatment with the two nano-lime products demonstrate a difference both in regards to consolidation effect and in the formation of white haze on the surface between the Nanorestore® and Nanorestore Plus®. Areas treated with Nanorestore Plus® show inferior consolidation effects as well as a more severe formation of a white haze of the surface, which probably correlates since the carbonation process occurring on the surface both creates a white haze and undermines the consolidation effects internally in the material. The results suggest a lower penetration ability of Nanorestore Plus®, which is somewhat contradictory since Nanorestore Plus® consists of particles with an average smaller particle size than Nanorestore®. Theoretically, Nanorestore Plus® should have a greater penetrating ability than Nanorestore®. These results could be explained either by the presence of gypsum in the rendering of the wall painting or by the back-migration of the nanoparticles.

Gypsum has a high solubility in water and it is possible that when water from the hydrated compress interacts with the surface that the calcium sulfate particles in the wall painting dissolves and migrates towards the surface as the water evaporates. The calcium sulfate crystallizes on the surface as the water evaporates, resulting in the formation of a white salt layer on the surface of the wall painting. This double exchange reaction, see reaction formula below, between the nanoparticles of calcium hydroxide and the calcium sulfate present in the wall painting, which is favored by water, could explain the formation of a white haze on the surface after treatment with the nano-lime products. It could also explain that it was possible to remove some of the white haze formed with carbonated water, see figure 22 & 23, since calcium sulfate is highly soluble in water. The more severe formation of a white haze on the surface on the areas treated with Nanorestore Plus® could also be explained by this double exchange reaction. The reaction will take place for both Nanorestore® and Nanorestore Plus® but because Nanorestore Plus® consists of smaller particles it has a higher chemical reactivity, which can be the reason for the more severe formation of white haze on the surface.

$$Ca(OH)_2 + CaSO_4 + 2H_2O \rightarrow CaSO_4 + Ca(OH)_2 + 2H_2O$$

Theoretically, since it has smaller average particle size, the Nanorestore Plus® should have a greater penetration ability than the Nanorestore® that has a larger average particle size and broader size distribution. However, the results of the experimental study show a more severe formation of white haze on the surface of the areas treated with Nanorestore Plus® , which indicates an inferior penetration ability to the Nanorestore®. A possible explanation for these results could be the back-migration of the calcium hydroxide nanoparticles, which is favored by generally low levels of relative humidity in the surrounding environment. Back-migration entails that the nano-particles penetrate the substrate but then migrate back to the surface, carbonating on the surface. Another contributing factor to the different results between the two nano-lime products is the dispersing alcohol. Ethanol, which is the dispersing agent for Nanorestore Plus®, has a higher volatility than isopropanol, which is the dispersing agent for Nanorestore®. A higher volatility will entail a faster evaporation, which will favor the process of back-migration of the calcium hydroxide nanoparticles.

It is necessary to mention that the possible explanations for the results of the experimental study are merely hypothetical at this stage. Additional tests and further investigation is required to gain a more comprehensive understanding about the possible processes and mechanisms taking place.

4.3. Future research

The results of this research study and the hypothesis presented in the discussion demonstrate the necessity of further research concerning the use of nano-lime products as a consolidation treatment in different climates and on different wall painting substrates. Knowledge about how nano-lime products should be used in environments with generally lower levels of relative humidity is lacking and it would be beneficial to conduct further tests investigating the influence of the application method in different climatic conditions. It seems probable that it is necessary to adjust application technique depending on the climatic conditions. Even if the deterioration problems are similar, the same approach and application method cannot be applied in distinctively different climatic conditions.

An adjustment to consider in regards to application method should be preparing the surface with alcohol before application of the nano-lime product. This could help the nanoparticles of calcium hydroxide to reach a sufficient penetration of the wall painting, which would increase consolidation effects and avoid the carbonation occurring on the surface creating a white haze. Another aspect that could be considered is the concentration of the dispersion of nanoparticles of calcium hydroxide. Some studies (D'Armada & Hirst, 2012, p.76) have suggested that the formation of a white haze on the surface could be avoided if using a lower concentration of the nano-lime product for the initial applications and then successively increasing the concentration, which is a possibility that should be further investigated. Another consideration that should be further examined is the possibility of using a higher concentration of the nano-lime product to reduce the loss of material. It is however important to consider the possible increased risk of formation of white haze on the surface when using a higher concentration of the nano-lime product.

For future experimental studies it would be beneficial to examine several areas of the same wall painting using the same nano-lime product, this would enable a more in-depth comparison. It would be preferred that the indoor climate of the church be monitored during a longer period of time so that both seasonal and diurnal changes in the temperature and relative humidity could be recorded. In addition to this it would have been advantageous to examine the treated areas of the wall painting after longer periods of time had passed after treatment. Examinations of the surface should be performed several weeks and even months after treatment since it can take a long period of time for the completion of the carbonation process. Future research projects should consider the possibility of using more technical analytical methods in-situ to examine the wall painting during the process of the conservation treatment. Useful analytics methods for examining consolidation effects and alterations occurring on the surface could be ultrasound velocity measures and a colorimeter instrument as well as spectrophotometry. The mechanisms of the use of carbonized water as a means for removal of the white haze formed on the surface should also be further investigated.

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6. Appendix

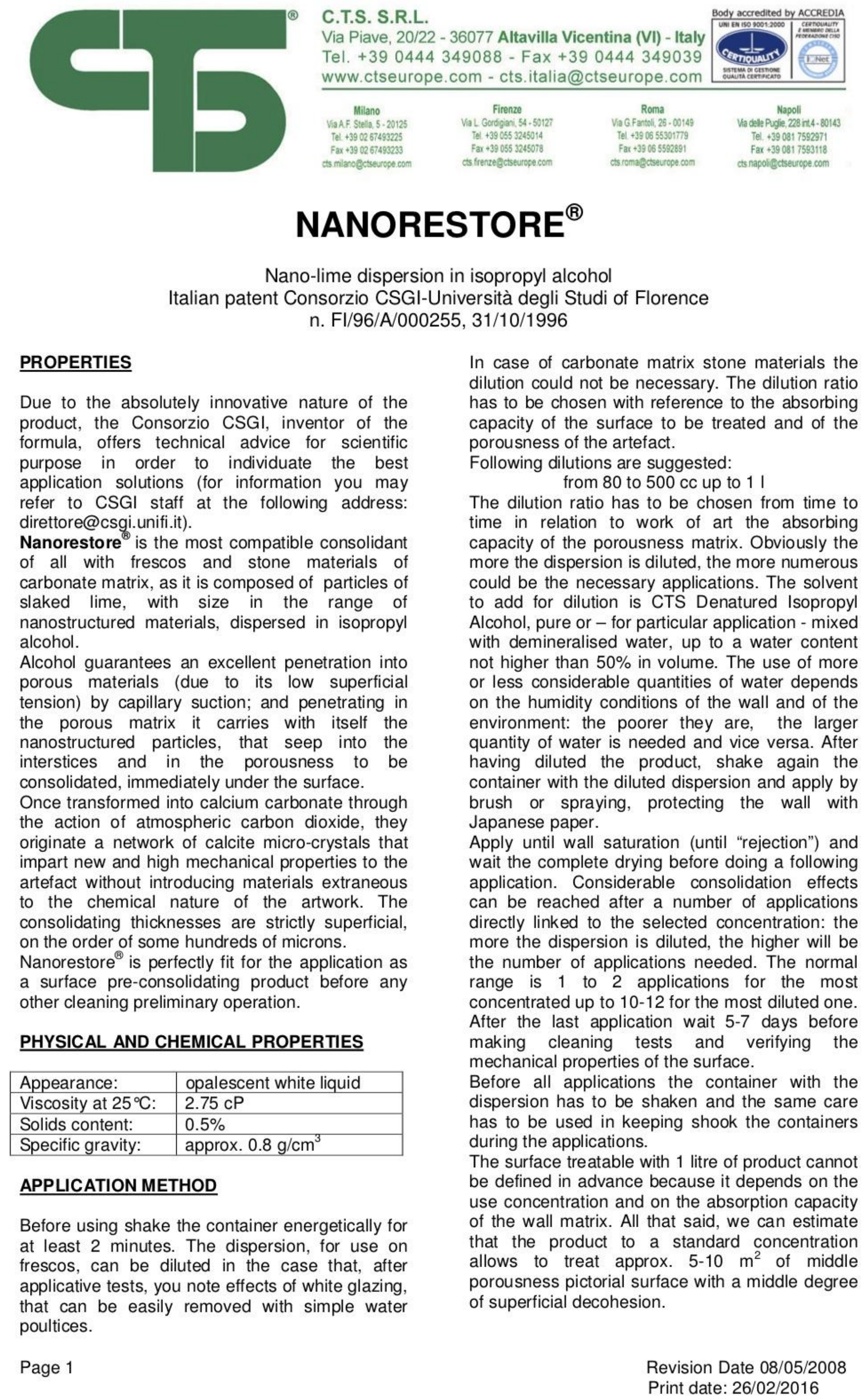
6.1. Temperature and relative humidity measurements in Dalby church

Time and date of measurement	**Temperature °C**	**Relative humidity %**
05-04-2023 (11.17 a.m.)	17,4°C	49%
05-04-2023 (12.00 p.m.)	17,2°C	50%
05-04-2023 (1.12 p.m.)	17,1°C	51%
05-04-2023 (2.10 p.m.)	17,0°C	50%
05-04-2023 (3.06 p.m.)	17,1°C	52%
06-04-2023 (10.44 a.m.)	17,2°C	52%
06-04-2023 (11.57 a.m.)	17,8°C	49%
06-04-2023 (12.30 p.m.)	17,5°C	51%
06-04-2023 (1.40 p.m.)	17,8°C	47%
06-04-2023 (2.39 p.m.)	17,4°C	51%
14-04-2023 (10.29 a.m.)	18,4°C	48%
14-04-2023 (11.35 a.m.)	18,7°C	47%
14-04-2023 (1.32 p.m.)	18,6°C	48%
14-04-2023 (3.32 p.m.)	18,1°C	49%

	Highest measurement	**Lowest measurement**
Temperature °C	18,7°C	17,0°C
Relative humidity %	52%	47%

6.2. Commercial nano-lime products

6.2.1. Nanorestore Technical Sheet



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NANORESTORE®

Nano-lime dispersion in isopropyl alcohol
Italian patent Consorzio CSGI-Università degli Studi of Florence
n. FI/96/A/000255, 31/10/1996

PROPERTIES

Due to the absolutely innovative nature of the product, the Consorzio CSGI, inventor of the formula, offers technical advice for scientific purpose in order to individuate the best application solutions (for information you may refer to CSGI staff at the following address: direttore@csgi.unifi.it).

