Abstract

Stone, ceramic and metal objects can be damaged by volatile acids and the salts these form by reacting with these objects or the soluble salts often contained in them. Because many people working with these objects in museums often do not recognize the problem or lack (re)sources to identify the salt species and therefore its origin, efforts to exclude sources of acetic acid from display or storage areas are usually not pursued. This article offers alternative, simple and inexpensive methods for the identification of these salts, including microchemical tests and polarized light microscopy, and compares the results with those of modern analytical methods.

Keywords

acetate salts, salt identification, microchemistry, preventive conservation, ceramics, limestone, calcareous objects, salt damage

Simple methods for the identification of acetate salts on museum objects

Lieve Halsberghe★
Ceramics conservation and restoration
Petrusberg 31
B-3001 Leuven
Belgium
E-mail: lievehalsberghe@hotmail.com

David Erhardt
SCMRE, Smithsonian Institution
4210 Silver Hill Road
Suitland
MD 20746, USA
E-mail: erhardtd@si.edu

Lorraine T Gibson
Department of Pure and Applied Chemistry
University of Strathclyde
295 Cathedral Street
Glasgow G1 1XL
United Kingdom
E-mail: lorraine.gibson@strath.ac.uk

Konrad Zehnder
Institut für Denkmalpflege, Forschungsstelle für Technologie und Konservierung
ETH Hoenggerberg HIL D33
CH-8093 Zurich
Switzerland
E-mail: zehnder@arch.ethz.ch

★Author to whom correspondence should be addressed

Introduction

Damage to museum objects caused by acid-induced salts is a widespread problem that has been recognized for quite some time. However, the identification of the salts, required to determine appropriate conservation procedures, remains a problem. The result is that the major cause, the emission of organic acids in the environment, is not being dealt with. This article gives an overview of the commonly encountered mixed acetate salt species and provides simple and inexpensive methods for their identification.

Background

Damage caused by acid vapours to museum collections was recorded as early as the 19th century (Byne 1899). In 1934 Nicholls described the mechanism on shells: acetic acid vapours from oak cabinets are absorbed by hygroscopic salts in the objects and react with calcium carbonate of the shell to form new salt species that effloresce and cause damage. Other acid-induced salt species have since been identified on objects in other museum collections, including natural history collections, archaeological collections with stone, ceramic or metal objects, and collections of decorative ceramics (see also Table 1).

Van Tassel (1945) identified calcium acetate chloride (calclacite) on a geological limestone specimen. It was later found on terracotta objects (West Fitzhugh 1971, Paterakis 1990, Halsberghe 2003). Calcium acetate nitrate was found on a coral brooch (Erhardt et al. 1981). Calcium acetate chloride nitrate (thecotrichite, originally identified as 'Efflorescence X' by West Fitzhugh and Gettens (1971)), was characterized in 1997 (Gibson et al. 1997) and has been reported on geological specimens, ceramics, limestone objects and fossils (Howie 1978). Calcium acetate and the double salt calcium acetate formate (Tennent and Baird 1985) form as the result of acid attack on molluscs, shells and bird's eggs, even when no hygroscopic salts are present in the object. However, most reports involve isolated cases, and the extent of the problem was not determined. Various

Table 1. Overview of known acetate salt species

Name	Formula	Type of objects it was found on	Literature and data on analyses	Method of analysis
Calcium acetate formate hydrate	$Ca(CH_3COO)(CHOO)H_2O$	Mollusca shells, bird's eggs	Tennent and Baird 1985	XRD, FTIR
Calcium acetate hydrate or hemihydrate	$Ca(CH_3COO)H_2O$ or $Ca(CH_3COO)\frac{1}{2}H_2O$	Molluscs, shells, bird's eggs	West Fitzhugh and Gettens 1971 Tennent and Baird 1985	XRD, FTIR
Calclacite (calcium acetate chloride pentahydrate)	$Ca(CH_3COO)Cl.5H_2O$	Fossils, terracotta objects, geological specimens	Van Tassel 1945 Van Tassel 1958	chemical analysis, optical microscopy XRD
Thecotrichite (calcium acetate chloride nitrate heptahydrate)	$Ca_3(CH_3COO)_3Cl(NO_3)_2.7H_2O$	Limestone, ceramic objects, geological specimens, fossils	Gibson et al. 1997	XRD, FTIR, IC
Calcium acetate nitrate hydrate	$Ca_2(CH_3COO)_3NO_3.2H_2O$	Coral object	Erhardt et al. 1981 Cooksey et al. 1999	
Sodium acetate	$Na(CH_3COO)$	Molluscs, terracotta objects, metals	West Fitzhugh and Gettens 1971	
Copper acetate (verdigris)	$Cu(CH_3COO)_2.H_2O$	Metals	Dunn 1981	XRD

