Quantitative Salt Analysis in Conservation of Buildings

C. Bläuer Böhm

Expert-Center für Denkmalpflege, ETH-Hönggerberg, Zürich, Switzerland

Abstract

For the conservation of monuments, quantitative analyses of salts in the original materials help to predict their destructive behaviour and to estimate the least harmful environmental conditions for preventive conservation of the object in question. Salt analyses can also be used to monitor the results of salt reduction treatments or to compare diverse methods of conservation treatment. Further it can be necessary to test new building or conservation materials for their soluble salt content and hence their suitability for use in historical monuments. The analytical procedure consists of three steps: sampling, actual analysis and interpretation of data. It will be more or less complicated depending on the materials considered and needs to be adapted to the specific case. The paper discusses frequently encountered questions regarding salt analysis in the context of historical monuments preservation. The types of materials that are often tested for their salt content are historical mortars, stones, repair mortars and materials used to extract salts from salt loaded original materials, such as poultices. A definition of these different material types and their sub-groups is given from the point of view of salt analysis, the questions asked regarding the different groups of materials are elaborated, sampling strategies and analytical procedures are discussed and finally some hints towards the possible interpretations and their difficulties are given. Special emphasis is put on the water extraction method as this seems to be the by the far most frequently used method for quantitative salt analysis.

Keywords: Quantitative salt analysis, water extraction method, historical mortars, stones, poulticing

Quantitative Salzanalyse bei der Konservierung von Bauwerken

Zusammenfassung

Im Kontext der Konservierung von historischen Bauten helfen quantitative Salzanalysen an Originalmaterialien zu verstehen und vorauszusagen, wie diese Materialien verwittern werden, sowie abzuschätzen, welche Umgebungsbedingungen bezüglich präventiver Konservierung den wertvollen Objekten am zuträglichsten sind. Salzanalysen können auch dazu dienen, die Ergebnisse von Behandlungen zur Salzreduktion zu überwachen oder unterschiedliche Konservierungsmethoden zu überprüfen. Weiter kann es nötig sein, Bauoder Konservierungsmaterialien auf ihren Salzgehalt und damit ihre Tauglichkeit für den Gebrauch an historischen Bauten zu überprüfen. Der Analysegang, bestehend aus den drei Schritten Probenahme, eigentliche Analyse und Interpretation, wird mehr oder weniger kompliziert, je nach den zu testenden Materialien und er wird dem individuellen Zweck der Analyse angepasst werden müssen. In diesem Beitrag werden die bezüglich Salzanalysen im Zusammenhang mit historischen Bauten am häufigsten angetroffenen Fragestellungen diskutiert. Die Materialarten, welche häufig auf ihren Salzgehalt überprüft werden, sind historische Mörtel, Steine, Reparaturmörtel und Entsalzungsmaterialien, wie Kompressen. Es werden Definitionen dieser Materialgruppen und ihrer Untergruppen aus der Sicht der Salzanalyse gegeben, die Fragestellungen bezüglich dieser unterschiedlichen Materialgruppen werden näher ausgeführt, Probenahmestrategien und analytische Vorgehensweisen werden diskutiert und schliesslich werden einige Hinweise für mögliche Interpretationen und ihre Schwierigkeiten gegeben. Spezielles Gewicht wird dabei der Analyse mittels eines wässerigen Auszugs gegeben, da dies die am weitaus häufigsten angewandte Methode für die quantitative Salzanalyse zu sein scheint.

Stichwörter: Quantitative Salzanalyse, Wasserauszugsmethode, historische Mörtel, Stein, Entsalzugskompressen

1 Introduction

Salts are undoubtedly of the most important factors threatening deterioration of historical monuments made out of inorganic porous materials such as stone and plaster [1]. Salt activity is usually detected when salt efflorescence appears on the materials' surfaces. The hygroscopic nature of the salts is known to be one of the important factors for the destructive potential of the salts. It allows them to absorb water from humid air, getting hydrated and finally getting dissolved in the absorbed water. The resulting salt solution is then redistributed in the porous system by capillarity and diffusion mechanisms [2]. The way this redistribution happens and the resulting effect of it depend very much on the porosity type and structure of the material. During dry periods water evaporates from the salt solution, which then becomes over saturated resulting in the crystallization of salts and causing mechanical damage to the porous material. Knowing the composition of the salt system can help in estimating its behaviour within the surrounding climate and hence its destructive potential. This knowledge is the basis for devising suitable environmental conditions that allow the long term conservation of the salt laden stone, mortar, stucco or wall painting. Here quantitative salt analysis gives the basis for the estimation of suitable environmental conditions [3].