Nanorestore® is the most compatible consolidant of all with frescos and stone materials of carbonate matrix, as it is composed of particles of slaked lime, with size in the range of nanostructured materials, dispersed in isopropyl alcohol.

Alcohol guarantees an excellent penetration into porous materials (due to its low superficial tension) by capillary suction; and penetrating in the porous matrix it carries with itself the nanostructured particles, that seep into the interstices and in the porousness to be consolidated, immediately under the surface.

Once transformed into calcium carbonate through the action of atmospheric carbon dioxide, they originate a network of calcite micro-crystals that impart new and high mechanical properties to the artefact without introducing materials extraneous to the chemical nature of the artwork. The consolidating thicknesses are strictly superficial, on the order of some hundreds of microns.

Nanorestore® is perfectly fit for the application as a surface pre-consolidating product before any other cleaning preliminary operation.

PHYSICAL AND CHEMICAL PROPERTIES

Appearance:	opalescent white liquid
Viscosity at 25°C:	2.75 cP
Solids content:	0.5%
Specific gravity:	approx. 0.8 g/cm^3

APPLICATION METHOD

Before using shake the container energetically for at least 2 minutes. The dispersion, for use on frescos, can be diluted in the case that, after applicative tests, you note effects of white glazing, that can be easily removed with simple water poultices.

In case of carbonate matrix stone materials the dilution could not be necessary. The dilution ratio has to be chosen with reference to the absorbing capacity of the surface to be treated and of the porousness of the artefact.

Following dilutions are suggested:

from 80 to 500 cc up to 1 l

The dilution ratio has to be chosen from time to time in relation to work of art the absorbing capacity of the porousness matrix. Obviously the more the dispersion is diluted, the more numerous could be the necessary applications. The solvent to add for dilution is CTS Denatured Isopropyl Alcohol, pure or – for particular application - mixed with demineralised water, up to a water content not higher than 50% in volume. The use of more or less considerable quantities of water depends on the humidity conditions of the wall and of the environment: the poorer they are, the larger quantity of water is needed and vice versa. After having diluted the product, shake again the container with the diluted dispersion and apply by brush or spraying, protecting the wall with Japanese paper.

Apply until wall saturation (until “rejection”) and wait the complete drying before doing a following application. Considerable consolidation effects can be reached after a number of applications directly linked to the selected concentration: the more the dispersion is diluted, the higher will be the number of applications needed. The normal range is 1 to 2 applications for the most concentrated up to 10-12 for the most diluted one. After the last application wait 5-7 days before making cleaning tests and verifying the mechanical properties of the surface.

Before all applications the container with the dispersion has to be shaken and the same care has to be used in keeping shook the containers during the applications.

The surface treatable with 1 litre of product cannot be defined in advance because it depends on the use concentration and on the absorption capacity of the wall matrix. All that said, we can estimate that the product to a standard concentration allows to treat approx. 5-10 m^2 of middle porousness pictorial surface with a middle degree of superficial decohesion.

It is not suitable to use Nanorestore® in those situations where the porousness surface is cancelled by the presence of polymeric fixatives, substantial deposits of dirt or strong lime paints.
The use of the product not as a simple pre-consolidant, but as a final consolidant in the presence of sulphation needs a desulphurization pretreatment with poultices of ammonium carbonate solutions or Amberlite 4400 OH anion exchange resin. At this point Nanorestore® can be used as usual even as an alternative to poultices of barium hydroxide solution, even though in this case it is suggested to contact Consorzio CSGI.
Possible problems are reported in the presence of very high quantities of magnesium salts. In any case, before using the product, it is strongly recommended to make a minimal diagnostic test campaign with the purpose of determining the pictorial technique and evaluating the deterioration.
Finally, it is emphasized that the product is preferably suitable for the “fresco” painted parts.

SAFETY PRECAUTIONS

Nanorestore® does not present particular hazards for users.
During spraying applications, wear a mask providing protection against isopropyl alcohol vapours and in rooms with poor aeration, facilitate the vapours dispersion by using filtering extractors.
Nanorestore® is a flammable product. For this reason it needs to be handled and stored according to the usual precautions for this kind of products.

STABILITY AND STORAGE

Sediment can forms on the bottom, it is suggested to shake the container energetically before using.
The containers tightly closed and without air or humidity have a shelf-life of 12 months.

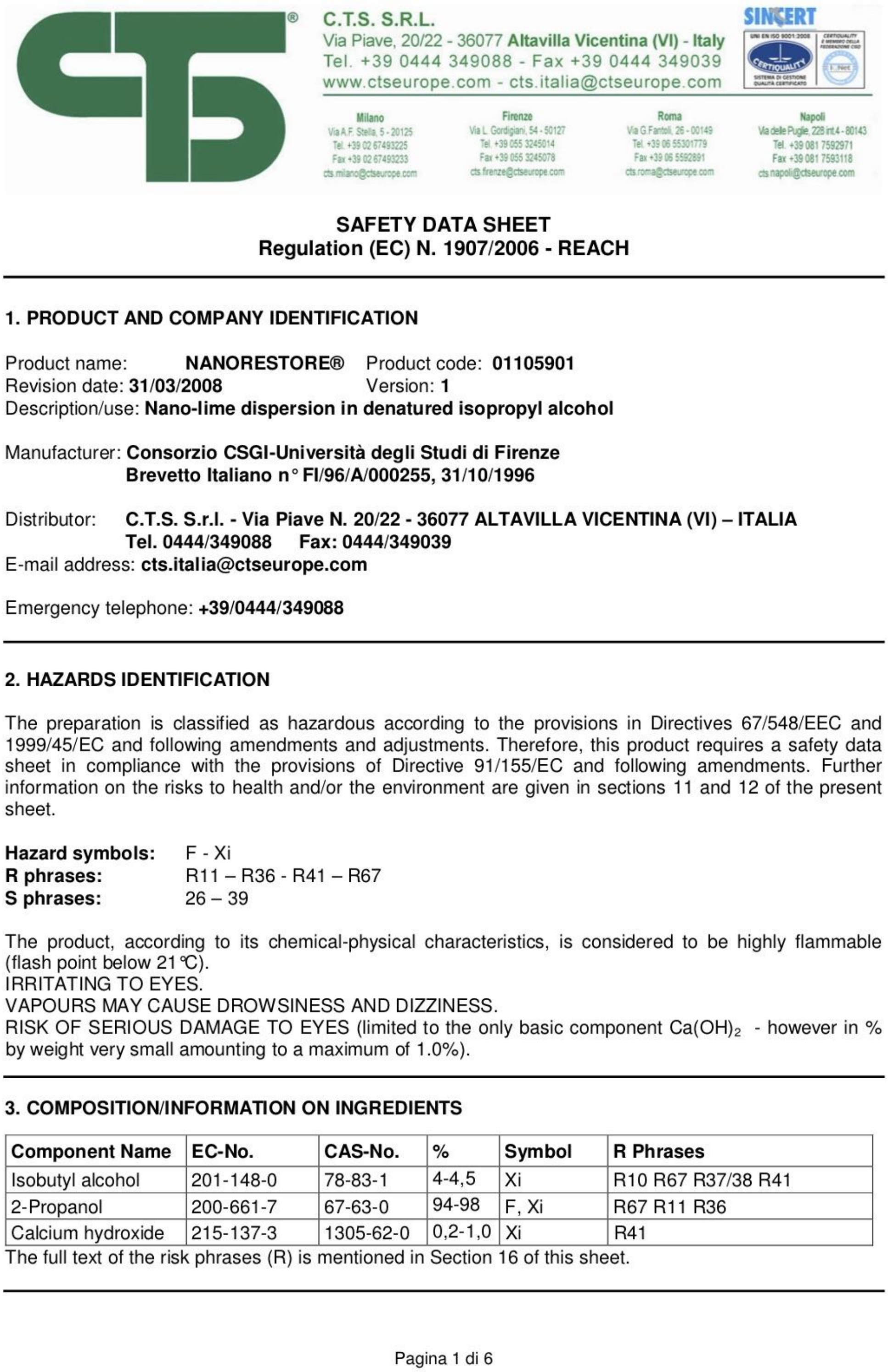
PACK SIZE

Nanorestore® is available in 1 litre containers.

