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CONSERVATION OF ARCHITECTURAL HERITAGE,
HISTORIC STRUCTURES AND MATERIALS

Introduction

INTRODUCTION

ARC
LABORATORY HANDBOOK

VOLUME 1/99

ISBN 92-9077-157-7

International Centre for the Study of the Preservation
and Restoration of Cultural Property
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ICCROM PREFACE

In recent decades, the conservation of architectural heritage has increasingly drawn on new knowledge arising from the development of specialized scientific disciplines.

Condition assessment, diagnosis, conservation and restoration treatment, as well as long-term monitoring of performance, often call for specific investigation techniques and interdisciplinary study with specialized conservation laboratories.

Over the years, conservation scientists working with cultural heritage have developed analytical methods, procedures and testing techniques for the study of materials: their characteristics, causes of deterioration, alteration and decay processes. Such data are of essential support to planning any conservation or restoration activity, as well as preventive measures.

Informed use of the various available testing techniques and measuring procedures combined with the findings of other surveys and past experience allow for establishing a more complete basis for correct diagnosis, sound judgement and decision-making in the choice of the most appropriate conservation and restoration treatments within the general strategy for the historic building.

Conservation professionals today are fully aware of the fundamental role materials science and laboratory analysis play in the conservation process.

Thus a certain knowledge of the basic and most frequently used laboratory tests and a capacity to interpret their results should be an integral part of the general preparation of any professional working in the field of conservation.

With the Laboratory Handbook, ICCROM hopes to fulfil the long-felt need to provide a simple and practical guide where basic concepts and practical applications are integrated and explained.

MARC LAENEN
DIRECTOR-GENERAL

INTRO INTRODUCTION

Concept

The ICCROM ARC Laboratory Handbook is intended to assist professionals working in the field of conservation and restoration of architectural heritage.

Target group

It has been prepared principally for architects and engineers, but may also be relevant for conservator-restorers, archaeologists and others.

Aims

- To offer simplified and selected material, structured to the needs of the target group: an overview of the problem area, combined with laboratory practicals and case studies.
- To describe some of the most widely used practices, and illustrate the various approaches to the analysis of materials and their deterioration processes.
- To facilitate interdisciplinary teamwork among scientists and other professionals involved in the conservation process.

Context

The handbooks have evolved from lecture and laboratory handouts developed and constantly updated for ICCROM's international or regional training programmes, principally the following mid-career professional courses:

- Conservation of Architectural Heritage and Historic Structures
- Technology of Stone Conservation
- Conservation of Mural Paintings and Related Architectural Surfaces
- Conservation of Architectural Surfaces

as well as in a series of collaborative laboratory activities, and consultancy and research projects.

Background

The Laboratory Handbook builds on valuable past experience. Certain ICCROM publications along similar lines, namely "Porous Building Materials: Materials Science for Architectural Conservation" by Giorgio Torraca (1982), and "A Laboratory Manual for Architectural Conservators" by Jeanne Marie Teutonico (1988) have been among the main references.

The long-term experience accumulated from other institutions, that of renowned experts and conservation/restoration practice in general have naturally also been a point of reference, as has the process of designing laboratory session modules for ICCROM courses in recent years; the latter has been enriched by feedback both from participants and from contributing leading specialists.

Structure

The concept behind the Laboratory Handbook is modular. Thus, it has been conceived as a set of independent volumes, each of which will address a particular subject area. The volumes relate particularly to topics covered in the International Refresher Course on Conservation of Architectural Heritage and Historic Structures (ARC), which are as follows:

- DECAY MECHANISMS, DIAGNOSIS: guiding principles of materials science, external climatic risk factors, atmospheric pollution, humidity, bio-deterioration, investigation techniques, surveying

- CONSERVATION AND RESTORATION TREATMENTS OF BUILDING MATERIALS AND STRUCTURES THEIR TESTING, MONITORING AND EVALUATION: timber, earthen architectural heritage, brick, stone, mortars, metals, modern materials, surface finishes.
  As an issue of broader interest, practical information and guidelines for setting up architectural conservation laboratories are also scheduled for publication.

In general, each volume includes:
- introductory information
- explanations of scientific terms used
- examples of common problems
- types of analysis (basic principles)
- practicals (laboratory tests)
- applications (case study)
- bibliography

Principles are explained, and some longstanding methodologies described. Up-to-date information on techniques, instruments and widely used reference standards has been included.

