International Course on Stone Conservation SC13

SESSION: Lab: Salt analysis

INSTRUCTOR: Alison Sawdy-Heritage

TIME: Friday, 17th May/ 14:30 – 16:00 (1.5 hours) & 16:30 – 18:00 (1.5 hours)

SESSION OUTLINE

TASK

Using the following test methods, and referring to the **FLOW CHART** provided below, try to identify the white fluffy stuff you can see on the 4 sample bricks **A, B, C and D**.

NOTE: If you are unsure about a test result, try the same test on a known reference salt for comparison (see **Table of Reference salts**).

Table of Reference salts (for comparing test results)

Salt Name	Formula	Test for ions	Comments
Nitratite	$NaNO_3$	Na, NO_3	
Halite	NaCl	Na, Cl	
Magnesium sulfate (epsomite)	$MgSO_4 \bullet 7H_2O$	Mg, SO_4	
Sodium hydrogen carbonate	$NaHCO_3$	Na, HCO_3,	moderately alkaline
Sodium carbonate	Na_2CO_3	Na, CO_3,	strongly alkaline
Mirabilite	$Na_2SO_4 \bullet 10H_2O$	Na, SO_4,	pH neutral: try the warming test!
Calcium chloride	$CaCl_2$		

Record the results of each test on your worksheet in the **TEST RESULTS** table provided below.

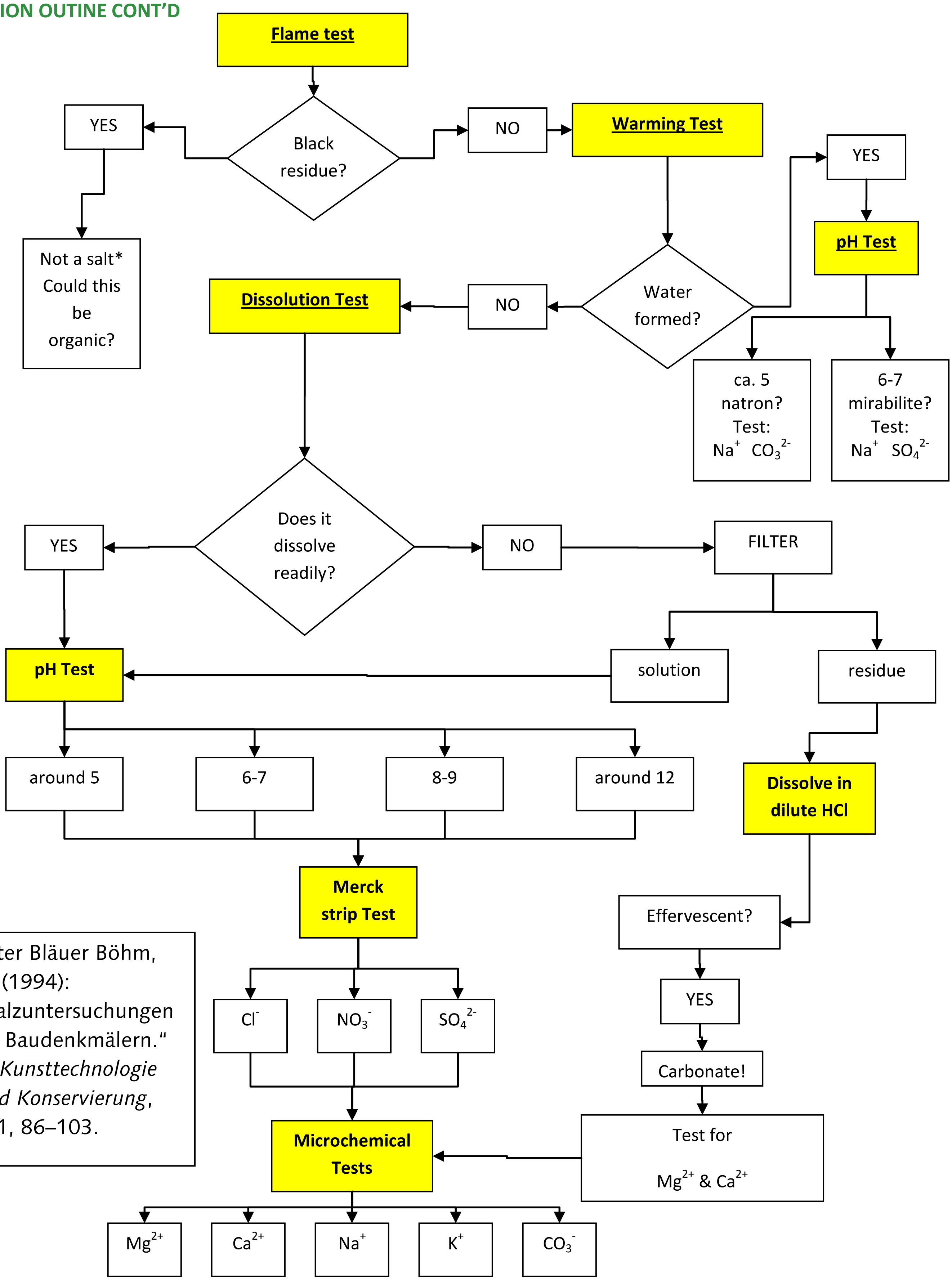
After each test make sure to carefully clean all equipment used: rinse into the waste containers provided with demineralised water, and wipe clean with tissue.