In the following list are some **references** relevant to the use of **Nanorestore®:**

Name of the monument/work/site	***Town - Country***	***Year***
Mural paintings of the Cappellone degli Spagnoli in the Church of Santa Maria Novella	Florence - Italy	1997
Mural paintings of the Cathedral of Santa Maria del Fiore	Florence - Italy	1999
Filippo Lippi's mural paintings in the Cathedral of Prato	Prato - Italy	2002-3
Medieval mural paintings (XIII and XIV century) in the Crypt of San Zeno	Verona - Italy	2005
Mural paintings in Santa Maria delle Grazie	Gravedona-Como - Italy	2005
Mural paintings in the Maya site of Calakmul (World Heritage Site declared by UNESCO)	Calakmul – Mexico	2005-2008
Frescos in the "Cappella del Podestà" in Bargello Museum	Florence – Italy	2006
"La leggenda della Vera Croce" by Agnolo Gaddi, Church of Santa Croce	Florence – Italy	2007
Mural paintings in "Villa del Bene"	Volargne-Verona - Italy	2007
Angera stone bas-relieves in Ca' Granda – "Università Statale" of Milan	Milan – Italy	2007
Paintings in the Church of Vendel	Vendel – Sweden	2007-2008
Mural paintings in the Aztec site of Tlatelolco	Mexico Ciy – Mexico	2007-2008
Mural paintings in the "Annunciazione" Chapel	Nazareth – Israel	2008
Mural paintings in the Aztec site of Cholula	Cholula - Mexico	2008

6.2.2. Nanorestore Safety Sheet



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SAFETY DATA SHEET
Regulation (EC) N. 1907/2006 - REACH

---

1. PRODUCT AND COMPANY IDENTIFICATION

Product name: **NANORESTORE®** Product code: **01105901**
Revision date: **31/03/2008** Version: **1**
Description/use: **Nano-lime dispersion in denatured isopropyl alcohol**

Manufacturer: **Consorzio CSGI-Università degli Studi di Firenze**
Brevetto Italiano n° FI/96/A/000255, 31/10/1996

Distributor: **C.T.S. S.r.l. - Via Piave N. 20/22 - 36077 ALTAVILLA VICENTINA (VI) – ITALIA**
Tel. 0444/349088 Fax: 0444/349039
E-mail address: **cts.italia@ctseurope.com**

Emergency telephone: **+39/0444/349088**

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2. HAZARDS IDENTIFICATION

The preparation is classified as hazardous according to the provisions in Directives 67/548/EEC and 1999/45/EC and following amendments and adjustments. Therefore, this product requires a safety data sheet in compliance with the provisions of Directive 91/155/EC and following amendments. Further information on the risks to health and/or the environment are given in sections 11 and 12 of the present sheet.

Hazard symbols: F - Xi
R phrases: R11 – R36 - R41 – R67
S phrases: 26 – 39

The product, according to its chemical-physical characteristics, is considered to be highly flammable (flash point below 21℃).
IRRITATING TO EYES.
VAPOURS MAY CAUSE DROWSINESS AND DIZZINESS.
RISK OF SERIOUS DAMAGE TO EYES (limited to the only basic component $Ca(OH)_2$ - however in % by weight very small amounting to a maximum of 1.0%).

---

3. COMPOSITION/INFORMATION ON INGREDIENTS

Component Name	EC-No.	CAS-No.	%	Symbol	R Phrases
Isobutyl alcohol	201-148-0	78-83-1	4-4,5	Xi	R10 R67 R37/38 R41
2-Propanol	200-661-7	67-63-0	94-98	F, Xi	R67 R11 R36
Calcium hydroxide	215-137-3	1305-62-0	0,2-1,0	Xi	R41

The full text of the risk phrases (R) is mentioned in Section 16 of this sheet.

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4. FIRST-AID MEASURES

In case of eye contact: Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician immediately.
In case of skin contact: Wash thoroughly with water. Take off contaminated clothing. If irritation persists, consult a physician. Wash contaminated clothing before reuse.
If inhaled: Move the person to fresh air. If breathing is difficult, consult a doctor. If the person is not breathing, apply artificial respiration. If breathing is difficult, give oxygen.
If swallowed: Rinse mouth with water provided person is conscious. Consult a doctor immediately. Induce vomiting only if indicated by the doctor. Never give anything by mouth to an unconscious person unless authorized by the physician.

5. FIRE-FIGHTING MEASURES

Closed containers exposed to heat from fire may build pressure and explode. For information on risks for the environment and health, respiratory protection, ventilation and personal protection equipment, refer to the other sections of this sheet.
Extinguishing media: CO_2, foam, chemical powder for flammable liquids. Water may not be effective to extinguish the fire, nevertheless it should be used to cool containers exposed to flames and prevent fires and explosions. For leakage and spillage that have not caught fire, nebulized water may be used to disperse the flammable vapours and protect the people involved in stopping the leakage.
Equipment: Wear equipment complete with helmet and face shield and protection of the neck, self breathing apparatus at pressure or demand, fireproof jacket and trousers, with bands around the arms legs and waist.
SPECIAL RISKS
Specific risk/s: emits toxic fumes in case of fire.

6. ACCIDENTAL RELEASE MEASURES

Remove all sources of ignition. Cover with inert absorbent material. Collect spilled material with non-sparking tools. Use water only to remove residuals, so as to avoid the danger of discharging the product into sewers. Do not let the product dry. Contaminated clothing should be left to soak in water before washing. For the selection of the safety measures and protection equipment, please see the other sections of this sheet. Spillage in waters: remove the liquid from the surface with flameproof or manual pumps or suitable absorbent material. If legally permitted, in water bodies resort to sinking and/or to dispersion of the product with suitable substances.
PROCEDURE/S OF PERSONAL PROTECTION
Wear respirator, safety goggles, rubber boots and heavy rubber gloves.

7. HANDLING AND STORAGE

Avoid the accumulation of electrostatic charges. Store in sealed containers and in well-ventilated areas. Vapours may ignite with explosion. It is necessary therefore to avoid accumulation keeping the windows and doors open, ensuring crossventilation. Without adequate ventilation, the vapours may accumulate at the bottom and ignite at a distance, if triggered off, with the risk of backfiring. Keep far away from sources of heat, sparks and flames.

Do not smoke, use matches or lighters. Ground containers during transfer operations and wear antistatic boots. Vigorous stirring and flow of the liquid in the pipes and equipment may cause the formation and accumulation of electrostatic charges due to the low conductivity of the product. To avoid the danger of fire and explosion, never use compressed air during movement. Open containers with caution, because they may be under pressure.

Do not inhale the product. Avoid contact with eyes, skin and clothing. Avoid prolonged or repeated exposure.

STORAGE

Storage conditions: Keep tightly closed.

8. EXPOSURE CONTROLS / PERSONAL PROTECTION

Exposure limits:

Description	Type	TWA/8 hour		STEL/15 min	
		Mg/m3	ppm	Mg/m3	ppm
Isobutyl alcohol	TLV-ACGIH	152	-	-	-
2-Propanol	TLV-ACGIH	491	-	982	-
Calcium hydroxide	TLV-ACGIH	5 (dust)	-	-	-

TLV of the solvent mixture: 451 mg/m^3

To minimize exposure, use personal protection equipment appropriate to the specific process, such as: masks suitable for the product, goggles, gloves and overalls. Do not eat, drink or smoke while handling the product; wash your hands thoroughly with soap and water before meals and at the end of your shift.

Type of protection for the respiratory tract: mask with filter type "A" (brown - for organic solvents) or otherwise suitable for the product.

9. PHYSICAL AND CHEMICAL PROPERTIES

Colour:	opalescent white
Odour:	characteristic
Physical state:	dispersion of a solid in a liquid
Solubility:	soluble in water
Viscosity:	2,75 cP
Vapour density:	N.A.
Evaporation rate:	N.A.
Oxidising properties:	N.A.
Partition coefficient: n-octanol/water:	N.A.
pH:	N.A.
Boiling point:	< 120°C
Melting point:	< -20°C
Flash point:	> 13°C
Lower explosion limit:	2% (v/v)
Upper explosion limit:	12% (v/v)
Ignition temperature:	> 250°C
Vapour pressure:	42 hPa a 20°C
Distillation range:	81 – 120°C
Molecular weight:	60,661
Specific gravity:	0,792 kg/l at 20°C
VOC (Directive 1999/13/EC):	100,00% - 785,00 g/l of substance
VOC (volatile carbon):	60,09% - 471,74 g/l of substance

10. STABILITY AND REACTIVITY

The product is stable in normal conditions of use and storage. Due to heat or in the event of fire carbon oxides and vapours potentially dangerous to health may be released. Vapours may form explosive mixtures with air. Reacts violently with strong oxidizing agents.
Conditions of instability: Absorbs carbon dioxide from the atmosphere. Materials to avoid: Strong acids. Hazardous decomposition products: Calcium oxide.

11. TOXICOLOGICAL INFORMATION

Acute effects: contact with eyes causes irritation but also serious damage to eyes; symptoms may include: redness, swelling, pain and tearing. Inhalation of vapours may cause moderate irritation of the upper respiratory tract; contact with the skin may cause slight irritation. Ingestion may cause health problems, including stomach pain and sting, nausea and vomiting. The product contains highly volatile substances, which may cause serious depression of the central nervous system (CNS), with effects such as drowsiness, dizziness, loss of reflexes, narcosis.

ISOBUTYL ALCOHOL: oral LD50 (mg/kg) 2460 (rat); dermal LD50 (mg/kg) 2460 (rabbit); inhalation LC50 (rat) 19.2 mg/1/4 hours.
2-PROPANOL: oral LD50 (mg/kg) 12800 (rat); dermal LD50 (mg/kg) 12800 (rat); inhalation LC50 (rat) 72.6 mg/l/4 hours.
CALCIUM HYDROXIDE: oral LD50 (mg/kg) 7340 (rat); oral LD50 (mg/kg) 7300 (mouse); RTECS DATA ON IRRITATION: rabbit skin 10% Notes: No irritating effect. Rabbit eyes Notes: Corrosive. Rabbit eyes 10 mg Notes: Severe irritation effect. CHRONIC EXPOSURE – MUTAGENIC EFFECT rat 1200 mg/kg Cell Type: ascetic tumor Cytogenetic analysis.

12. ECOLOGICAL INFORMATION

Use this product according to good working practices, avoiding littering. Inform the competent authorities, should the product reach waterways or sewers or contaminate soil or vegetation.