In other cases quantitative salt analysis is needed to monitor the results of salt reduction treatments or to compare diverse conservation methods. Further, it can be necessary to test building or conservation materials for their water soluble salt content and hence suitability to be used in the context of the conservation of historical monuments.

The present paper does not intend to give solutions to all problems arising when quantitative salt analysis is performed. It is rather aimed to show what kind of problems have to be tackled, when confronted with the vast range of possible questions occurring, in spite of the easy and straight forward appearance of a quantitative analysis of the salt content of a material.

2 Questions to be answered by Quantitative Salt Analysis

There are three main questions to be answered by quantitative salt analysis in conservation:

1. What is the salt content of a material (stone, mortar) from a historical building?

- 2. What is the salt content of a fresh building or repair material which will be in contact to the historical materials and what is the estimated destructive potential of this new material?
- 3. How much salt has been extracted by a certain salt extracting material (poultice)?

In the following some of the wider aims of such analyses are given.

2.1 Salt Content of Materials from Historical Buildings - Stones or Mortars

Salt profiles that provide the in depth salt distribution of the salts can help to explain certain weathering forms. The types of salts found and their place of concentration can give information on their sources. It can be necessary to know the salt content of a certain material without special salt contamination, be it for the decision making about certain treatments (consolidation, salt reduction) or for climate control. Quantitative salt analysis is further needed for the calculations of equilibrium relative humidities of the salt systems contaminating individual monuments to estimate suitable conditions to prevent salt crystallization cycles and related damage [3].

2.2 Salt Content of a Fresh Building or Repair Material

Most building or repair materials already contain certain amounts of soluble salts in their fresh state. In situations where no water can reach repair materials containing salts, their salt contents cannot be washed out and can hardly cause a threat to their neighbouring original materials. However, even in protected places certain events (leaking of the roof, flooding, water from fire extinction, etc.) can lead to water penetrating the repair materials and hence wash the salts out and transport them into neighbouring original materials. For repair work in salt sensible surroundings it is therefore usually necessary to select the repair material that contains the smallest amount of salts possible.

2.3 Amount of Salts extracted by Poulticing

There are several questions that frequently arise when performing salt extraction treatments by poulticing. In our experience these are:

Which type of poultice material is the most efficient?

How long should the poultice be left on the materials surface to be the most effective?

How many changes of poultices should be performed?

In analytical terms, the above questions are directly related to the question:

How much salt did the individual poultice absorb?

3 Materials

The materials that most frequently are tested for their salt content in the context of the preservation of historical monuments are original plasters or mortars, stones, repair materials and poultices that have been used for salt extractions measures. For the purpose of this paper, these are grouped from the point of view of comparable problems to be solved regarding salt analysis, mainly considering salt analysis by the water extraction method.

3.1 Historical Mortars, Plasters and Renders

For the purpose of this paper the term "historical mortar" groups all materials such as plasters, renders, stucco and others, which were basically produced as a mixture of aggregate, inorganic binder, water and maybe with some additives. They result from a chemical setting reaction [4] and are completely set by the time they are analysed. Not included in this group are materials that contain a large amount of clay minerals with ion exchanging capacities. The problematic of salt analysis for these latter materials is rather similar to the one for clay poultices (see group j below).

a) Fine grained mortars without water soluble components

This group consists of fine grained mortars made out of sand and inorganic binder, both of which are not soluble in water. The grain size of the aggregate is usually not bigger than about 2 mm. Such mortars can contain animal hair or plant fibres. This type of mortar is normally very homogeneous in the scale of centimetres and is often found as intonaco of wall paintings or as plasters.

b) Coarse grained mortars without water soluble components

In mortars of this type the maximum grain size can be as big as several centimetres, in our experience, most frequently around 1 or 2 centimetres. These mortars are only homo-

geneous in the scale of decimetres or more, and they are often found as jointing or bedding mortars of masonry.

c) Historic mortars with water soluble components

Mortars can contain soluble components as part of the aggregate or of the binder. Gypsum or anhydrite are common rock forming minerals and they can therefore also be found as aggregate in mortars.

Even more frequently the binder contains or forms water soluble minerals after the setting reaction. Examples are portlandite (Ca(OH)₂, see also group f below), as the reaction product of the setting of hydraulic mortars and cements, then the manifold setting products of dolomitic lime mortars (see [5], [6]) or gypsum binders.