Further information on practical techniques not strictly related to laboratory work is also provided in some cases.

The practicals - involving basic tests and simple analyses - are conceived as part of ICCROM's laboratory sessions.

It is understood that architects will not generally be performing laboratory analyses on their own. However, knowledge of the types of analysis available for obtaining specific data, their cost, reliability and limitations is essential for today's conservation architects. They should also be aware of sampling requirements and techniques, able to understand and interpret results, and effectively communicate them to other colleagues in interdisciplinary teams.

The individual volumes are being prepared by various authors, depending on the subject and their specialization. The Scientific Committee is composed of specialists in the relevant fields, who also have strong ties with ICCROM through direct involvement in the training courses.

Special features

Progress in conservation science and technology means that currently available information must be regularly evaluated and updated. This is why the Handbook has been structured as a series of volumes.

This will allow:

- the authors to periodically update specific volumes to reflect changing methodology and technology in an easy, time-saving and economical way, thanks to the digital reprinting process
- the users to work selectively with the volume relating to the particular problem they are facing
- new volumes to be gradually added to the set in line with developing needs, until all the relevant subjects have been covered by the series.

We are aware that the information provided is not all-embracing but selective. It is hoped that feedback from users will assist us in improving and continually adapting the project to changing needs.

The project team - Ernesto Borrelli and Andrea Urland - welcomes any constructive criticism, comments and suggestions that might help us achieve this goal.

ANDREA URLAND
ARC PROJECT MANAGER

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The authors would especially like to express their gratitude to the members of the Scientific Committee, who kindly agreed to give this publication their support, sharing their expertise by reviewing the draft texts and providing valuable comments and suggestions.

The authors further wish to recognize the scientific collaboration of Beatrice Muscatello, the precious contribution of the advisors and the text editing by Christopher McDowall and Cynthia Rockwell.

They are equally grateful to the ICCROM staff for their whole-hearted collaboration and to those at the UNESCO World Heritage Centre for their support.

And finally we wish to thank all the others who have, in some way, contributed to the preparation and completion of this publication.

1998 - 99 VOLUMES:

1. Introduction
2. Porosity
3. Salts
4. Binders
5. Colour specification and measurement

ICCROM

The International Centre for the Study of the Preservation and Restoration of Cultural Property (ICCROM) is a leading voice in the conservation of cultural heritage around the world. Founded by UNESCO in 1956, and based in Rome, ICCROM is the only intergovernmental organization concerned with conserving all types of movable or immovable heritage.

ICCROM takes action today for heritage tomorrow. Its broad-ranging activities span five continents and cover a wide range of cultural heritage, from cave painting to sculpture, earthen architecture, plastered façades, libraries, archives and entire historic centres.

ICCROM tackles the challenges facing cultural heritage – neglect, pollution, catastrophe, theft or decay – and strengthens the conditions for its effective conservation. It provides an international platform for debate while also tailoring activities to regional needs.

It achieves this by collecting and disseminating information; coordinating research; offering consultancy and cooperation in field conservation and restoration; providing professional training; and promoting awareness of the social value of cultural heritage preservation amongst all sectors of society.

Above all, ICCROM integrates the conservation of our cultural heritage into global approaches to sustainable human development and community service.

Dr Harold Plenderleith (1898-1997)

ICCROM’s LABORATORY: A BRIEF HISTORY

The new ICCROM Laboratory, inaugurated in 1997, is dedicated to Dr Harold Plenderleith, the Organization’s founding director.

In 1966, during his tenure, a first basic laboratory was set up for didactic purposes at the original headquarters in Via Cavour.

In the 1980s, after ICCROM had moved to Via di San Michele, a new and better-equipped laboratory was installed under the coordination of Dr Giorgio Torraca, then ICCROM’s Deputy Director. Many activities, including research, were launched in the framework of the newly created “Training and Research Units”. Later, a smaller specialized laboratory was also developed by Jeanne Marie Teutonico for the architectural conservation courses.

ICCROM’s current Laboratory (about 200 m^2) is organized as a series of specialized areas, grouping together all the previous activities. The works were subsidized by a major financial contribution from the Italian Government.

The improved level of equipment and furnishing offers opportunities to expand and further raise the standard of work.