13. DISPOSAL CONSIDERATIONS

Consider the possibility of burning the product in a suitable incinerator equipped with post-combustion system and scrubber. Acid or basic products must always be neutralized before undergoing any treatment, including biological treatment whenever feasible. If the waste is solid, it can be disposed in a landfill provided local technical regulations are observed. Empty containers, after proper washing, are to be treated in the same way as the contents. Never discharge to sewers or surface water or groundwater. Observe all Federal, State, and Local Environmental regulations.

14. TRANSPORT INFORMATION

These goods must be transported by vehicles authorized to the carriage of dangerous goods according to the provisions set out in the current edition of the Code of International Carriage of Dangerous Goods by Road (ADR) and in all the applicable national regulations.

These goods must be packed in their original packagings or in packagings made of materials resistant to their content and not reacting dangerously with it. People loading and unloading dangerous goods must be trained on all the risks deriving from these substances and on all actions that must be taken in case of emergency situations.

Road and rail transport:

ADR/RID Class: 3	N. UN: 1993	Packing Group: II	Label: 3
Nr. Kemler: 33	Proper Shipping Name: FLAMMABLE LIQUID, N.O.S.		

Transport by sea:

IMO Class: 3	N. UN: 1993	Packing Group: II	Label: 3
EMS: F-E, S-E	Proper Shipping Name: FLAMMABLE LIQUID, N.O.S.		

Transport by air:

IATA: 3	N. UN: 1993	Packing Group: II	Label: 3

---

15. REGULATORY INFORMATION

Health hazard symbol:	Xi	IRRITATING
Physical hazard symbol:	F	HIGHLY FLAMMABLE

R11 - Highly flammable.
R36 - Irritating to eyes.
R41 Risk of serious damage to eyes.
R67 - Vapours may cause drowsiness and dizziness.

S7/9 - Keep container tightly closed in a well-ventilated place.
S16 - Keep away from sources of ignition – No smoking.
S25 - Avoid contact with eyes.
S26 - In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S33 - Take precautionary measures against static discharges.
S39 - Wear eye/face protection.

Danger labeling according to 67/548/EEC and 1999/45/EC directives and following amendments and adjustments. Workers exposed to this chemical agent dangerous to health must undergo health checks carried out in accordance with the provisions of Article 72-decies of Legislative Decree No. 25 of February 2, 2002.

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16. OTHER INFORMATION

Text of Risk (R) phrases mentioned in section 3 of the present sheet:

R10 - Flammable.
R11 - Highly flammable.
R36 - Irritating to eyes.
R37/38 - Irritating to respiratory system and to skin.
R41 - Risk of serious damage to eyes
R67 - Vapours may cause drowsiness and dizziness.

GENERAL BIBLIOGRAPGY:

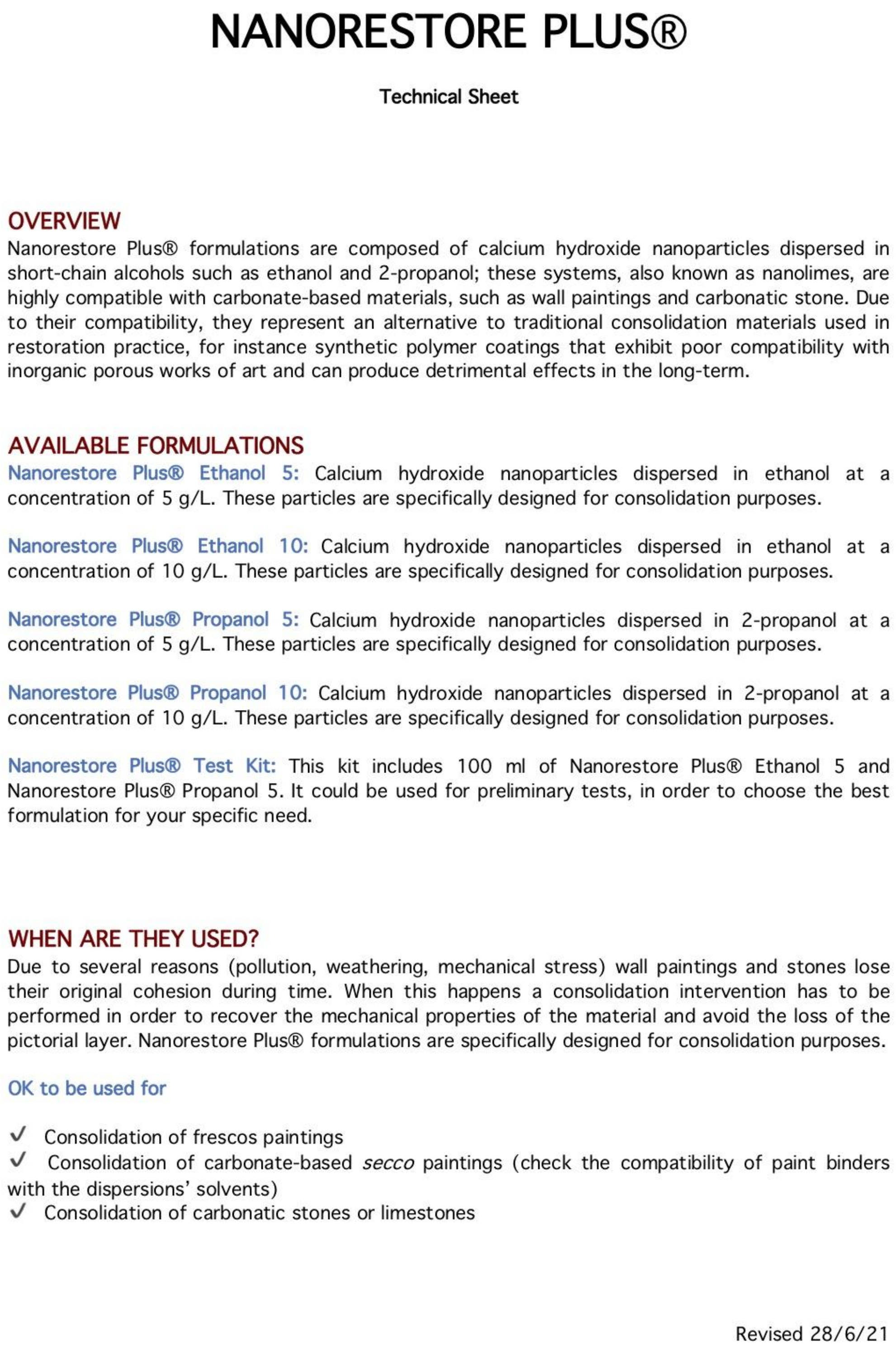
1. Directive 1999/45/CE and following amendments
2. Directive 67/548/CEE and following amendments and adjustments (XXIX technical adjustment)
3. Regulation (EC) 1907/2006 of the European Parliament (REACH)
4. The Merck Index. Ed.10
5. Handling Chemical Safety
6. Niosh - Registry of Toxic Effetcs of Chemical Substances
7. INRS - Fiche Toxicologique
8. Patty - Industrial Hygiene and Toxicology
9. N.I. Sax - Dangerous properties of Industrial Materials-7 Ed., 1989

Changes to previous review:
The following sections were modified: 3 8 9 10 11 16.

The information contained in the present sheet are based on our knowledge on the date of the last version. Users must verify the suitability and thoroughness of provided information according to each specific use of the product. This document must not be regarded as a guarantee on any specific product property. The use of this product is not subject to our direct control; therefore, users must, under their own responsibility, comply with the current health and safety laws and regulations. The producer is relieved from any liability arising from improper uses.

Issue date: 08/05/2008

6.2.3. Nanorestore Plus Technical Sheet



NANORESTORE PLUS®

Technical Sheet

OVERVIEW

Nanorestore Plus® formulations are composed of calcium hydroxide nanoparticles dispersed in short-chain alcohols such as ethanol and 2-propanol; these systems, also known as nanolimes, are highly compatible with carbonate-based materials, such as wall paintings and carbonatic stone. Due to their compatibility, they represent an alternative to traditional consolidation materials used in restoration practice, for instance synthetic polymer coatings that exhibit poor compatibility with inorganic porous works of art and can produce detrimental effects in the long-term.

AVAILABLE FORMULATIONS

Nanorestore Plus® Ethanol 5: Calcium hydroxide nanoparticles dispersed in ethanol at a concentration of 5 g/L. These particles are specifically designed for consolidation purposes.

Nanorestore Plus® Ethanol 10: Calcium hydroxide nanoparticles dispersed in ethanol at a concentration of 10 g/L. These particles are specifically designed for consolidation purposes.

Nanorestore Plus® Propanol 5: Calcium hydroxide nanoparticles dispersed in 2-propanol at a concentration of 5 g/L. These particles are specifically designed for consolidation purposes.

Nanorestore Plus® Propanol 10: Calcium hydroxide nanoparticles dispersed in 2-propanol at a concentration of 10 g/L. These particles are specifically designed for consolidation purposes.

Nanorestore Plus® Test Kit: This kit includes 100 ml of Nanorestore Plus® Ethanol 5 and Nanorestore Plus® Propanol 5. It could be used for preliminary tests, in order to choose the best formulation for your specific need.

WHEN ARE THEY USED?

Due to several reasons (pollution, weathering, mechanical stress) wall paintings and stones lose their original cohesion during time. When this happens a consolidation intervention has to be performed in order to recover the mechanical properties of the material and avoid the loss of the pictorial layer. Nanorestore Plus® formulations are specifically designed for consolidation purposes.

OK to be used for

- ✓ Consolidation of frescos paintings
- ✓ Consolidation of carbonate-based *secco* paintings (check the compatibility of paint binders with the dispersions' solvents)
- ✓ Consolidation of carbonatic stones or limestones

Revised 28/6/21

× *For different applications, it is advised to contact us for assistance. We will be glad to help you in finding the best solution for your conservative need.*

E-mail: *products@csgi.unifi.it*

HOW DO THEY WORK?