Make sure you label your samples and glass slides etc. clearly to avoid any confusion.

If in any doubt ask!

TEST RESULTS TABLE

Sample	Flame Test	Warming Test	Dissolution test	pH Test	Merck strip Chloride	Merck strip Nitrate	Merck strip Sulfate	CO_3^{2-} Carbonate	Ca^{2+} Calcium	Mg^{2+} Magnesium	Na^+ Sodium	K^+ Potassium
A												
B												
C												
D												



After Bläuer Böhm, C. (1994): „Salzuntersuchungen an Baudenkmälern." *Z. Kunsttechnologie und Konservierung*, 8/1, 86–103.

1) FLAME TEST

White biological growth, such as mould, often looks very similar to fluffy salt efflorescence. This is a useful and quick field test to differentiate between a white fluffy microbiological growth and a salt efflorescence.

☐ **Caution** Be careful! Do not set fire to yourself or other things!

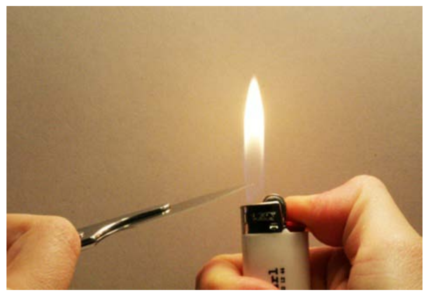
NOTE: this test is only valid in the context of porous building materials! Salts that occur on porous building materials are generally not flammable, however some organic salts (e.g. those that occur on certain museum objects) are flammable.

The following tests should ideally be performed outdoors, using small samples of material.
They should not be performed directly on facades or facade elements.

Tools needed:

Clean scalpel or knife, and a lighter.

Test Method:



Pick up a small amount of sample material using the tip of the knife blade or scalpel. Hold the knife tip with the sample in the *blue part* of the flame (in order to avoid deposition of soot on the sample and the tool do not hold in the yellow part of the flame).

White biological growth, such as mould, often looks very similar to fluffy salt efflorescence. **Mould burns and becomes black, whereas salt melts or bursts**

Mistakes to avoid:

If the sample is burnt in the yellow part of the flame, it will blacken due to soot deposition, even if it is free of organic material!

Other observations:

- Many materials, such as several pigments and stones, change their colour when exposed to an oxidising flame (they become reddish if they are rich in iron minerals, and blacken if they contain organic matter).

Reference salt to use: NaCl

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2) DISSOLUTION TEST

Like test 1, this test is also useful for distinguishing between fluffy salts, and fluffy fungal growths.