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CONSERVATION OF ARCHITECTURAL HERITAGE,
HISTORIC STRUCTURES AND MATERIALS

Porosity

POROSITY

ARC
LABORATORY HANDBOOK

VOLUME 2/99

Ernesto Borrelli

The ICCROM ARC Laboratory Handbook is intended to assist professionals working in the field of conservation of architectural heritage and historic structures. It has been prepared mainly for architects and engineers, but may also be relevant for conservator-restorers or archaeologists.
It aims to:

- ***offer an overview of each problem area combined with laboratory practicals and case studies;***
- ***describe some of the most widely used practices and illustrate the various approaches to the analysis of materials and their deterioration;***
- ***facilitate interdisciplinary teamwork among scientists and other professionals involved in the conservation process.***

The Handbook has evolved from lecture and laboratory handouts that have been developed for the ICCROM training programmes. It has been devised within the framework of the current courses, principally the International Refresher Course on Conservation of Architectural Heritage and Historic Structures (ARC).

The general layout of each volume is as follows: introductory information, explanations of scientific terminology, the most common problems met, types of analysis, laboratory tests, case studies and bibliography.

The concept behind the Handbook is modular and it has been purposely structured as a series of independent volumes to allow:

- ***authors** to periodically update the texts;*
- ***users** to work selectively with the volume relating to the particular problem they are facing*
- ***new volumes** to be gradually added in line with developing needs.*

1998 - 99 volumes:
*(1) Introduction, **(2) Porosity**, (3) Salts, (4) Binders, (5) Colour specification and measurement*

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ARC
Laboratory Handbook

Porosity

Ernesto Borrelli

ICCROM

Rome, 1999

CONTENTS

① : Footnotes

🗁 : Bibliographic references

1 INTRODUCTION

Many building materials, both natural (stones) and artificial (bricks, lime and cement mortar) contain a certain volume of empty space. This is distributed within the solid mass in the form of pores, cavities, and cracks of various shapes and sizes. The total sum of these empty spaces is called porosity, a fundamental characteristic of building material that affects its physical properties (durability, mechanical strength, etc.).

The characteristics of pores in rocks depend mainly on their genesis (i.e. igneous①, sedimentary②, metamorphic③ etc.) whereas the porosity in man-made building materials depends on their manufacture 🗀1.

The knowledge of the pore structure is an important parameter for characterizing materials, predicting their behaviour under weathering conditions, evaluating the degree of decay and establishing the effectiveness of conservation treatments.

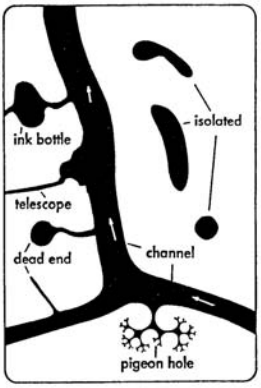
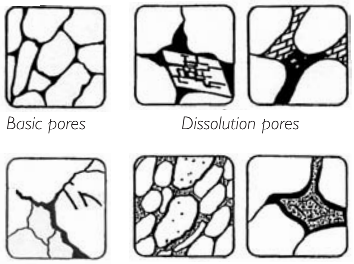


Fig. 1 - Pore models (taken from Fitzner)

2 CLASSIFICATION OF PORES 🗀2

Pores can essentially be classified according to their typology, geometry and size.



Basic pores *Dissolution pores*

Fracture pores *Shrinkage pores*

Fig. 2 - Pore types (taken from Fitzner)

Typology

- **Closed pores:** pores completely isolated from the external surface, not allowing the access of water in either liquid or vapour phase. They influence neither permeability nor the transport of liquids in materials but do affect their density and mechanical and thermal properties 🗀3.
- **Open pores:** pores connected with the external surface of the material and therefore accessible to water have a direct bearing on deterioration phenomena. Open pores permit the passage of fluids and retain wetting liquids by capillary action. They can be further divided into dead-end or interconnected pores *(Fig. 1)* 🗀4.