Calcium hydroxide nanoparticles of Nanorestore Plus® formulations penetrate into the pores and cracks of the artifacts, where they act as a binder for the de-cohered layers and powdering surface of the works of art by turning into calcium carbonate through the reaction with atmospheric CO_2. The carbonation process is highly favored by the nanosize of the particles.

HOW ARE THEY USED?

General features

Nanorestore Plus® formulations, composed of calcium hydroxide nanoparticles dispersed in short-chain alcohols, i.e., ethanol and 2-propanol, are systems specifically designed for the consolidation intervention on carbonate-based mural paintings and stone artifacts.

Storage

Nanorestore Plus® dispersions are shipped in HPDE bottles, which should be kept firmly closed to prevent the contact between calcium hydroxide nanoparticles and air, to avoid the clustering of particles and their carbonation. The contact between nanoparticles dispersions and humidity has to be avoided too. Water doesn't affect the effectiveness of Nanorestore Plus®, but it may cause changes in nanoparticles size. Bigger particles than the ones originally present may result in white haze on the treated surfaces, which has to be promptly removed. Nanorestore Plus® formulations contains no additives and are formulated to prevent sedimentation. Even though, after long storage, it is recommended to shake energetically the dispersion before use.

Safety

Nanorestore Plus® dispersions should be handled with care, following the same standard operating procedure recommended for ethanol and 2-propanol. Therefore, the formulations must be used in the presence of good air ventilation, and should be handled wearing googles and gloves. Nanorestore Plus® dispersions cannot be used in presence of open flames, sparks, and hot surfaces.

Preliminary tests

Before the application of Nanorestore Plus® dispersions, preliminary test should be carried out to evaluate the conservation status of the artifact that needs to be consolidated. In particular, the presence of sulfates must be evaluated. Their presence could hamper the consolidation action Nanorestore Plus® formulations. Therefore, in case of sulfate pollution, their removal should be carried out before the consolidation intervention.

Dilution (optional)

Nanorestore Plus® dispersions are available at a concentration of 5 g/L or 10 g/L. It is worth noting that for standard applications, a concentration of 2.5 g/L is advisable. In the case of low porous substrate, white hazes can be seen on treated surface. To avoid the formation of these hazes, each Nanorestore Plus® dispersion can be diluted to the appropriate concentration by using the corresponding pure and anhydrous solvent (it is important that the chosen solvent does not contain water).

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Product consumption

Considering that several factors affect product consumption, it is hard to predict the amount of dispersion needed for a standard intervention. Based on available data, it can be said that, for the consolidation of wall paintings, 1L of Nanorestore Plus® Ethanol 5 or Propanol 5 can be used for 5-10 m^2 of pictorial surface.

Pre-treatment of the surface

A consolidation intervention should be performed on surfaces free from detrimental coatings, such as polymers, glues and fixatives, which could hinder nanoparticles penetration. For the removal of undesired coatings, please refer to the Technical Sheet of Nanorestore Cleaning® formulations.
Pre-treatment of the surface to be treated is required when the substrate contains large amount of moisture or is wet. In this case, the application of alcohol could help in drying the substrate, favoring the penetration of nanoparticles (**Fig. 1.1**).

Application

Nanorestore Plus® formulations are usually applied on the surface to be consolidated by brushing (**Fig. 1.2**) or by spraying (**Fig. 2.1**). In the case of brushing, the usage of a Japanese paper sheet, having a grammage of 9 g/m^2 is recommended. The spraying of Nanorestore Plus® dispersion should be carried out on fragile, flaking, degraded surfaces, which cannot tolerate mechanical stresses. The dispersion should be applied until the matrix seems completely full with the product (**Fig. 1.3**); after the evaporation of the alcohol, a second application can be carried out. As a general rule, it is advisable to perform several application (up to 10-12) with less concentrated dispersion than one or two application with more concentrated systems.

After the application

Right after the application of Nanorestore Plus® dispersions, a cellulose poultice soaked with distilled water should be applied over Japanese paper on the treated surface and removed only when dry (**Fig. 1.4 - 1.7**). The cellulose pulp compress prevents the formation of white haze and favors the carbonation of nanoparticles.

Assess consolidation effectiveness

For the assessment of consolidation effectiveness it is recommended to wait for one month after the application of Nanorestore Plus® dispersions. As a matter of fact, full carbonation may require, depending on the environmental conditions, from 2 to 4 weeks.

APPLICATION GUIDELINES AT A GLANCE

Goggles	Yes
Gloves	Yes
Ventilated hood or environment	Recommended
Application methods	If possible, dispersions should be applied by brushing over Japanese paper. On very fragile surfaces, spraying of dispersion is preferable

Revised 28/6/21

After treatment	After the consolidation, a cellulose pulp poultice soaked with distilled water should be applied with the aim of favoring carbonation of particles and hindering the formation of white hazes

FIGURES

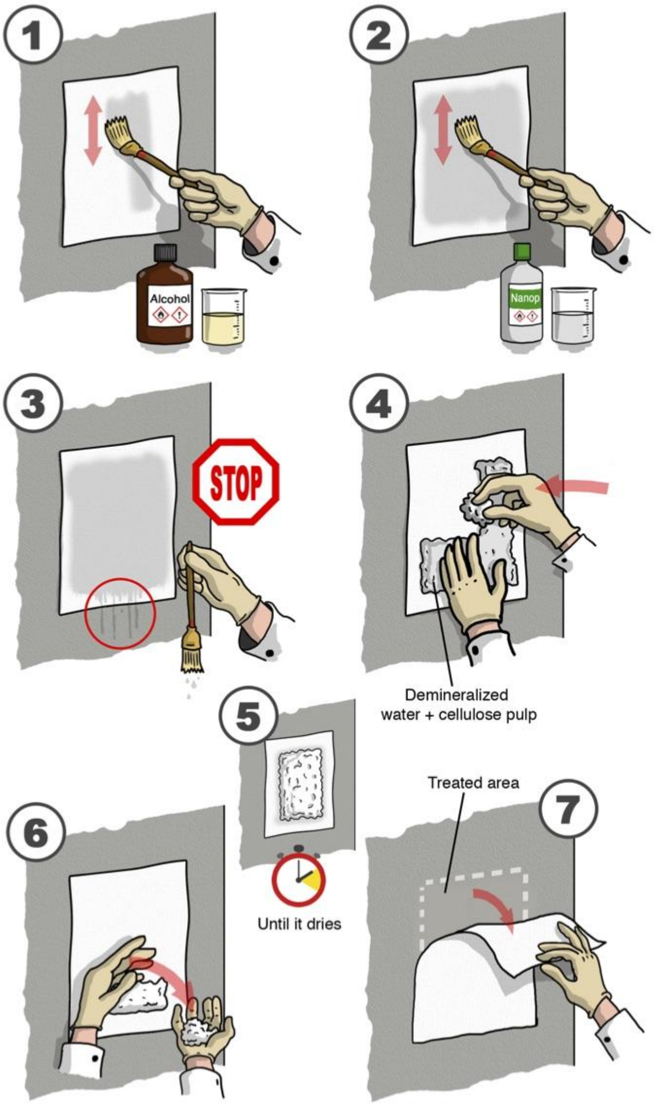

Figure 1. Application of Nanorestore Plus® by brushing.
(1) Pre-treatment with alcohol, if the substrate is wet or contains moisture. (A sheet of Japanese paper is interposed between the brush and the substrate).
(2) Application of the dispersion using a brush over a Japanese paper sheet.
(3) Stop when the substrate is completely wet. (Several applications can be carried out).
(4) Application of a humid (not dripping) cellulose pulp poultice.
(5) Let the poultice dry.
(6) Remove the dried poultice.
(7) Gently remove the Japanese paper sheet.

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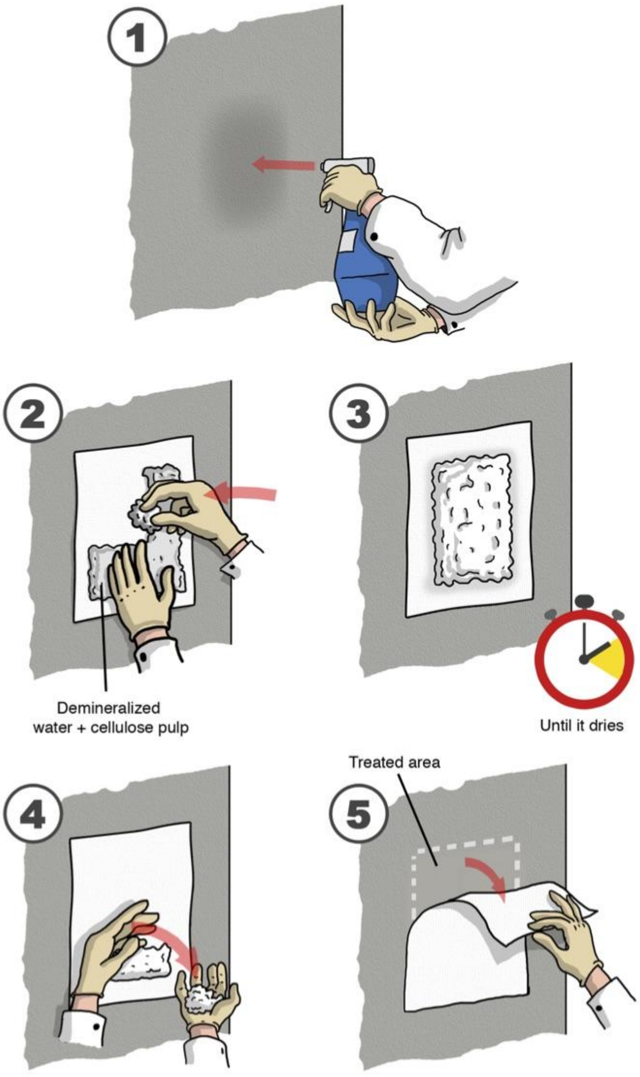


Figure 2. Application of Nanorestore Plus® by spraying.
(1) Application of the dispersion by spraying.
(2) Application of a humid (not dripping) cellulose pulp poultice.
(3) Let the poultice dry.
(4) Remove the dried poultice.
(5) Gently remove the Japanese paper sheet.