acetates and formates also have been found on metal objects (West Fitzhugh and Gettens 1971, Dunn 1981, Thickett and Odlyha 2000), though metal corrosion products are not the focus of this paper.

Acetic acid damages materials such as metals, especially lead, and calcareous materials such as shells, coral, limestone and ceramics, and has the potential to damage many other materials. The use of materials for display or storage cases that might emit acetic acid has been widely, though not always effectively, discouraged (Taboury 1931, Lamy 1933, Nicholls 1934, West Fitzhugh and Gettens 1971, Blackshaw 1978, Padfield et al. 1982). Unsafe materials continue to be used for reasons of economy, convenience, availability, and working qualities (not to mention ignorance). Ceramics, for example, are not usually considered to be at risk. Hygroscopic salts such as calcium chloride and calcium nitrate are often present in ceramics and limestone objects, especially those that have been buried. In typical museum conditions, these are present as solutions that may cause no damage themselves. However, these solutions can react with atmospheric acetic acid to form mixed salts that are not deliquescent under museum conditions and therefore precipitate.

Determining the identity of the efflorescences or the ions they are composed of is essential to establish the causes of the deterioration so that appropriate measures can be determined.

Problems with identification

The recognition of the threat and the identification of the salts still present major problems. The efflorescences are often too small to be noticed or may be mistaken for mould (Halsberghe 2003). Small crystals are sometimes difficult to sample. The small quantities and often unavoidable impurities present an analytical problem. Recently identified mixed salt species are not yet in standard analytical databases; some have not been fully characterized. Conservators without access to scientific instrumentation or large budgets often test first for chlorides or nitrates. If the test is positive and no tests for other ions are conducted, the salts may be considered 'common'. Tests for other ions, such as acetate, are not routinely performed. Action may then be limited to salt concentration reduction (formerly desalination) of the contaminated object, which is then returned to the same storage environment. But deterioration does not necessarily occur simultaneously on all objects stored in the same environment (Tennent and Baird 1985), even if their composition and salt content is similar (Halsberghe 2003). If acid emission continues, treated objects may be relatively safe for some time, but the acid is likely to damage other objects stored in the same environment. Prevention of deterioration by RH control alone is not sufficient and is complex, if even possible. Most objects contain mixed salt solutions, which may crystallize and deliquesce over a range of relative

humidities. Calculating this range requires knowing the composition of the salt solutions inside the object. This is a difficult task for one object and a practical impossibility for large collections since salt compositions, concentrations and resulting RH calculations differ from object to object.

A series of simple tests that are easy, inexpensive, and require only small samples may aid in the identification of the problem and its extent. These are described in this paper and compared with traditional methods of analysis. Comparative analyses and testing of a series of samples from a variety of museum objects provide a guide to easier identification.

Microchemistry and contemporary analytical methods

Arnold's (1984) article on salt determination is probably the most referenced article on soluble salts in the conservation literature. Unfortunately, few people have implemented its useful recommendations. Arnold advocates qualitative identification methods such as optical microscopy combined with microchemical tests as alternatives to the usual but often expensive or unavailable analytical methods, primarily X-ray diffraction (XRD). Microchemical analysis combined with optical microscopy is a way to overcome the analytical problem of tiny and impure efflorescence samples. Difficulties with X-ray diffraction analysis occur when salts are too fine or poorly crystalline, and with hydrated salts that easily dehydrate.