Geometry

Pores can also be classified according to their shape:

- SPHERICAL PORES, CYLINDRICAL PORES AND ELONGATED PORES

or according to their genesis *(Fig.2; photos 1-4 on inside back cover)*:

- BASIC PORES: pores inherent to the process of rock formation;
- DISSOLUTION PORES: pores deriving from the chemical dissolution of carbonates (see transformation of carbonates into soluble bicarbonates④) sulphates, and organic materials (by transformation into CO_2);
- FRACTURE PORES: pores and microcracks deriving from intro and intercrystalline mechanical fracture, linked to the tectonic deformation of rocks and due to stress caused by applied loads;

① *Rocks that have solidified from molten rock material both below and on the earth's surface (e.g. granite, gabbro, basalt, tuffs).*

② *Rocks formed by the accumulation and consolidation of sediment at relatively low temperature and pressure (sandstone, limestone, travertine).*

③ *Rocks that are the result of the structural transformation in the solid state of pre-existing rocks under conditions of high temperature and pressure (marble, gneiss, schist).*

④ *See Laboratory Handbook Salts p. 7*

- SHRINKAGE PORES: pores deriving from the contraction of the various components of masonry materials, mainly artificial ones e.g. the shrinkage of mortars due to rapid water loss.

Size

There is considerable variability in pore sizes; they vary from a few angstrom⑤(Å) to several millimetres. Pores of greater dimensions are defined as cavities rather than pores, and do not contribute to capillary action. Pores with radii⑥ less than 10 angstrom are not considered permeable.

There are conflicting views concerning pore size classification. In practice, when conservation scientists speak of porosity, they are not generally referring to the values defined below, but to a dividing line of < 2.5 µm and > 2.5 µm between microporosity and macroporosity, which is more realistic when dealing with building material⑦ 🗀6.

International standards (IUPAC) 🗀5 classify pores according to their radius as

MICROPORES:	radius	< 0.001	µm	(< 10 Å)
MESOPORES:	radius between	0.001	µm and 0.025 µm	(10 Å and 250 Å)
MACROPORES:	radius	> 0.025	µm	(> 250 Å)

The percentage distribution of pores of differing radius within the material is an extremely important parameter for the evaluation of its behaviour in contact with water and therefore for the forecast of freeze-thaw cycles, chemical reactivity etc.

There is obviously a great variation in porosity from one material to another. Igneous (e.g. granite, basalt) and metamorphic (e.g. marble, gneiss) rocks are not very porous with maximum porosity between 1% and 2%. Unless they are fractured, these low-porosity rocks are scarcely permeable. A lot of sedimentary rocks, however, and particularly calcarenites, have high porosity with maximum values even reaching 45%.

The % porosity and pore types of some common rocks are summarized in the following table:

Rock type	**Genesis**	**Geological formation**		**% porosity**	**Predominant pore type**
		pressure	**temperature**	**(average value)**	
basalt	igneous	low	very high	≅ 1 - 3	macro
granite	igneous	high	very high	≅ 1 - 4	micro
tuff	igneous	low	high	≅ 20 - 30	micro
gneiss	metamorphic	high	high	≅ 0,4 - 2	micro
marble	metamorphic	high	high	≅ 0,2 - 0,3	micro
slate	metamorphic	high	medium-high	≅ 0,1 - 1	micro
coral stone	sedimentary	low	low	≅ 40 - 50	macro
limestone	sedimentary	low	low	≅ 15 - 20 ± equal	micro/macro
sandstone	sedimentary	low	low	≅ 10 - 15	macro

Table 1 - Porosity and pore type of some common rocks

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⑤ 1 Å = 10^{-10}m, or 1µm = 10^{4} Å.

⑥ At a first approximation, all pores of any shape are considered equivalent to round pores of equal nature. The radius of the equivalent pores can be measured by several methods (see section 6).

⑦ These values are proposed by Russell (1927), De Quervain (1967), Ashurst & Dimes (1977), Zehnder (1982) and Veniale & Zezza (1987).

3 BASE TERMS

- **Pore volume (V_p)**
  is the fraction of the total volume of a solid occupied by the pores (i.e. the empty space of a solid).

- **Apparent volume (V_a)**
  is the volume of a solid including the space occupied by pores.
  (a piece of stone measuring 5 cm each side has an apparent volume of 5x5x5 = 125 cm^3)

- **% total porosity (P)**
  is defined as the ratio between the volume of the pores **(V_p)** and the *apparent volume* **(V_a)** expressed as a percentage.

$$\boxed{\% P = 100 \times (V_p / V_a)}$$

(a piece of limestone measuring 5 cm each side with a total porosity of 22% contains 27.5 cm^3 of empty space)

- **Open pore volume (V_{op})** is the volume occupied by open pores.