FREQUENTLY ASKED QUESTIONS

Q After the consolidation intervention with Nanorestore Plus® dispersions, I applied a humid cellulose pulp compress, as suggested. Even though, on the treated surface a white haze is present. How can I remove it?

A Gentle mechanical action by means of a brush soaked with the same alcohol of the applied dispersion can help in removing white hazes. In case white haze persists, the application of another cellulose pulp compressed soaked with distilled water left for few hours is recommended.

REFERENCES

Further information can be found in the following textbooks:

1. Piero Baglioni and David Chelazzi. *Nanoscience for the Conservation of Works of Art*. Royal Society of Chemistry, 2013.

2. Piero Baglioni, David Chelazzi and Rodorico Giorgi. *Nanotechnologies in the Conservation of Cultural Heritage: A Compendium of Materials and Techniques*. Springer, 2014.

For technical questions:

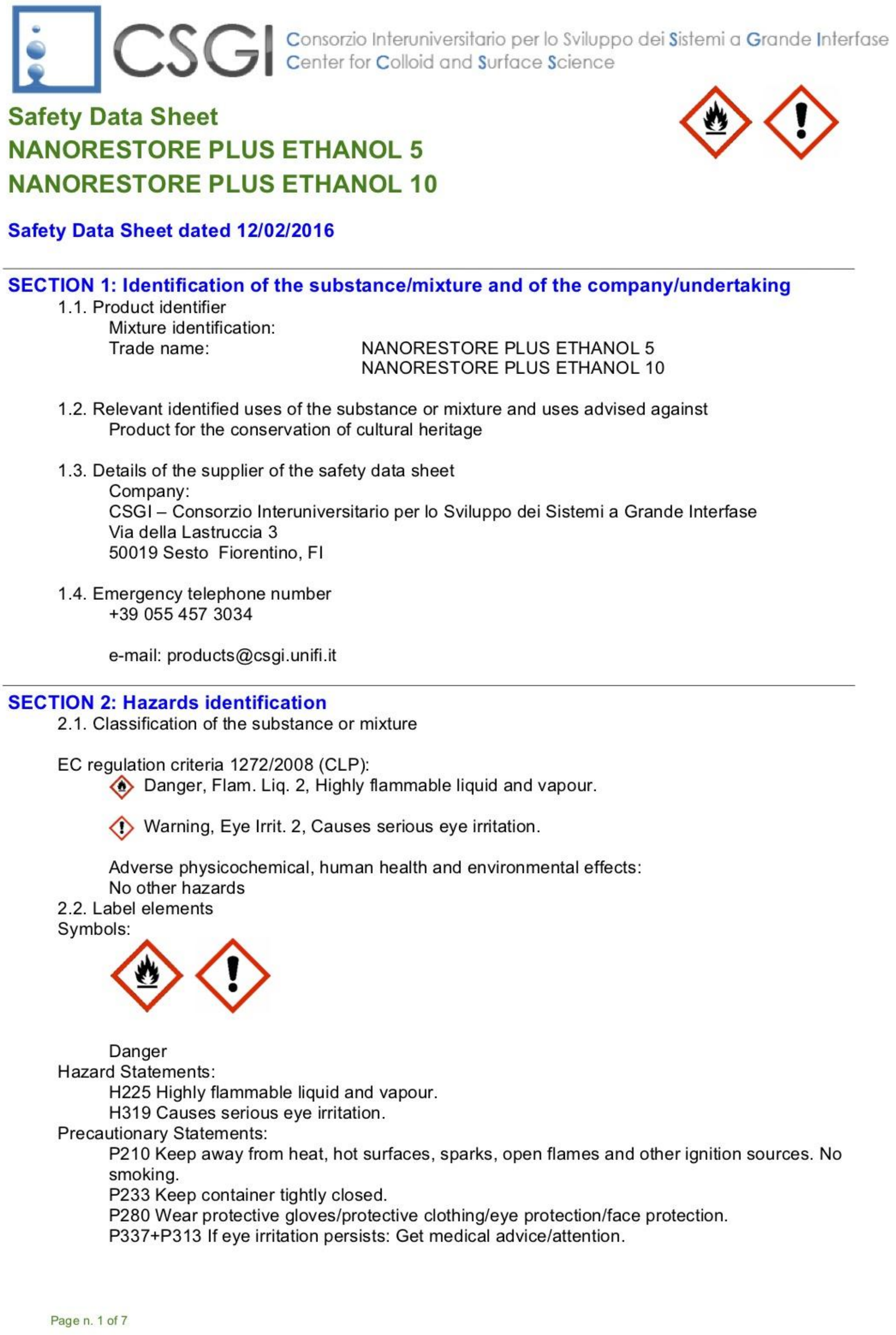
assistance@csgi.unifi.it

For placing an order or for administrative support:

products@csgi.unifi.it

Revised 28/6/21

6.2.4. Nanorestore Plus Safety Sheet



CSGI Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase
Center for Colloid and Surface Science

Safety Data Sheet
NANORESTORE PLUS ETHANOL 5
NANORESTORE PLUS ETHANOL 10

Safety Data Sheet dated 12/02/2016

SECTION 1: Identification of the substance/mixture and of the company/undertaking

1.1. Product identifier

Mixture identification:	
Trade name:	NANORESTORE PLUS ETHANOL 5 NANORESTORE PLUS ETHANOL 10

1.2. Relevant identified uses of the substance or mixture and uses advised against
Product for the conservation of cultural heritage

1.3. Details of the supplier of the safety data sheet
Company:
CSGI – Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase
Via della Lastruccia 3
50019 Sesto Fiorentino, FI

1.4. Emergency telephone number
+39 055 457 3034

e-mail: products@csgi.unifi.it

SECTION 2: Hazards identification

2.1. Classification of the substance or mixture

EC regulation criteria 1272/2008 (CLP):
Danger, Flam. Liq. 2, Highly flammable liquid and vapour.

Warning, Eye Irrit. 2, Causes serious eye irritation.

Adverse physicochemical, human health and environmental effects:
No other hazards

2.2. Label elements
Symbols:

Danger

Hazard Statements:
H225 Highly flammable liquid and vapour.
H319 Causes serious eye irritation.

Precautionary Statements:
P210 Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P233 Keep container tightly closed.
P280 Wear protective gloves/protective clothing/eye protection/face protection.
P337+P313 If eye irritation persists: Get medical advice/attention.

Page n. 1 of 7

P370+P378 In case of fire: Use CO_2, foam, chemical powder for flammable liquids to extinguish.
P501 Dispose of contents/container in accordance with applicable regulations.

Special Provisions:
None

Special provisions according to Annex XVII of REACH and subsequent amendments:
None

2.3. Other hazards
vPvB Substances: None - PBT Substances: None
Other Hazards:
No other hazards

SECTION 3: Composition/information on ingredients

3.1. Substances
N.A.
3.2. Mixtures
Hazardous components within the meaning of EEC directive 67/548 and CLP regulation and corresponding classification:

>= 75% ethanol
603-002-00-5, CAS: 64-17-5, EC: 200-578-6
F; R11; substance with a Community workplace exposure limit
2.6/2 Flam. Liq. 2 H225

>= 1% - < 2.5% Calcium Hydroxide
CAS: 1305-62-0, EC: 215-137-3
Xi; R37/38-41
3.2/2 Skin Irrit. 2 H315

3.3/1 Eye Dam. 1 H318

3.8/3 STOT SE 3 H335

SECTION 4: First aid measures

4.1. Description of first aid measures
In case of skin contact:
Wash with plenty of water and soap.
In case of eyes contact:
In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
In case of Ingestion:
Do not under any circumstances induce vomiting. OBTAIN A MEDICAL EXAMINATION IMMEDIATELY.
In case of Inhalation:
Remove casualty to fresh air and keep warm and at rest.
4.2. Most important symptoms and effects, both acute and delayed
None

4.3. Indication of any immediate medical attention and special treatment needed
Treatment:
None

SECTION 5: Firefighting measures

5.1. Extinguishing media
Suitable extinguishing media:
CO_2 or Dry chemical fire extinguisher.
Extinguishing media which must not be used for safety reasons:
None in particular.

5.2. Special hazards arising from the substance or mixture
Do not inhale explosion and combustion gases.
Burning produces heavy smoke.

5.3. Advice for firefighters
Use suitable breathing apparatus .
Collect contaminated fire extinguishing water separately. This must not be discharged into drains.
Move undamaged containers from immediate hazard area if it can be done safely.

SECTION 6: Accidental release measures

6.1. Personal precautions, protective equipment and emergency procedures
Wear personal protection equipment.
Remove all sources of ignition.
Remove persons to safety.
See protective measures under point 7 and 8.

6.2. Environmental precautions
Do not allow to enter into soil/subsoil. Do not allow to enter into surface water or drains.
Retain contaminated washing water and dispose it.
In case of gas escape or of entry into waterways, soil or drains, inform the responsible authorities.
Suitable material for taking up: absorbing material, organic, sand

6.3. Methods and material for containment and cleaning up
Wash with plenty of water.

6.4. Reference to other sections
See also section 8 and 13

SECTION 7: Handling and storage

7.1. Precautions for safe handling
Avoid contact with skin and eyes, inhalation of vapours and mists.
Don't use empty container before they have been cleaned.
Before making transfer operations, assure that there aren't any incompatible material residuals in the containers.
Contamined clothing should be changed before entering eating areas.
Do not eat or drink while working.
See also section 8 for recommended protective equipment.

7.2. Conditions for safe storage, including any incompatibilities
Always keep the containers tightly closed.
Keep away from unguarded flame, sparks, and heat sources. Avoid direct exposure to sunlight.
Keep away from food, drink and feed.
Incompatible materials:

None in particular.
Instructions as regards storage premises:
Cool and adequately ventilated.