Only the main anions, acetate (or formate), chloride and nitrate, are discussed here. Establishing their presence or absence generally provides sufficient information on the source of the efflorescence and for the conservation of the damaged object. It also permits to distinguish between the common acetate salt species and determine whether sources of volatile acids are present and should be dealt with. Acetate and formate are usually found only at the surface of objects, indicating an environmental source. Chlorides and nitrates are found at varying depths inside the objects since they mainly originate from ground water absorbed by the objects before collection, though conservation treatments or former use may also have been the cause.

Tests for other ions are found in the literature (Chamot et al. 1958, Arnold 1984, Bläuer Böhm 1994). Other analytical methods may be used if necessary and possible with the available sample quantity and budget. X-ray diffraction yields qualitative identification of the major salt species in the sample. In recent years, ion chromatography (IC) and Fourier transform infrared spectroscopy (FTIR) have been increasingly used. The data for thecotrichite are not in crystallographic data bases, but can be found in Gibson et al. (1997). The same article provides FTIR spectra of both calclacite and thecotrichite and the IC method used to quantitatively separate acetates and formates from other ions.

Recommended methods

These are summarized in Table 2.

Table 2. Summary of the recommended tests

Test name	Ions to detect	Test type	Reagent concentration	
1. Ferric chloride test	Acetate Formate	Colorimetric	0.5 M solution of FeCl₃, (or about 4 g of FeCl₃ dissolved in 50 ml water)	Deep terracotta coloration, no distinction between acetate or formate
2. Silver nitrate test	a. Chloride b. Acetate	Precipitation reaction	0.025 M of AgNO₃ (or about 0.1 g of AgNO₃ dissolved in 25 ml water)	a. White precipitation b. Pearly scales, arrow point like crystals
3. Nitron test	Nitrate	Precipitation reaction	2% nitron sulphate (diphenylendanilodihydrotriazol) in 5% acetic acid	Heavy white radiates (in reflected light and brown in transmitted light)

General advice

• Observe efflorescences with a binocular microscope, if possible before sampling with clean tweezers, scalpel or thin brush. If crystals with different
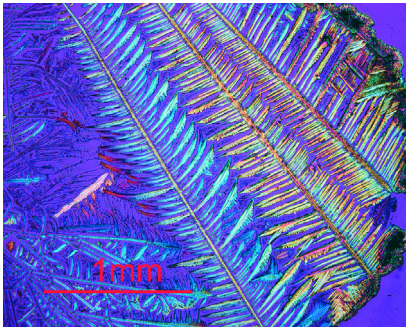
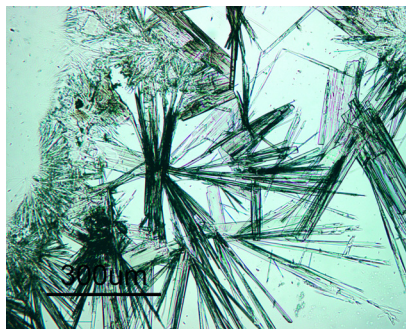*Figure 1. Crystals formed by dried silver nitrate reagent (photo with λ filter)*

Figure 2. Crystals formed by dried nitron reagent
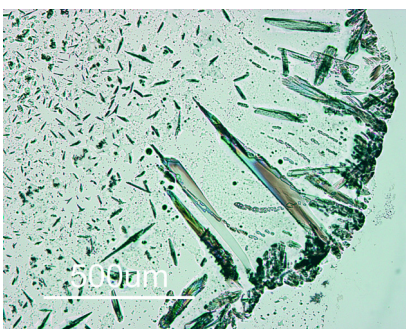

Figure 3. Silver acetate crystals at the edge of the test drop (silver nitrate test on sample 4)
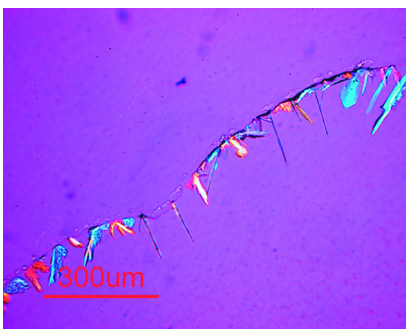

Figure 4. Silver acetate crystals growing at the edge of the test drop (silver nitrate test on sample 6, photo with λ filter)

morphologies are present, observe them separately with the polarizing light microscope.