- Collect a small amount of sample material on the knife point
- Place in central well of a reservoir glass slide; add a few drops of deionised water (from the small dropper bottle) and stir with a glass rod.
- Observe the dissolution: soluble salts will dissolve readily, however other salts (such as gypsum) are only slightly soluble, and will remain as a residue.

Note: to observe this better, it can be helpful to place the slide on a dark surface

3) WARMING TEST; AN INDICATOR FOR HYDRATED SALTS

indicator for mirabilite (Na2SO4.10H2O) or natron (Na2CO3.10H2O)

A good simple field test to indicate the presence of mirabilite ($Na_2SO_4.10H_2O$) or natron ($Na_2CO_3.10H_2O$) on site is as follows:

- Place a small amount of the efflorescence in a clear plastic sample bag, and hold the bag against a warm surface (warm coffee cup, or in trouser pocket). Examine to see if beads of water develop inside the bag.
- If water drops form, measure the pH with pH-paper: if it is neutral (pH 6-8) then the sample is likely to be mirabilite; if it is alkaline (pH 9-11)it is most probably natron.

Sodium sulfate and also sodium carbonate can exist in a number of different hydrated mineral phases. Sodium sulfate can crystallize in the form of mirabilite ($Na_2SO_4.10H_2O$), however above 32 °C mirabilite spontaneously dehydrates to thenardite (Na2SO4), and releases its water.
Natron ($Na_2CO_3.10H_2O$) also readily dehydrates.

4) pH TEST: ALKALINE VERSUS ACIDIC SALTS

Photo: Christine Bläuer

In situ measurement:
- moisten the pH paper with demineralised water
- hold it against the efflorescence, or sprinkle some efflorescence onto the paper
- read the value

Photo: Christine Bläuer

Laboratory measurement:
- place a sample of the salts on a glass slide, and dissolve in a drop of water
- dip the edge of the pH paper into the drop (if using indicator strips wet the coloured part of the strip with a drop of sample solution).
- read the value

Note: Only a general estimation of the pH value is needed:

pH < 5 = acidic salts
pH 6–8 = neutral salts
pH 9–10 = slightly alkaline salts
pH >11 = strongly alkaline

The source of alkaline (i.e. pH>8) soluble salts (such as sodium and potassium carbonates) on monuments is always an alkaline building material (or restoration/conservation material), such as cement, hydraulic lime or water glass (Schaffer, 1932; Arnold, 1985). However, if the pH is neutral or acid (≤8) the origin of the soluble salts is not so certain, and can only be determined after more sophisticated analyses (however their origin can still be alkaline building materials).

Many carbonates and hydrogen carbonate salts are alkaline:

- Hydrogen carbonate (HCO_3^-): up to pH 8.4
- Carbonate (CO_3^{2-}): stable above pH 8.4
- Hydroxide (OH^-) : above pH 12

Name	Formula	pH (ca.)
Sodium carbonate (Natrite)	Na_2CO_3	12
Natron	$Na_2CO_3 \bullet 10H_2O$	12
Thermonatrite	$Na_2CO_3 \bullet H_2O$	12
Nesquehonite	$MgCO_3 \bullet 3H_2O$	10
Lansfordite	$MgCO_3 \bullet 5H_2O$	10
Trona	$Na_3H(CO_3)_2 \bullet 2H_2O$	10
Nahcolite (sodium bicarbonate)	$NaHCO_3$	8
Kalicinite (potassium bicarbonate)	$KHCO_3$	8

Watchpoint/ common mistakes:

De-ionised water can give a slightly acidic pH value due to its low ion content . Therefore for this test it is better to not use ultra pure de-ionised water, but rather demineralised or even clean drinking water (as long as it its dissolved ion content is not too high). Take care also when testing coloured sample materials (particularly those that form a fine suspension in water), that the reading is not confused/obscured by the coloration of the paper with sample itself.

Salt mixtures can produce some problems in that samples containing natron (sodium carbonate $Na_2CO_3 \bullet 10H_2O$) *with an excess of gypsum will give rise to a neutral solution, rather than an alkaline solution (as expected for pure natron).*

If your sample consists of a fine white powder (e.g. from a salt contaminated limestone) it can be interesting to tip a few grains on a damp pH-paper and observe the aureole forming around the grains (e.g. samples containing natron with an excess of gypsum will give a neutral pH in solution but using this method will show a few blue aureoles (i.e. high pH).