7.3. Specific end use(s)
None in particular

SECTION 8: Exposure controls/personal protection

8.1. Control parameters
ethanol - CAS: 64-17-5
TLV TWA - ppm 1000 A4
TLV STEL - A4

8.2. Exposure controls
Eye protection:
Not needed for normal use. Anyway, operate according good working practices.
Protection for skin:
No special precaution must be adopted for normal use.
Protection for hands:
Not needed for normal use.
Respiratory protection:
Not needed for normal use.
Thermal Hazards:
None
Environmental exposure controls:
None

SECTION 9: Physical and chemical properties

9.1. Information on basic physical and chemical properties

Appearance and colour:	Milky liquid
Odour:	Characteristic
Odour threshold:	N.A.
pH:	11
Melting point / freezing point:	N.A.
Initial boiling point and boiling range:	78 °C
Solid/gas flammability:	N.A.
Upper/lower flammability or explosive limits:	3.5 Vol % - 15.0 Vol %
Vapour density:	N.A.
Flash point:	13 °C
Evaporation rate:	N.A.
Vapour pressure:	59 hPa
Density:	0.79 g/cm^3
Solubility in water:	Fully miscible
Solubility in oil:	N.A.
Partition coefficient (n-octanol/water):	-0.35 log POW
Ignition temperature:	425 °C
Decomposition temperature:	N.A.
Viscosity:	1.2 mPas
Explosive properties:	*Product is not explosive. However, formation of explosive air/vapour mixtures are possible.*
Oxidizing properties:	N.A.

9.2. Other information

Miscibility:	N.A.

Fat Solubility: N.A.
Conductivity: N.A.
Substance Groups relevant properties N.A.

SECTION 10: Stability and reactivity

10.1. Reactivity
Stable under normal conditions
10.2. Chemical stability
Stable under normal conditions
10.3. Possibility of hazardous reactions
None
10.4. Conditions to avoid
Stable under normal conditions.
10.5. Incompatible materials
Avoid contact with combustible materials. The product could catch fire.
10.6. Hazardous decomposition products
None.

SECTION 11: Toxicological information

11.1. Information on toxicological effects

ethanol - CAS: 64-17-5
LD50 (RABBIT) ORAL: 6300 MG/KG
LD50 (RAT) ORAL SINGLE DOSE: 7060 MG/KG

SECTION 12: Ecological information

12.1. Toxicity
Adopt good working practices, so that the product is not released into the environment.
N.A.
12.2. Persistence and degradability
None
N.A.
12.3. Bioaccumulative potential
N.A.
12.4. Mobility in soil
N.A.
12.5. Results of PBT and vPvB assessment
vPvB Substances: None - PBT Substances: None
12.6. Other adverse effects
None

SECTION 13: Disposal considerations

13.1. Waste treatment methods
Recover, if possible. Send to authorised disposal plants or for incineration under controlled conditions. In so doing, comply with the local and national regulations currently in force.

SECTION 14: Transport information

14.1. UN number
ADR- ONU: 1170

14.2. UN proper shipping name
ADR-Shipping Name: ETHANOL

14.3. Transport hazard class(es)
FLAMMABLE

14.4. Packing group
II

14.5. Environmental hazards
N.A.

14.6. Special precautions for user
N.A.

14.7. Transport in bulk according to Annex II of MARPOL73/78 and the IBC Code
Environmental Pollutant:
No

SECTION 15: Regulatory information

15.1. Safety, health and environmental regulations/legislation specific for the substance or mixture
Dir. 67/548/EEC (Classification, packaging and labelling of dangerous substances)
Dir. 99/45/EC (Classification, packaging and labelling of dangerous preparations)
Dir. 98/24/EC (Risks related to chemical agents at work)
Dir. 2000/39/EC (Occupational exposure limit values)
Dir. 2006/8/EC
Regulation (EC) n. 1907/2006 (REACH)
Regulation (EC) n. 1272/2008 (CLP)
Regulation (EC) n. 790/2009 (ATP 1 CLP) and (EU) n. 758/2013
Regulation (EU) n. 453/2010 (Annex I)
Regulation (EU) n. 286/2011 (ATP 2 CLP)
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15.2. Chemical safety assessment
No

SECTION 16: Other information

Text of phrases referred to under heading 3:
R11 Highly flammable.
R37/38 Irritating to respiratory system and skin.

R41 Risk of serious damage to eyes.

H225 Highly flammable liquid and vapour.
H315 Causes skin irritation.
H318 Causes serious eye damage.
H335 May cause respiratory irritation.

This document was prepared by a competent person who has received appropriate training.

Main bibliographic sources:

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Insert further consulted bibliography

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WGK:	German Water Hazard Class.

CSGI Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase
Center for Colloid and Surface Science

Safety Data Sheet
NANORESTORE PLUS PROPANOL 5
NANORESTORE PLUS PROPANOL 10

Safety Data Sheet dated 12/02/2016

SECTION 1: Identification of the substance/mixture and of the company/undertaking

1.1. Product identifier

Mixture identification:

Trade name:	NANORESTORE PLUS PROPANOL 5 NANORESTORE PLUS PROPANOL 10

1.2. Relevant identified uses of the substance or mixture and uses advised against

Product for the conservation of cultural heritage

1.3. Details of the supplier of the safety data sheet

Company:
CSGI – Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase
Via della Lastruccia 3
50019 Sesto Fiorentino, FI

1.4. Emergency telephone number

+39 055 457 3034

e-mail: products@csgi.unifi.it

SECTION 2: Hazards identification

2.1. Classification of the substance or mixture

EC regulation criteria 1272/2008 (CLP):

Danger, Flam. Liq. 2, Highly flammable liquid and vapour.

Warning, Eye Irrit. 2, Causes serious eye irritation.

Warning, STOT SE 3, May cause drowsiness or dizziness.

Adverse physicochemical, human health and environmental effects:
No other hazards

2.2. Label elements

Symbols:

Danger

Hazard Statements:

H225 Highly flammable liquid and vapour.
H319 Causes serious eye irritation.
H336 May cause drowsiness or dizziness.

Precautionary Statements:

P210 Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.

P233 Keep container tightly closed.
P280 Wear protective gloves/protective clothing/eye protection/face protection.
P312 Call a POISON CENTER/ doctor/if you feel unwell.
P337+P313 If eye irritation persists: Get medical advice/attention.
P370+P378 In case of fire: Use CO_2, foam, chemical powder for flammable liquids to extinguish.

Special Provisions:
None

Contents:
propan-2-ol

Special provisions according to Annex XVII of REACH and subsequent amendments:
None

2.3. Other hazards
vPvB Substances: None - PBT Substances: None

Other Hazards:
No other hazards

SECTION 3: Composition/information on ingredients

3.1. Substances
N.A.

3.2. Mixtures
Hazardous components within the meaning of EEC directive 67/548 and CLP regulation and corresponding classification:

>= 98% propan-2-ol
603-117-00-0, CAS: 67-63-0, EC: 200-661-7
F,Xi; R11-36-67
2.6/2 Flam. Liq. 2 H225

3.3/2 Eye Irrit. 2 H319

3.8/3 STOT SE 3 H336

>= 1% - < 2.5% Calcium Hydroxide
CAS: 1305-62-0, EC: 215-137-3
Xi; R37/38-41
3.2/2 Skin Irrit. 2 H315

3.3/1 Eye Dam. 1 H318

3.8/3 STOT SE 3 H335

SECTION 4: First aid measures

4.1. Description of first aid measures
In case of skin contact:
Immediately take off all contaminated clothing.

Areas of the body that have - or are only even suspected of having - come into contact with the product must be rinsed immediately with plenty of running water and possibly with soap.
Wash thoroughly the body (shower or bath).
Remove contaminated clothing immediately and dispose off safely.

In case of eyes contact:

After contact with the eyes, rinse with water with the eyelids open for a sufficient length of time, then consult an opthalmologist immediately.
Protect uninjured eye.

In case of Ingestion:

Do not under any circumstances induce vomiting. OBTAIN A MEDICAL EXAMINATION IMMEDIATELY.

In case of Inhalation:

After contact with skin, wash immediately with soap and plenty of water.

4.2. Most important symptoms and effects, both acute and delayed

None

4.3. Indication of any immediate medical attention and special treatment needed

In case of accident or unwellness, seek medical advice immediately (show directions for use or safety data sheet if possible).
Treatment:
None

SECTION 5: Firefighting measures

5.1. Extinguishing media

Suitable extinguishing media:
CO2 or Dry chemical fire extinguisher.
Extinguishing media which must not be used for safety reasons:
None in particular.

5.2. Special hazards arising from the substance or mixture

Do not inhale explosion and combustion gases.
Burning produces heavy smoke.

5.3. Advice for firefighters

Use suitable breathing apparatus .
Collect contaminated fire extinguishing water separately. This must not be discharged into drains.
Move undamaged containers from immediate hazard area if it can be done safely.

SECTION 6: Accidental release measures

6.1. Personal precautions, protective equipment and emergency procedures

Wear personal protection equipment.
Remove all sources of ignition.
Remove persons to safety.
See protective measures under point 7 and 8.

6.2. Environmental precautions

Do not allow to enter into soil/subsoil. Do not allow to enter into surface water or drains.
Retain contaminated washing water and dispose it.
In case of gas escape or of entry into waterways, soil or drains, inform the responsible authorities.
Suitable material for taking up: absorbing material, organic, sand

6.3. Methods and material for containment and cleaning up

Wash with plenty of water.

6.4. Reference to other sections

See also section 8 and 13

SECTION 7: Handling and storage

7.1. Precautions for safe handling

Avoid contact with skin and eyes, inhalation of vapours and mists.
Don't use empty container before they have been cleaned.
Before making transfer operations, assure that there aren't any incompatible material residuals in the containers.
Contamined clothing should be changed before entering eating areas.
Do not eat or drink while working.
See also section 8 for recommended protective equipment.