- If possible, remove obvious impurities (fragments of ceramics or stone) with the use of a binocular microscope.
- Test drops must be sufficiently concentrated, otherwise no precipitate may form. Dry a drop of each reagent in order to distinguish reagent crystals from the precipitated crystals one is looking for (Figures 1 and 2).
- Microchemical tests require only quite small samples. Even small amounts should suffice for all necessary tests.
- Test first with standard solutions of acetates, formates, chlorides and nitrates, for reference purposes. These can be, respectively: sodium acetate, 0.1 g in 10 ml demineralized water; ammonium formate, same concentration; a few grains of table salt (sodium chloride) dissolved in water; 5 mg of sodium nitrate in 50 ml water.

Microchemical (colorimetric) test for the presence of acetates and formates

This test, described by Feigl (1939) and Vogel (1969), employs ferric chloride ($FeCl_3$). Already used by Byne (1899), it was adapted by Kirsten Linnow. Strips of filter paper are dipped into a 0.5 M solution of $FeCl_3$ (4 g of $FeCl_3$ in 50 ml water) and placed on a clean glass or glazed ceramic surface. A sample of efflorescence is placed on the wet paper. This instantly dissolves and a deep (terracotta) red coloration (ferric acetate or ferric formate) forms if acetates or formats are present. This works only with salts with a neutral pH, which is the case of all acetate and formate salts presented here.

Microchemical tests (with precipitation reactions) for the identification of acetates (formates), chlorides and nitrates

A drop of reagent is joined to a drop of the test solution (efflorescence sample dissolved in demineralized water). The precipitation of less soluble crystals with a specific shape, upon connection of the two drops, is the principle of this method. These crystals may be observed with a microscope and sometimes with the naked eye. The method is adapted to tiny quantities of efflorescence, but other variations are available (Chamot and Mason 1958, Arnold 1984).

A small amount of efflorescence is added to a small drop of demineralized water on a clean microscope slide. A drop of the reagent is placed at a distance of 3–4 mm from the first drop. With the tip of a clean needle or glass rod, a bridge is drawn from the reagent drop to the solution. The precipitated crystals are observed with a microscope. For the following reactions, heating of the slides is not necessary.

SILVER NITRATE TEST

This test establishes the presence of chlorides in efflorescences or solutions (Paterakis 1987). Tiny crystals of the insoluble silver chloride, AgCl, form and, depending on the concentration, a white precipitate may be visible to the eye. If the test solution is pH neutral and contains acetates, crystals of the more soluble silver acetate can be observed growing at the edge of the drying drops (Figures 3 and 4). They resemble pearly scales, which develop into long thin plates (Chamot and Mason 1958), usually about 200–400 μm long. Some have pointed ends, others more rounded, like the end of a feather. Formates in the test drop precipitate with the silver into grey, pulpy tablets and star-shaped aggregates composed of thin prisms and needles (Behrens and Kley 1922), as in Figure 5. Both silver acetate and formate will turn dark, formate more quickly. Therefore, it is best to observe the connected drops drying in the air without heating.

Note that silver forms precipitates with other ions that could be confused with silver chloride (see Chamot and Mason 1958). However, bromides and iodides are usually not present in efflorescences, and sulphates only react if present in high concentrations. Carbonates, however, form a white amorphous precipitate indistinguishable from silver chloride. To make this test specific for chlorides, the test solution is acidified (Bläuer Böhm 1994), but this makes the acetate test invalid. Water-soluble carbonates are rarely found on museum objects.
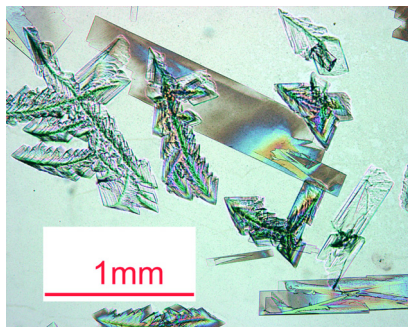
Figure 5. Silver formate crystals (precipitated from union of one drop of ammonium formate and one drop of silver nitrate)
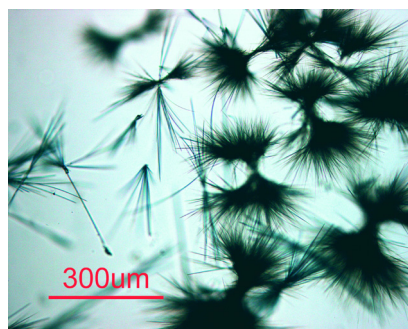