- **% open porosity**
  is less than or equal to the total porosity and is defined as the ratio between the volume of the open pores **(V_{op})** and the apparent volume **(V_a)** expressed as a percentage.

$$\boxed{\% P = 100 \times (V_{op} / V_a)}$$

It is also known as effective porosity: percentage of interconnected pore space
(a piece of limestone measuring 5 cm each side with a total porosity of 22% that contains 20 cm^3 of open pores has an open porosity of 16 %)

- **Real volume (V_r)**
  is the difference between apparent volume **(V_a)** and pore volume **(V_p)**

$$\boxed{V_r = V_a - V_p}$$

(a piece of stone measuring 5 cm each side with a total porosity of 22% has a real volume of 97.5 cm^3)

- **Specific surface**
  (S_s) is the surface (m^2) of the walls of the open pores and is expressed per unit volume of the material (m^2/m^3).

4 MOVEMENT OF WATER IN POROUS BUILDING MATERIALS

The study of porosity is fundamental for understanding phenomena of water transport within pore structure and interactions between materials and water.

Water can penetrate a solid because there are interconnected channels (pores) inside the solid that facilitate its transportation. Stone material can absorb moisture from the environment in **vapour form** depending on the relative humidity and in **liquid form** when exposed to the direct action of water (rainfall, rising damp from the soil and water vapour condensation from the air) 🗀**7.**

In liquid form:

a) By capillary suction: when an initially dry porous material comes into contact with water, it gets progressively wetter. First, it fills up the smaller pores, and then creates a liquid film on the surface of the larger pores, eventually filling these too;

b) By diffusion, due to the passage of water from a higher to a lower water content area;

c) By osmosis: when salts are present in water, they are dissociated into electrically charged particles (ions) that attract water through electric force.

In vapour form:

a) By diffusion as vapour, from pores with a high water vapour content to pores with a lower one;

b) By hygroscopic absorption, which can occur even at temperatures above dew point⑧. This phenomenon is accentuated in the presence of soluble salts that are hygroscopic and can absorb water also under average conditions of relative humidity;

c) By condensation: when the temperature of the material is less than dew point, water vapour then condenses within the pores. In small pores, condensation can take place before the temperature reaches dew point.

⑧ *The temperature at which the water vapour in the air is saturated. As the temperature falls the dew point is the point at which the vapour begins to condense as droplets of water.*

5 DETERIORATION

The size of the pores, their distribution and geometry are fundamental factors in determining the properties of materials and their suitability for building applications.

The degree of porosity in different materials can be a positive characteristic for their use in some applications (e.g. very porous plaster allows for water vapour transmission) but may have adverse effects on their performance in others (e.g. very porous stone generally deteriorates more easily) 🗀**8.**

One of the main causes of stone decay is the interaction between water and the porous structure.

Water adsorption can induce weathering on stone materials in several ways:

a) by chemical reaction (e.g. aggressive pollutants);

b) by a physical mechanism: through mechanical stress due to freeze/thaw cycles;

c) by acting as a transport medium for salts in dissolution and recrystallization processes within the pore space;

d) by providing an essential substrate for biological growth 🗀**9.**

6 METHODS OF MEASUREMENT

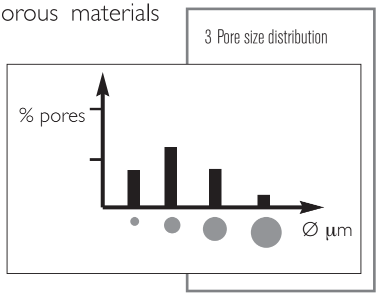
The three structural properties that are fundamental in describing porous materials are **porosity**, **pore size distribution** and **specific surface**; pore shape is also significant but less easily quantifiable.

As these properties are geometrical, they can be evaluated by **direct** observation. Other methods of assessment are termed **indirect**, as they are obtained from calculations based on other parameters 🗀**10**.

Direct methods

Those methods that make it possible to directly observe the porous structure, using either a petrography microscope or scanning electron microscopy (SEM).

A) PETROGRAPHY MICROSCOPE ANALYSIS


3 Pore size distribution

Direct observation by microscope of thin sections of porous materials makes it possible to evaluate total porosity which includes closed pores. This is a traditional method of studying the porosity on thin sections⑨ of material, enabling the calculation of the area occupied by pores as a percentage of the total surface area under examination and, at the same time, recording their size distribution *(Fig. 3)*.

The advantage of this technique is that it permits the direct quantification of what is visible. A further important characteristic is that specific data such as the size distribution of larger pores can only be obtained with this method 🗀**11**.