3.2 Stone

d) Stones not containing water soluble components

The majority of natural stones do not contain water soluble components to a relevant extent. It is however, important to note that probably all stones contain at least small amounts of soluble components (e.g. fluid inclusions can be released, when the stone is crushed to powder) and that many rock forming minerals are at least to a certain extent water soluble (e.g. solubility of calcite = 0.0014 g/100 ml at 25 °C value from [7]). Generally if the solubility of a stone material is small, like in the case of calcite, the stone would be included in this group.

e) Stones containing water soluble components
As stated above, gypsum or anhydrite are rather common rock forming minerals and it has to be expected that also other more or less water soluble minerals can form quite big parts of certain types of stones.

3.3 Freshly prepared Building Materials

f) Mortars containing hydraulic binders
Artificially produced hydraulic binders such as cement or hydraulic lime contain calcium silicate phases that react with water to form calcium silicate hydrate phases (CSH-phases) and calcium hydroxide (Ca(OH)₂, portlandite). Calcium hydroxide is quite soluble in water (0.185 g/100 ml at 0 °C [7]) and gives very alkaline solutions, this is important to keep in mind, when pre-

paring water extractions from such materials as some analytical methods do require neutral solutions

g) Mortars containing latently hydraulic binders

Latently hydraulic binders (such as pozzolana, diatomeous earth, etc.) are natural siliceous materials, that have the capacity to react with water in the presence of hydrated lime (Ca(OH)₂) to form calcium silicate hydrate phases. By this setting reaction components such as sodium, potassium, magnesium or others are released and within the set mortar they will be present in more easily water soluble forms [8].

3.4 Salt Extracting Materials - Poultices

- h) Poultices without ion exchanging capacities
 Poultice materials such as natural cellulose
 fibres or newspaper pulp can be used for the
 salt extraction ([9], [10]). These materials
 probably do not have a relevant ion exchange
 capacity.
- i) Poultices with ionic exchange capacities
 Synthetic resins can be added to poultices as an ion exchanger ([11], [12]). For example, anion exchanging raisins will, after adequate preparation, take up sulphate, chloride or nitrate from the treated material and release hydroxide ions instead.
- j) Poultices prepared with clay or clay additions

There are various types of clay or clay containing materials used for poulticing [10]. The ion exchange capacity of clay minerals can be very large, however, it depends on the exact nature of the clay minerals [13] and of the nature of the exchangeable ions in the clay.

4 Sampling Strategies for Quantitative Salt Analyses

Good sampling strategies are extremely important to avoid major errors in quantitative salt analysis, because even the most sophisticated analytical procedure cannot save the analytical results from being completely useless, if the samples are not representative of the question under consideration.

There exists a major difference between samples and specimens [14].

The **specimen** is a part of the whole. It is usually not collected for a certain purpose and therefore cannot be used as a representative part of the object in consideration.

A **sample** is a part of the whole that has the properties of the whole regarding the property in consideration. Samples must therefore be taken with a clear idea in mind about the property that should be investigated.

For our purpose, two ways of sampling can be differentiated: direct—by taking away a part of the salt containing material; and, indirect—by applying poultices to extract the salts from the material. While direct sampling is destructive, indirect sampling is only destructive to water sensitive materials.

One of the very obvious problems with direct sampling is that it cannot be repeated on exactly the same place. This feature makes all investigations that, for example, compare situations before and after treatments, particularly difficult. The problem could be overcome by taking several samples well distributed over the surface. However when sampling original materials from historical monuments. it is usually impossible to take many, statistically distributed samples and not to mention a repeat this sampling, since this should be restricted to the minimum necessary. Often samples can only be taken at places which are already damaged but which may not be very representative. Therefore it has to be considered very seriously if the analytical results obtained from these samples will be at all helpful to conserve the monument.

As salts very often show cyclic periods of crystallisation and dissolution depending on the climatic variation throughout the year, the moment of sampling can have an important effect on the results. This can easily be shown at places with periodically visible salt efflorescence. Surface samples from such places taken at the moment when the salts are visible, will of course give different salt contents and probably compositions, than samples taken at the same place while no efflorescence is visible on the surface. In our experience, important differences in salt content and chemical composition of the salt system can also be observed in places where efflorescences never occur depending on the climatic conditions.