5) MERCK STRIPS FOR THE DETECTION OF CHLORIDE, NITRATE, AND SULFATE

Merck strips are a quick easy low cost method for indicating the presence of a range dissolved ions. The results are semi-quantitative, but the accuracy of this depends on the dilution used. Therefore in the field they are best used to give a general indication regarding the presence of specific ions. Test strips exist for a range of different ions, however, the detection limit for many of these is quite high.

Photo: Christine Bläuer

- Collect a small amount of efflorescence material on the knife point
- Place in central well of a reservoir glass slide; add a few drops of deionised water (dropper bottle) and stir with a glass rod.
- Using a pipette, take up some of the dissolved salt solution (leaving any residue), apply a series of drops to the coloured parts of the Merckstrip,. Wait a few seconds, and then compare indicator strip with the colour guide given on the package. Record the result.

Note:

- *Chlorides: the detection limit is very high so a very strong solution is needed*
- *Sulphates: the detection limit is very high too. Therefore not really good for gypsum (due to its low solubility) depending on how much water used to dilute sample.*
- ➢ *TIP: Merckstrips can be cut in half lengthways to cut costs!*

6) MICRO CHEMICAL TESTS

CAUTION: All the reagents used for these tests are hazardous!
Please make sure you are wearing gloves and eye protection at all times.
Familiarise yourself with the relevant chemical Hazard Data sheets.
Avoid any contact of chemicals with skin and especially eyes. Avoid any inhalation.
Handle all chemicals carefully, and dispose of them appropriately in the marked waste containers.

Carbonates (CO_3^{2-})

Acid test for carbonates (salt solution)

- Place a drop of salt solution on a glass slide.
- Add a drop of **dilute hydrochloric acid (1M HCl)**.
- ➢ If carbonate is present the solution will start to bubble due to the formation of carbon dioxide gas (CO_2 (g)) and water.

Acid test for carbonates (salt grain)

- Place a grain of salt on a glass slide.
- Add a drop of **dilute hydrochloric acid (HCl 1M)** to the grain of salt.
- ➢ If a carbonate salt is present, a vigorous effervescence will be observed, with the exception of Dolomite ($CaMg(CO_3)_2$) and Magnesite ($MgCO_3$), which will only effervesce in the presence of concentrated warm acids.

<u>Sodium (Na^+); Potassium (K^+)</u>

Adapted from Chamot et al 1946

<u>Preparation of the reagent solution</u>
(Not: must always be made up fresh, but can however be used for several tests on the same day):

- Place a glass reservoir slide on a piece of black paper (so you can better see what you are doing!)
- Place **1 small particle** (max. 1 mm^3) of **bismuth nitrate** on the glass reservoir slide.
- Add **1 small drop concentrated sulphuric acid (H_2SO_4 conc.) from the small dropper bottle**
- Stir vigorously for 1 to 2 minutes with a glass rod (bismuth nitrate dissolves slowly).
- Add **1 drop of deionised water**
- When the solution is saturated, the acidic drop will be white, firm and swells considerably.
- Add **1 drop of deionised water** and stir vigorously. The white salt should now almost completely dissolve to form a colourless/opalescent solution
- Add **1 drop 2M nitric acid (HNO_3 2M)**.
- <u>The reagent solution is now ready</u>.

<u>To avoid any accidents during this lab session, please bring JUST your salt sample and a glass slide to the microscope area, to do the test for sodium and potassium (where there is already some reagent solution made up).</u>

Test for Na+ und K+:
- Place a small grain of salt on a reservoir glass slide (or a drop of sample, which is then evaporated until dry).
- Carefully add **1 drop of the reagent solution to the salt particle**.
- Observe the reaction products under the microscope.