7.2. Conditions for safe storage, including any incompatibilities

Always keep the containers tightly closed.
Keep away from unguarded flame, sparks, and heat sources. Avoid direct exposure to sunlight.
Keep away from food, drink and feed.
Incompatible materials:
None in particular.
Instructions as regards storage premises:
Cool and adequately ventilated.

7.3. Specific end use(s)

None in particular

SECTION 8: Exposure controls/personal protection

8.1. Control parameters

propan-2-ol - CAS: 67-63-0
TLV TWA - ppm 200 A4
TLV STEL - ppm 400 A4

8.2. Exposure controls

Eye protection:
Use close fitting safety goggles, don't use eye lens.

Protection for skin:
No special precaution must be adopted for normal use.

Protection for hands:
Use protective gloves that provides comprehensive protection, e.g. P.V.C., neoprene or rubber.

Respiratory protection:
Use adequate protective respiratory equipment.

Thermal Hazards:
None

Environmental exposure controls:
None

SECTION 9: Physical and chemical properties

9.1. Information on basic physical and chemical properties

Appearance and colour: Milky liquid
Odour: Characteristic
Odour threshold: N.A.
pH: 11
Melting point / freezing point: -89.5 °C

Initial boiling point and boiling range: 82 °C
Solid/gas flammability: N.A.
Upper/lower flammability or explosive limits: 2 Vol % - 12 Vol %
Vapour density: N.A.
Flash point: 12 °C
Evaporation rate: N.A.
Vapour pressure: 43 hPa (at 20 °C)
Density: 0.785 g/cm^3
Solubility in water: 1 g/L
Solubility in oil: N.A.
Partition coefficient (n-octanol/water): N.A.
Ignition temperature: 425 °C
Decomposition temperature: N.A.
Viscosity: 2.43 mPas
Explosive properties: N.A.
Oxidizing properties: N.A.

9.2. Other information

Miscibility: N.A.
Fat Solubility: N.A.
Conductivity: N.A.
Substance Groups relevant properties N.A.

SECTION 10: Stability and reactivity

10.1. Reactivity

Stable under normal conditions

10.2. Chemical stability

Stable under normal conditions

10.3. Possibility of hazardous reactions

None

10.4. Conditions to avoid

Stable under normal conditions.

10.5. Incompatible materials

Avoid contact with combustible materials. The product could catch fire.

10.6. Hazardous decomposition products

None.

SECTION 11: Toxicological information

11.1. Information on toxicological effects

N.A.

SECTION 12: Ecological information

12.1. Toxicity

Adopt good working practices, so that the product is not released into the environment.
N.A.

12.2. Persistence and degradability

None
N.A.

12.3. Bioaccumulative potential

N.A.
12.4. Mobility in soil
N.A.
12.5. Results of PBT and vPvB assessment
vPvB Substances: None - PBT Substances: None
12.6. Other adverse effects
None

SECTION 13: Disposal considerations

13.1. Waste treatment methods
Recover, if possible. Send to authorised disposal plants or for incineration under controlled conditions. In so doing, comply with the local and national regulations currently in force.

SECTION 14: Transport information

14.1. UN number
ADR- ONU: 1219
14.2. UN proper shipping name
ADR-Shipping Name: ISOPROPANOL
14.3. Transport hazard class(es)
FLAMMABLE
14.4. Packing group
II
14.5. Environmental hazards
N.A.
14.6. Special precautions for user
N.A.
14.7. Transport in bulk according to Annex II of MARPOL73/78 and the IBC Code
Environmental Pollutant:
No

SECTION 15: Regulatory information

15.1. Safety, health and environmental regulations/legislation specific for the substance or mixture
Dir. 67/548/EEC (Classification, packaging and labelling of dangerous substances)
Dir. 99/45/EC (Classification, packaging and labelling of dangerous preparations)
Dir. 98/24/EC (Risks related to chemical agents at work)
Dir. 2000/39/EC (Occupational exposure limit values)
Dir. 2006/8/EC
Regulation (EC) n. 1907/2006 (REACH)
Regulation (EC) n. 1272/2008 (CLP)
Regulation (EC) n. 790/2009 (ATP 1 CLP) and (EU) n. 758/2013
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Paragraphs modified from the previous revision:

SECTION 2: Hazards identification
SECTION 3: Composition/information on ingredients
SECTION 4: First aid measures
SECTION 8: Exposure controls/personal protection
SECTION 11: Toxicological information

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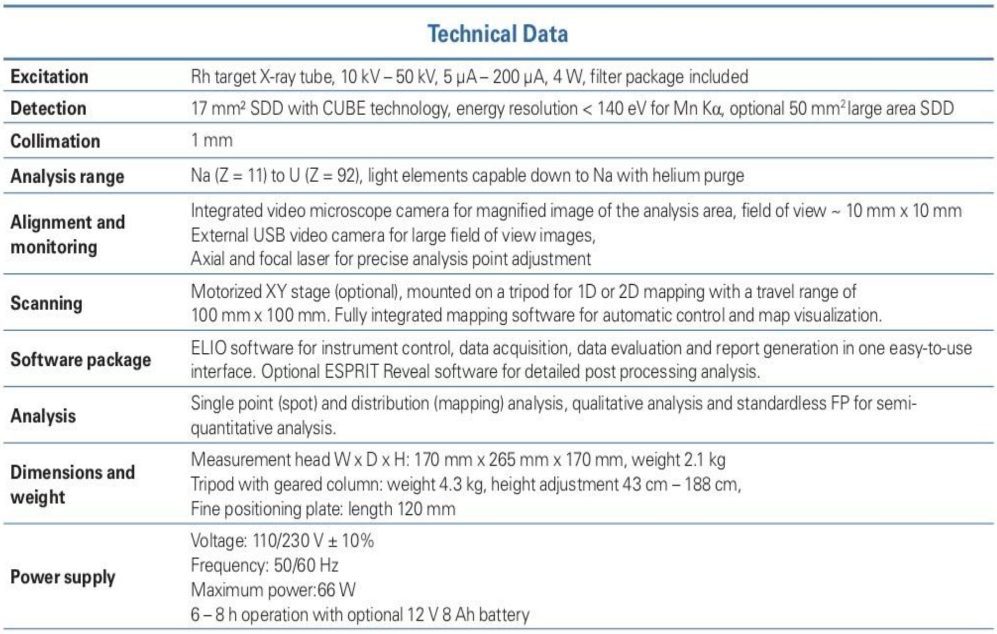
6.3. Technical description of analytical instruments

6.3.1. MICRO-XRF ELIO: Portable Micro X-ray Fluorescence Spectrometer



Technical Data

Excitation	Rh target X-ray tube, 10 kV – 50 kV, 5 µA – 200 µA, 4 W, filter package included
Detection	17 mm² SDD with CUBE technology, energy resolution < 140 eV for Mn Kα, optional 50 mm² large area SDD
Collimation	1 mm
Analysis range	Na (Z = 11) to U (Z = 92), light elements capable down to Na with helium purge
Alignment and monitoring	Integrated video microscope camera for magnified image of the analysis area, field of view ~ 10 mm x 10 mm External USB video camera for large field of view images, Axial and focal laser for precise analysis point adjustment
Scanning	Motorized XY stage (optional), mounted on a tripod for 1D or 2D mapping with a travel range of 100 mm x 100 mm. Fully integrated mapping software for automatic control and map visualization.
Software package	ELIO software for instrument control, data acquisition, data evaluation and report generation in one easy-to-use interface. Optional ESPRIT Reveal software for detailed post processing analysis.
Analysis	Single point (spot) and distribution (mapping) analysis, qualitative analysis and standardless FP for semi-quantitative analysis.
Dimensions and weight	Measurement head W x D x H: 170 mm x 265 mm x 170 mm, weight 2.1 kg Tripod with geared column: weight 4.3 kg, height adjustment 43 cm – 188 cm, Fine positioning plate: length 120 mm
Power supply	Voltage: 110/230 V ± 10% Frequency: 50/60 Hz Maximum power: 66 W 6 – 8 h operation with optional 12 V 8 Ah battery

6.2.2. Bruker ALPHA-R med Platinum-ATR

THE SWISS-KNIFE OF FT-IR SPECTROSCOPY.
A reliable device like the ALPHA II needs an equally reliable support network. Luckily, Bruker services extend globally making sure your service and validation needs are addressed in time and all over the world.

Technical Data

Spectrometer Housing	Rigid and durable metal housing
Detector and Interferometer	Temperature-controlled DLaTGS-detector; RockSolid™ cube corner interferometer
Spectral Range	350 – 8,000 cm^{-1}, with standard KBr beamsplitter; 500 – 6,000 cm^{-1}, option: "High Humidity" ZnSe
Signal-to-Noise Ratio	Typically > 55,000:1 (1 min measurement time, spectral resolution 4 cm^{-1})
Accuracy and Precision	<0.05 cm^{-1} @ 1576 cm^{-1}, <0.0005 cm^{-1} @ 1576 cm^{-1}
Dimensions	With Panel-PC: ~ 267 x 340 x 340 mm without Panel-PC: ~ 208 x 330 x 260 mm
Weight	Approx. 7-11 kg (Depending on configuration)

The ALPHA II at a glance

- Robust and compact FT-IR
- Integrated touch panel with state-of-the-art software
- Low cost of ownership
- Conveniently exchangeable sampling modules
- Absolute reliability through high system intelligence

Laser class 1 product.

Bruker Optics GmbH & Co. KG
info.bopt.de@bruker.com

bruker.com

Bruker Optics is ISO 9001, ISO 13485, ISO 14001 and ISO 50001 certified.

Worldwide offices
bruker.com/bopt-offices

Online information
bruker.com/ALPHA