4.1 Direct Sampling of Salt Contaminated Original Materials

In general, fine grained mortars or stone samples do not present a sampling problem since their homogeneity lies within the standard minimal size of sample needed to perform a salt content analysis.

On the other hand, coarse grained mortars or stone samples can bring about major problems because at an ordinary sample scale—often less than one cubic centimetre—they are very inhomogeneous. Here the decision has to be made either to crush and grind a big sample to powder and make a proper sample splitting of the powder, or to only analyse the salt content in one part of the sample, e.g., in the binder. And this decision is highly dependent on the question that the analysis is supposed to answer.

4.2 Freshly prepared Building Materials

For most of these materials the salts will only be released during setting (pozzolana, dolomitic lime, and possibly also for hydraulic binders) therefore it is best to analyse the set material. But of course it is not clear when this setting reaction can actually be considered to be completed. Hence it will be necessary to decide on a standard setting time before analysis, which at least will allow to compare the results from different analyses. For hydraulic lime materials 28 days setting time has been suggested [15].

4.3 Monitoring Salt Reduction Treatments

This seems to be the easiest and most straightforward task regarding sampling for salt analysis. For these samples it is important that a part of the unused poultice is tested as well by exactly the same method to serve as the blank sample.

If the poultice material contains ion exchanging materials the analytical procedure can become very complicated, depending on the case under in consideration.

For poultices it is usually necessary to know how much salt they were able to extract per unit of surface. Therefore the sampling will normally be the whole poultice layer together with the underlying separating sheets of Japanese paper or equivalent, covering a known surface area.

5 Analytical Methods for Quantitative Salt Analysis

5.1 X-ray Diffraction

Within porous building materials salts are present as individual salt minerals, they are dissolved and form a part of the pore solution or they are present as both salt crystals and salt solution.

Frequently used methods to analyse salt minerals (phases) qualitatively are polarizing light microscopy ([16], [17]), X-ray diffraction or infra red spectroscopy (FTIR). From these mainly X-ray diffraction can be used for quantitative salt analysis. The method has the disadvantage however, that a calibration material (e.g. LiF) has to be added to the sample and the resulting mixture needs to be homogenised mechanically. During this procedure changes of the salt mineral species cannot be excluded (hydration or dehydration of the salts). A further problem lies in the fact, that calibration curves would be needed for every individual salt mineral occurring in the sample (over 40 different salt minerals are known to commonly occur within or on building materials [17]).

A further disadvantage is that only the ions that have crystallised to form minerals will be detected, and the ions being part of the pore solution will be not be identified. This makes the analytical results somewhat ambiguous, as the state of the salt system within the materials is mainly defined by the environmental conditions at the time of the analysis. So the analysis would give an arbitrary picture of the salt system, probably reflecting more the laboratory conditions at the time of the analysis, than the conditions in the monument of consideration.

5.2 Water Extraction Method

For most cases, the aim of the quantitative salt analysis of original material is to estimate the destructive potential of the salts so as to be able to take conservation measures. It is hardly ever possible or even desired to quantitatively analyse the crystallized salt minerals within a sample. Direct analyses of the pore water [18] is usually not possible, because of the huge sample size needed to gain only minor amounts of pore solution. Furthermore this procedure requests very sophisticated analytical instruments both for the extraction and the subsequent water analysis. In most cases, the salt species' need only to be known qualitatively (and in relation to the room climate) but the total content of water soluble ions within a sample should be measured quantitatively.

The easiest practical and most frequently used method to quantitatively analyse the salt content within porous materials is to extract the salts by means of deionised water and analyse the ionic content of the extracted solution [19].

5.2.1 Water Extraction Procedures

Mortars and stone (material types a to g)

Several authors have shown, that more salt ions will be extracted, if the samples are finely ground, than if they are only crushed to rather coarse pieces (see e.g. Laue, 1997 [29]). To make results comparable it will therefore be necessary to use always the same preparation treatment of the sample materials (drying, grinding, homogenization, etc.). It will also be necessary to use the same ratio of sample to water for the water extraction because the dilution factor can strongly influence results.

Water extractions out of stones and mortars not containing any water soluble components (types of material a, b and d in the above given list) or components with ion exchanging capacities (types i and j) can usually be made without major problems.