➢ Na^+ usually quickly forms characteristic tiny rod shaped crystals of sodium bismuth sulphate ($3Na_2SO_4.2Bi_2(SO_4)_3.2H_2O$).
➢ K^+ forms (often first after careful warming on a lukewarm heating plate) six-sided platelets of potassium bismuth sulfate {$K_2SO_4.Bi_2(SO_4)_3.2H_2O$}, some of which are iridescent (i.e. have shimmering rainbow colours visible under the polarising light microscope).

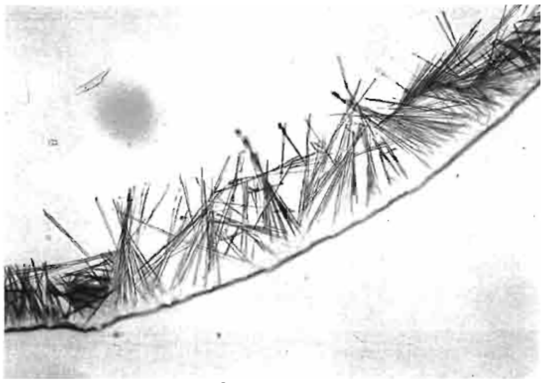
Watchpoints/ Complications:

➢ *Calcium, barium, strontium, lead, silver, titanium and mercury (Ca, Ba, Sr, Pb, Ag, Tl und Hg) can interfere with the reaction, either impeding or completely preventing the reaction.*

Calcium (Ca^{2+})

- Place a drop of salt solution on a glass slide
- Add **1 drop of 1M sulfuric acid (H_2SO_4) (small dropper bottle)**.
- Transfer the glass slide to a warming plate, until the edge of the drop begins to dry.
- Under a microscope, observe the crystals that form at the droplet edge.

➢ When calcium is present, bundles of characteristic needle shaped gypsum crystals will start to form.
➢ Detection limit for Ca^{2+} = 0.05 µg.



Indication of Ca^{2+}: Formation of gypsum crystals at edge of test droplet after the addition of 1M sulphuric acid
Image: Bläuer Böhm, C. (1994): „Salzuntersuchungen an Baudenkmälern." Z. Kunsttechnologie und Konservierung, 8/1, 86–103.

Magnesium (Mg^{2+})

Test with titan yellow

This test is very easy and simple! However you should also compare the result with the reaction of a salt solution drop containing calcium ions, because these give a similar but slightly different test result.

- Place a drop of the salt sample solution on a spotting plate
- Add **1 drop of dilute hydrochloric acid (1M HCl)** (small dropper bottle)
- Add **1 drop of Titan yellow solution** (small dropper bottle)
- Then add **1-2 drops of sodium hydroxide solution (2M NaOH)** and stir with a glass rod.

➢ In the presence of Mg^{2+}, a red fluffy precipitate is formed (detection limit ca. ca. 1,5 µg)

Complications:

➢ *In the presence of Calcium ions produces a light orange-red coloration which is then difficult to distinguish from the fluffy precipitate produced by Mg^{2+}. Compare with the results obtained for a solution containing calcium ions*
➢ *Nickel, Zink, Manganese und Cobalt ions also disrupt this test.*

READINGS

🕮 = Essential reading material
💻 = Available online

🕮 Arnold, Andreas. 1984. Determination of mineral salts from monuments. *Studies in Conservation* 29 (3): 129-38.

🕮 Arnold, Andreas. 1985. Moderne alkalische Baustoffe und die Probleme bei der Konservierung von Denkmälern. In *Natursteinkonservierung: Internationales Kolloquium, München, 21./22. Mai 1984*. ed. Rolf Snethlage and York Langenstein. 152-62. Arbeitsheft (Bayerisches Landesamt für Denkmalpflege) 31. München: Bayerisches Landesamt für Denkmalpflege.

🕮 Bläuer Böhm, Christine. 2005. Quantitative Salt Analysis. *Conservation of Buildings. Restoration of Buildings and Monuments / Bauinstandsetzen und Baudenkmalpflege 11* (6): 1–10.

💻 Salt wiki portal (http://www.saltwiki.net/) (also available in German at http://www.salzwiki.de/)

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