Figure 6. Nitron nitrate crystals (nitron test on sample 7)

NITRON TEST

If the sample contains nitrates, a heavy white precipitate of nitron nitrate forms instantly. This is brown in transmitted light. With a binocular microscope, slender needles forming bulky, imperfect radiates can be observed. Nitron nitrate is almost insoluble, and even small concentrations of nitrates can be detected because of the typical shape of the crystals (Figure 6).

Polarized light microscopy permits qualitative identification of the salts species

Under a binocular microscope (about 50× magnification), thecotrichite appears as white fluffy aggregates of very fine needles. With a polarizing light microscope (500×), the needles exhibit diameters of about 1 μm with lengths up to several hundred microns. The needles often lump in irregular clusters or parallel fibrous aggregates (similar to asbestos, see Figure 7), which are often articulated. With an immersion liquid of $n = 1.518$, the relief is rather low and negative. The refractive indices are $n_x = 1.491 \pm 0.001$ and $n_z = 1.494 \pm 0.003$. The elongation is negative: that is, the higher index is perpendicular to the c-axis of the needles. With crossed polarizers, the extinction is parallel (namely parallel to the direction of the polarizers). The birefringence (double refraction) is rather low (similar, for example, to gypsum). The as yet undetermined crystallographic system of thecotrichite can be deduced from these features as orthorhombic, hexagonal or tetragonal.
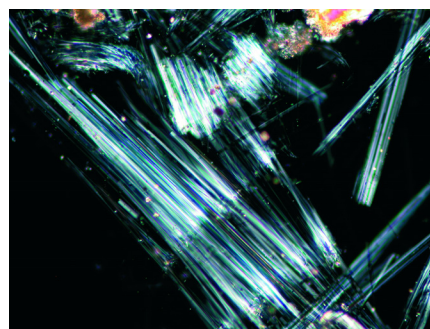

Figure 7. Bundle of thecotrichite needles from sample 11 seen with crossed nicols (image width about 0.75 mm)
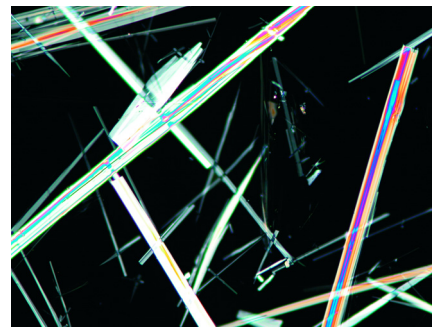

Figure 8. Bundle of calclacite needles (sample 6) seen with crossed nicols. (High birefringence colours are visible on the colour version, image width 1.5 mm)

Other important and often co-existing salts are distinguished from thecotrichite as follows:

- Halite (NaCl) normally crystallizes with coarser needles and grains. It has a stronger and positive relief ($n = 1.544$), and is isotropic.
- Nitratine ($NaNO_3$) and other nitrate salts have a very high birefringence.
- Calclacite – $Ca(CH_3COO)Cl.5H_2O$ – has a stronger but also negative relief and a higher birefringence, with $n_x = 1.484$ and $n_z = 1.515$. In consequence, when the grain is rotated, its relief changes from clearly negative to almost invisible (Figure 8).

Comparative testing and analysis

Samples were selected from a growing collection of acid induced efflorescence samples (Table 3), and each submitted to the recommended tests, polarized light microscopy and available analytical techniques.