No standardised method has yet been agreed upon to produce water extractions for the salt analysis, as can be seen by comparing a selection of procedures for water extractions published during the past 20 years ([15], [19], [20], [21], [22], [23]). According to these papers:

The samples are either ground to a grain size of $125 \mu m$ and homogenised or only crushed to pieces of about 2 mm in size;

The water used for the extraction is either distilled, deionised or deionised water that was previously boiled and then left to cool;

The dilution factor varies from 1:5 to 1:100;

The contact times between water and material powder vary from two minutes to twenty-four hours;

The suspension is shaken periodically or constantly during this time, or it is stirred constantly.

Poultices without ion exchanging capacities (type h) The most common materials of this type are cellulose fibres or newspaper pulp. Even small amounts by weight of such materials usually take up a comparatively big volume. The amount of sample put into contact with water to produce the extraction cannot be reduced below a certain amount if the sample size is to remain representative.

For these poultice materials, we usually select 5g of dry material, mix it with 100 ml of water and let it stir for half an hour. The filtration of such samples lasts normally between 10 minutes and an hour. During filtration of the suspension such materials have a tendency to block the filter paper and therefore the filtration can take a very long time. To our experience filtration procedure take often much longer for the blank poultice materials, than for the poultices after salt extraction.

Poultices with ionic exchange capacities or clay minerals (types i and j)

There exists a vast variety of materials of this type that are used in conservation, therefore no general procedure to measure their ionic content can be suggested here.

If the question to be answered is, how much of a certain ion has been taken up by the ion exchanging material, the procedure can consist in mixing the material with an appropriate eluent, that has the capacity to exchange the ions bound to the ion exchanger during the desalination procedure the poultice was used for.

As ion exchangers normally are not used together with an inert material, it will probably be necessary to make a further extraction with water only in a similar procedure as that laid out above.

5.2.2 Analysis of the Extracted Solution

The most commonly measured properties of the aqueous extracts are pH, electrical conductivity and the content of Na⁺, K⁺, Ca²⁺, Mg²⁺, NH₄⁺, Cl⁻, SO₄²⁻ and NO₃⁻ ions. Soluble salts from monuments are most frequently composed of Na⁺, K⁺, Mg²⁺, Ca²⁺, NH₄⁺, Cl⁻, NO₃⁻, SO₄²⁻, CO₃²⁻, HCO₃⁻ and H₂O [24]. Other ions such as nickel [25], lithium (e.g. from the use of lithium water glass), phosphates, oxalates [26], aluminium or copper [19] can also be found but are far less frequent.

No direct method exists to analyse carbonic acid (H₂CO₃) or its anions (HCO₃⁻, CO₃²⁻) in aqueous extracts. Hydrogen carbonate or carbonate are measured by titration in water analysis, but these tests need a lot of testing water so that they normally cannot be performed with water extraction samples.

All methods normally used for water analysis (see e.g. [27]) can be used to measure the ion content of the solutions. The diverse methods can, however, give quite different results (see e.g. [23] or [28]), so that the analytical error of the methods used has to

be estimated very carefully and taken into consideration for a cautious interpretation. Depending on the method used, several ions can be detected together in one analytical step and can hardly be accidentally overlooked, but if the ionic contents is analysed by ion selective tests, only those ions for which specific tests are performed can be found while the presence of ions not tested will go undetected.

In this context Steiger et al. [19] strongly emphasize the need to calculate the ionic balance by comparing the sum of anion equivalents with the sum of cation equivalents, which should amount to the same, if all ions present had been measured accurately. Bläuer Böhm [23] suggests in addition to calculating the ionic balance to compare the sum of measured ions with the electrical conductivity and with the weight loss of the sample after the water extraction. Kraus et al. [15] used the computer programme PHREEQC to calculate the carbonate and hydrogen carbonate contents on the basis of the ionic balance of the extraction solution from modern hydraulic lime mortars.

One frequent constituent of soluble salts that will hardly ever be analysed quantitatively is the crystalline water. This has to be kept in mind, when comparing the results from the ion measurements with the weight loss of the sample after extraction.

The highly alkaline solutions resulting from the water extract of fresh mortars containing hydraulic binders can cause major analytical problems, depending on the method used for the analyses of the ions

For salt contents in mortars or stone samples, the results of the analyses are normally given in either grams or moles per unit of sample or as weight percent of sample. As stated by Steiger et al. [19] results given in mg per litre are not helpful, because they are difficult to compare particularly if no dilution factor is given.

For the salt content of poultices it is better to calculate the results in weight per surface [g/cm²], because it is far more relevant to know the poultice capacity for salt extraction for a given surface, than to know the weight percentage of salts within the poultice. A further reason to calculate the results in grams per surface unit lies in the fact that diverse poultice materials have highly different specific weights (clay minerals have a density around 2.9 g/cm³ whereas that for cellulose fibres lies around 1 g/cm³).

6 Interpretation of the Results

For result interpretation it will often be important to specify what are "low" and what are "high" concentrations. However, these values are dependent on the material being tested. Very small amounts of salt can cause a large problem in a material that has little pore space for the salts to crystallize in. Contrariwise, very high salt contents in certain highly porous materials might not do no damage at all. Hence the definition of high or low concentrations is strongly dependent on the material in consideration and no generally valid standard value can be given.

For the interpretation of the results it has further to be kept in mind that by adding water to a sample, salts that may be separately located within the pore space of the material might be brought together, which can result in their precipitation. This, of course changes the results of the subsequent water analysis. To illustrate this point a case observed in our laboratory is presented. The sample contained gypsum $(CaSO_4.2H_2O)$ and thermonatrite (Na₂CO₃) both as identified mineral phases. The water extract of this sample (which in this case was analysed only qualitatively) had a neutral pH and showed only sodium, sulphate and calcium ions – hence the amount of gypsum in the original sample was obviously bigger than the amount of thermonatrite so that the pH was neutralized by the precipitation of calcium carbonate. The reaction that had taken place when the sample was mixed with water could be written as follows:

$$xCaSO_4.2H_2O + yNa_2CO_3 \rightarrow yCaCO_3 + 2yNa^+ + (x-y)Ca^{++} + xSO_4^{--} + xH_2O$$
 (1)

In most cases it is necessary to know the original salt content of the material to be able to interpret the results. This appears easy enough with poultice and stone materials, however, it is impossible to achieve for historic mortars. For the latter the soluble salt content of the non contaminated material can only be estimated rather rudimentarily by comparison with similar materials or by analysing a sample from a place where no visible damage caused by salts can be observed. The salt content of this sample gives the level of what is meant by "not contaminated with salts" but this value is only true for the individual situation and material in consideration and cannot generally be taken as being representative for all similar kinds of mortars.

If ever possible the water extractable ion content of the fresh material (blank) has to be tested with exactly the same extraction method, otherwise the interpretation of the results becomes somewhat haphazard, which makes it difficult to use in for future reference.

6.1 Materials Containing Water Soluble Components

The interpretation of the results becomes rather difficult for all materials that contain water soluble components. Because these are usually present in such high amounts that the extraction becomes saturated with these components. In our experience, this is valid for most freshly prepared mortars containing hydraulic binders, where Ca(OH)₂ can form such a big proportion of the material, that saturation is reached even with a dilution factor of 1 to 100. Furthermore, it has to be taken into consideration that the water extraction inevitably results in the solution acquiring a very high pH (around pH 12), and this has rather a different leaching potential towards the minerals present in the aggregate of the mortar than a nearly neutral solution.

Similar problems have to be faced with samples of dolomitic lime mortars or gypsum containing mortars.

6.2 Poultices

For the interpretation of salt analyses of poultice materials it is necessary to know how much dry poultice material by weight covers what surface area size. And it is necessary to know how much surface area was covered by the specific sample analysed.

Apart from these very general remarks no more indications for the interpretations of results from salt analysis from salt extraction poultices can be given, as very different types of materials are included in this group and the interpretation will depend very much on the questions to be answered and on a case by case basis.

7 Conclusions

In the context of historical monuments it is the norm that sampling is restricted to the absolutely minimum necessary. This means that the few samples that can actually be taken and analysed have to be selected very carefully following a sophisticated sampling strategy. This sampling strategy has to be adapted to the individual case and therefore it seems impossible to give general advice on how to proceed.

However, some aspects appear to be generally correct and are listed below:

The purpose the analysis should serve must be known exactly before any sampling can take place. It is not enough to know, that the "total salt content" is wanted, but it must be known precisely what this information is needed for.

Samples taken for a certain purpose normally are useless to answer other questions. Some exceptions might be provided by those cases where the exact conditions of sampling procedure and analysis are known, and where it is therefore possible to deduce from the results, the information needed.

In summary, salt analyses needs primarily a very sophisticated strategy. This includes definitions of the final aim of the analysis and the questions to be answered, the type of sampling procedure and the conditions at the time at which the sampling was performed, the adapted analytical procedure for the laboratory analysis and last but not least a wise interpretation of the obtained data.