Table 3. details on samples tested

Sample number	Sample name	Description of efflorescence	Description of object	Description of damage	Museum collection
1	Eggshell	Salt pustules on all of outer surface	Pigeon's egg	Disintegration of shell	Musée National d'Histoire Naturelle, Luxembourg
2	Inv. 5559	Deep green crust	Copper plate attached to back of tile panels	Surface corrosion	Stedelijke Musea Kortrijk, Belgium
3	C3, inv. NS 80	Thin long needles (http://www.iaq.dk/image/cyprus_vase.htm)	Small Cypriot terracotta vase (between 9th–7th c. BC)	Surface powdering and flaking	Musée Royal de Mariemont, Morlanweltz, Belgium
4	Inv. Ac67/30	Thin whiskers on outer and inner surface	Attic terracotta vase (about 8th c. BC)	Surface powdering and flaking	Musée Royal de Mariemont, Morlanweltz, Belgium
5	Inv. A 1582–1982	Thin whiskers on outer and inner surface	Greek vase	Surface flaking	Birmingham Museums and Art Galleries, UK
6	Inv. 1953.929 (i)	Abundant whisker growth on whole surface	Pottery sherd (Cypriot origin)	Surface flaking and disintegration	Ashmolean Museum, Oxford, UK
7	Inv. 3922/B1	Layer of fluffy whiskers and salt pustules	Tin glazed Dutch tile, 18th c.	Pitting, powdering and flaking on all unglazed sides	Stedelijke Musea Kortrijk, Belgium
8	Inv. KD 1610	Salt pustules and tiny whiskers	Lead glazed tile, Flemish, 18th c.	Pitting and flaking of the surface, both in glazed and unglazed zones	Stedelijke Musea Kortrijk, Belgium
9	Inv. 5363	Abundant whisker growth on large part of surface	Lead glaze on slip decorated terracotta plate, Nishapur, Persia, 12th c.	Flaking of glaze and ceramic body	Stedelijke Musea Kortrijk, Belgium
10	Inv. 7394R 1860	Tiny whiskers growing on unglazed side	Tin glazed terracotta lion head, medallion for wall, Italian, prob. Surr. Della Robbia, 16th c.	Minor damage, micro flaking	Victoria and Albert Museum, London, UK
11	Inv. Ev370	Abundant whisker growth on unglazed sides	Tin glazed tile, Dutch, 18th c.	Pitting of the surface	Musées Royaux d'Art et d'Histoire, Brussels, Belgium
12	Inv. 72.60	Surface covered in fluffy whiskers	Limestone funerary stela, Roman period (3rd–4th c. AD)	Surface flaking	Brooklyn Museum of Art, Brooklyn, NY, USA
13	Inv. 431484	Surface covered in fluffy whiskers	Limestone relief, origin: Yemen	Surface flaking	National Museum of Natural History, Washington D.C., USA
14	No inv. number	Coarse salt grains cover surface	Terracotta mould, Hathor head, Egypt, unknown date	Surface pitting	Brooklyn Museum of Art, Brooklyn, NY, USA
15	Inv. 3528	Coarse grains cover part of surface	Coral brooch	Surface pitting, increase in porosity	National Museum of American History, Washington D.C., USA

Discussion

See Table 4 for results of comparative analysis.

- The iron chloride test usually works well because the concentration of acetates and formates is high in the tested salt species. It was also effective for the shell and metal corrosion, as well as green corrosion on a small bronze Egyptian jug (Smithsonian inv. 88659-61). Results for tiny samples or samples containing impurities or other salt species are difficult to interpret.
- With practice, the silver nitrate test works well. It gave unsatisfactory results with the eggshell efflorescence and the copper plate corrosion, even though the presence of acetates was confirmed by other methods.
- The nitron test is very sensitive and easy to interpret. The crystals are quite distinct.
- With practice, polarized light microscopy can be used to distinguish and identify crystals of calclacite, thecotrichite, halite and nitratine, but experience is required to identify all other salt crystals. Polarizing light microscopes may be available at a local university, often in a geology or mineralogy laboratory. With the information in this text, specialists should be able to help with identifications. In our experience, people are usually willing to help (when the right questions are asked). The advantage of this method is that different salt species in one sample can be observed and identified. Little sample is needed (a few whiskers suffice). Identification is nearly certain when combined with microchemical tests.
- FTIR spectra usually yield matches with published spectra of known acetate salt species. But they do not reveal halite, for example.