Acknowledgements

Many thanks to Adam Krzystek, our laboratory assistant who always helps me again and again to find the most appropriate analytical procedure for the individual case and to Bénédicte Rousset for very helpful comments and discussion.

References

- 1. Arnold, Salze: Lästige weiße Ausblühungen oder Hauptschadensursache? in Snethlage, R. (Hrsg.) Jahresberichte aus dem Forschungsprogramm Steinzerfall Steinkonservierung, Band 2 1990, Verlag Ernst & Sohn, Berlin, 1-9 (1992)
- 2. D. Jeannette, Structures de porosité, mécanismes de transfert des solutions et principales altérations des roches des monuments.

 La pietra dei monumenti in ambiente fisico e culturale. Atti del 2° Corso Intensivo Europeo tenuto a Ravello e a Firenze dal 10 al 24 aprile 1994, Edipuglia, Bari, 49-77 (1997)
- 3. C. E. Price, An expert chemical model for determining the environmental conditions needed to prevent salt damage in porous materials. Research report No 11, European Commission. Technologies to protect and

- rehabilitate European Cultural Heritage. Project ENV4-CT95-0135 (1996-2000), (2000)
- 4. C. Bläuer Böhm, *Factors influencing the durability performance of mortars*, in Maintenance and strengthening of materials and structures. Plaster. Proceedings of the international workshop on urban heritage and building maintenance VII, ETH Zürich, 1.9.2000, Aedificatio Publishers Freiburg, 17-24, (2000).
- 5. C. Bläuer Böhm and E. Jägers, *Analysis and recognition of dolomitic lime mortars*, in Béarat, H. et al. (Ed.): Roman wall painting materials, techniques, analysis and conservation, Proc. int. workshop, Fribourg 7.-9.3.1996, 223-235 (1997).
- A. Diekamp, J. Konzett, T. Bidner and P. W. Mirwald, *Kalkmörtel und Kalkputz in Tirol*, 4th International Eurolime-Meeting, Freilichtmuseum Ballenberg, 4.-6. August (2005)
- 7. R. C. E. Weast (Ed.), *Handbook of chemistry* and physics, 55th Edition.- CRC Press, Cleveland, Ohio, (1974).
- 8. H.-E. Schwiete, P. Kastanja, and U. Ludwig, Das mörteltechnische und chemische Verhalten verschiedener Trasse und Gesteinsmehle in Verbindung mit Kalk in wässrigen Lösungen, Forschungsbericht des Landes NRW, Nr. 1441, Westdeutscher Verlag, Köln und Opladen. (1965)
- 9. Diverse Authors, *Le dessalement des matériaux poreux*, 7es Journées d'Etudes de la SFIIC, Poitiers 9 10 mai 1996, Champs-sur-Marne (1996)
- 10. E. Witte de, M. Dupas and S. Peters, *Dessalement de voûtes d'un fumoir de harengs*, in Le dessalement des matériaux poreux. 7es journées d'études de la SFIIC, Poitiers, 9 10 mai 1996.- SFIIC, Champs-sur-Marne, 177-190 (1996)
- 11. M. Oeter, Die Reinigung von Wandmalerei mit Ionenaustauschern. Beobachtungen und Ergebnisse nach den ersten Jahren der Anwendung. Arbeitshefte des Bayerischen Landesamtes für Denkmalpflege, Band 104, Beiträge einer Fortbildungsveranstaltung der Restaurierungswerkstätten des BLD am 9.12.1994, 122-124 (2001)
- 12. M. Matteini, A. Moles, M. Oeter and I. Tosini, *Ionenaustauschharze in der Reinigung von Kunstwerken aus Stein und in der*

- Wandmalerei: Experimentelle Verifizierung und Anwendungen, Arbeitshefte des Bayerischen Landesamtes für Denkmalpflege, Band **104**, Beiträge einer Fortbildungsveranstaltung der Restaurierungswerkstätten des BLD am 9.12.1994, 234-239 (2001)
- 13. K. Jasmund and G. H. Lagaly, *Tonminerale* und Tone Struktur, Eigenschaften, Anwendung und Einsatz in Industrie und Umwelt, Steinkopff Verlag, Darmstadt (1993)
- 14. P. Gy, L'échantillonnage des lots de matière en vue de leur analyse, Masson, Paris, Mailand, Barcelona (1996)
- 15. K. Kraus, J. Eisenberg, D. Schenk and K. Droll, *Untersuchung wasserlöslicher Salzgehalte in modernen hydraulischen Kalkmörteln*, 6th International Conference on Materials Science and Restoration MSR-VI, Aedificatio Publishers Freiburg, 377-388 (2003)
- 16. A. Arnold, *Determination of mineral salts from monuments*, Studies in Conservation, **29/3**, 129-138. (1984)
- 17. C. Bläuer Böhm, *Salzuntersuchungen an Baudenkmäler*; Zeitschrift für Kunsttechnologie und Konservierung, **8/1**, 86-103 (1994)
- H. Umierski, S. Brüggerhoff and P.W. Mirwald, Untersuchungen zur Probennahme und Analyse von Porenwässern aus Natursteinen, Jahresbericht Forschungsprogr. Steinzerfall-Steinkonservierung, Bd. 1, 1989, Verlag Ernst & Sohn, Berlin, 131-145 (1991)
- M. Steiger, H.-H. Neumann, T. Grodten,. C. Wittenburg, U. Richter and W. Dannecker, Salze in Natursteinmauerwerk Probennahme, Messung und Interpretation, in R. Snethlage (Hrsg.): Denkmalpflege und Naturwissenschaft Natursteinkonservierung II, 61-91 (1998)
- 20. K. Kraus, Experimente zur immissionsbedingten Verwitterung der Naturbausteine des Kölner Doms im Vergleich zu deren Verhalten am Bauwerk, Dissertation, Universität Köln (1985)
- 21. D. Knöfel, P.H. Schubert, *Handbuch Mörtel* und Steinergänzungsstoffe in der Denkmalpflege, Sonderheft BMFT-Verbundforschung zur Denkmalpflege, Verlag Ernst & Sohn, Berlin (1993)
- 22. H. Rösch and H.-J. Schwarz, *Mineralogische* und anorganisch-chemische Untersuchungen zur Klärung der Schadensursachen an

- romanischen Wandmalereien, Hrsg. C. Segers-Glocke, BMFT-Forschungsprojekt Wandmalerei-Schäden, Schlussber. interdisziplinäre Ergebnisse, CW Niemeyer Verlag, Hameln, 104-114 (1994)
- 23. C. Bläuer Böhm, Assessment of quantitative salt analysis by the water extraction method on lime mortars, 8th Int. Congr. Deterior. Conserv. of Stone, 30.9.-4.10., Berlin, 1505-1519 (1996)
- 24. A. Arnold and K. Zehnder, *Monitoring wall paintings affected by soluble salts*, The Conservation of Wall Paintings. Proceedings of a symposium organized by the Courtauld Institute of Art and the Getty Conservation Institute, July 13-16, 1987, London, 103-135 (1991)
- 25. M. T., Blanco Varela, E. Menendez and M. Hoyos, *Study of surface decay of the marbles and serpentine from the Descalzas Reales convent at Madrid*, La conservation des monuments dans le bassin méditerranéen,

- Actes du 2ème symp. int, 19.-21. Nov., Genève, 167-175 (1991)
- 26. M. Del Monte and C. Sabbioni, *Weddellite* on limestone in the Venice environment, Environ. Sci. Technol., Vol. 17, 518-522 (1983)
- 27. L. A. Hütter, *Wasser und Wasseruntersuchung*, Sechste Auflage. Otto Salle Verlag, Frankfurt a.M. + Verlag Sauerländer, Aarau, Frankfurt a.M., Salzburg (1994)
- 28. A. Amman, F. Bürgi, T. Rüttimann and U. Schönenberger, Ein Vergleich der photometrischen und ionenchromatographischen Bestimmung von Chlorid, Nitrat und Sulfat in schweizerischen Fließgewässern, Jahresbericht 1995, EAWAG, 28-29 (1995)
- 29. S. Laue *Einfluss des Porenraums und des Raumklimas auf die Verwitterung von Steinen durch lösliche Salze*. Dissertation, Fachbereich Geowissenshaften der Johannes Gutenberg-Universität, Mainz (1997)



Dr. Christine Bläuer Böhm is a conservation scientist who after an apprenticeship in designing of houses has studied mineralogy-petrography and made her PhD in 1987 on the deterioration of Bernese Sandstones. Then she worked several years in research projects on the deterioration and conservation of wall paintings. Since 2000 she is the director of the Zurich laboratory of the Expert-Center for the conservation of monuments and sites. E-Mail: blaeuer@ecd.ethz.ch

Received September 19, 2005