Table 4. Comparative analysis

N°	Material	FeCl₃ test	AgNO₃ test		Nitron test	PI microscopy	FTIR	XRD	IC (anions) in mg/g of sample	Conclusion
			Cl⁻	acetate	Nitrates					
1	eggshell	+	-	n.d.	-	n.a.	calcium acetate formate	calcium acetate formate	acetate: 400 formate: 182 chloride: 0 nitrate: 0	calcium acetate formate hydrate
2	copper	+	-	n.d.	-	Medium birefringence	copper acetate	n.a.	n.a.	copper acetate
3	terracotta	+	+	+	-	Straight needle bundles, high birefringence, neg. relief (poss. calclacite)	calclacite	calclacite, halite, calcite, quartz	acetate: 229 formate: 0 chloride: 173 nitrate: < 15	calclacite and some halite (calcite and quartz are part of ceramic body)
4	terracotta	+	+	+	-	Calclacite	calclacite	calclacite, quartz		
5	terracotta	+	+	+	-	Calclacite	n.a.	n.a.	n.a.	calclacite
6	terracotta	+	+	+	+	1) Bundles straight needles, high brief., neg. relief (poss. calcl.) 2) Bundles of very thin needles, very low brief., neg. relief (poss. theco) 3) Grains, pos. relief, isotropic: halite	thecotrichite	thecotrichite	n.a.	calclacite, thecotrichite and some halite
7	tin glazed ceramic	+	+	+	+	Bundles of very thin needles, very low brief., neg. relief (theco)	thecotrichite	thecotrichite, halite	acetate:140 formate: 0 chloride: 59 nitrate: 110	thecotrichite and some halite
8	lead glazed ceramic	+	+	+	+	Bundles of very thin needles, very low brief., neg. relief (theco)	thecotrichite	thecotrichite, calcite	n.a.	thecotrichite
9	lead glazed (on slip) ceramic	+	+	+	+	Bundles of very thin needles, very low brief., neg. relief (theco)	thecotrichite	thecotrichite	acetate:216 formate: 0 chloride: 49 nitrate: 270	thecotrichite
10	lead glazed ceramic	+	+	+	+	Bundles of very thin needles, very low brief., neg. relief (theco)	thecotrichite	thecotrichite	n.a.	thecotrichite
11	lead glazed ceramic	+	+	+	+	Bundles of very thin needles, very low brief., neg. relief (theco)	thecotrichite and quartz	thecotrichite and quartz	n.a.	thecotrichite
12	limestone	+	+	+	+	1) Bundles of very thin needles, very low brief., neg. relief (theco) 2) Grains, pos. relief, isotropic: halite	thecotrichite	thecotrichite	n.a.	thecotrichite and some halite
13	limestone	+	+	+	+	Bundles of very thin needles, very low brief., neg. relief (theco)	n.a.	thecotrichite	n.a.	thecotrichite
14	terracotta	+	-	+	-	Grains with high brief., neg. relief	sodium acetate	n.a.	n.a.	poss. sodium acetate
15	coral	+	-	+	+	1) Bundles, very low brief., neg. relief 2) Grains, high brief., neg. relief	n.a.	calcium acetate nitrate	n.a.	calcium acetate nitrate

Abbreviations used   +: positive; -: negative; n.d.: not detected; n.a.: not analysed; biref.: birefringence; neg.: negative; pos.: positive; poss.: possibly; theco: thecotrichite; calcl.: calclacite

- XRD works well if data for the known acetate salts is available. Calcite and quartz are often detected. They are not part of the efflorescence, but tiny particles of the ceramic body mixed in the sample. Their presence in the efflorescence confirms damage to the ceramic body.
- IC is the only method that gives precise quantitative information, but only on the ions present. The analysis requires great accuracy, is quite time and budget consuming, and identification of the salt species requires knowledge of the stoichiometry of the specific salts.

Conclusion

Microchemical tests and microscopy are useful for the identification of salt efflorescences and corrosion products on museum objects caused by organic acids such as acetic and formic acid. They are recommended so that the problem may be identified and dealt with appropriately. The tests are a simple, economical and reliable alternative to instrumental analysis.

Acknowledgements

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