It is limited in that a large number of thin sections from different layers and angles of the sample must be examined in order to obtain a statistically viable result from these measurements.

Although this analysis is suitable for larger pores, pores with radii smaller than 4 µm are not measurable. This depends on the resolution of the optical microscope, which limits the measurement to pores with radii ranging between 4 and 500 µm 🗀**12**.

When combined with the digital analysis of the images, this technique automatically calculates the area occupied by pores comparing it to that occupied by the solid. For this reason, it is possible to carry out a large number of measurements and therefore obtain statistically valid data.

B) SCANNING ELECTRON MICROSCOPY ANALYSIS (SEM)

This is an effective technique for analysing materials that have a large number of micropores. It can be combined with the digital analysis of the images and computer-aided techniques to reconstruct three-dimensional images (3D-modelling), as opposed to the two-dimensional system in petrography microscopy. This makes it possible to delineate the empty space occupied by the pores and obtain direct information on their shape, size and three-dimensional distribution.

The advantage of this method is that it does not rely on fictitious pore models, which are generally assumed to be cylindrical (see Indirect methods p.8), but provides a true description of the pore structure. It is again necessary to examine a large number of thin slices⑩ of the material for the result to be representative 🗀**13**.

⑨ *These are obtained by embedding the sample in a synthetic resin and cutting across its outer surface. The sections are then polished until their thickness is less than 30 mm. They provide information on mineralogical composition and microstructural characteristics such as porosity.*

⑩ *dimensions: 10mm x 10mm x 2mm.*

The problem of the representativity of the sample is the same as in the preceding case. This is a highly sophisticated method and is only used in specific areas of research 🗀**14.**

Indirect methods

Indirect methods measure certain derived properties, such as density, permeability to fluids (liquid or gas), liquid imbibition rates, adsorptive capacity and so on, in order to evaluate the porous structure 🗀**15.**

Mercury porosimetry and nitrogen adsorption measurement are the two most common indirect methods in which porosity is essentially correlated to the pressure necessary to introduce a fluid into the pores of the material.

A) MERCURY POROSIMETRY MEASUREMENT 🗀16

This technique makes it possible to measure the distribution of pore sizes inside the material. The mercury⑪ is forced inside by applying steadily increasing pressure.

The principle of measurement is based on Washburn's equation:

$$\boxed{r = 2\sigma\cos\theta/P}$$

where:
P = pressure exercised
σ = surface tension of mercury
θ = contact angle between the mercury and the solid
r = pore radius

The distribution of the pores, as well as the total porosity values, the real and apparent density and the volume of intrusion can be obtained from the proportionality between pressure necessary for penetration and the dimension of the pores. The theory upon which the Washburn equation is based assumes that all pores are cylindrical. In the case of ink bottle pores, for example, their true dimensions are unobtainable, as the measurement only refers to the radius of the pore entrance.

Current instruments allow the pressure to reach 4000 bar⑫ (400 MPa), which permits them to fill macro and micropores. However, this method cannot be recommended for very fragile materials.

The amount of sample necessary for the analysis ranges from 0.5 to 1 g and the current cost is around 150 US dollars per test.

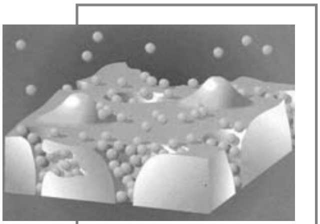
⑪ *Mercury is used because of its non-wetting properties.*

⑫ *1 bar = 0.9678 atm*

B) MEASUREMENT OF NITROGEN ADSORPTION *(Fig.4)* 🗀17

This procedure is based on the quantity of gas adsorbed by a porous material at constant temperature and at increasing levels of pressure. A curve is obtained called the isotherm of adsorption which is correlated to the distribution of pore sizes within the solid. Various fluids can be used depending on the dimensions of the pores to be measured, but nitrogen has given the best results making it possible to determine micropores.

A gram of sample is necessary for the analysis.



4 Gas adsorption

Simple methods

All the previously mentioned methods, both direct and indirect, have the advantage of requiring only a small quantity of sample for the analysis but the initial cost of the instruments is extremely high.

Other indirect methods to study porosity can be used, based on the derived properties of the material, by measuring, for example, *water absorption by total immersion, water desorption, water absorption by capillarity, and water vapour permeability*. These tests, which are easy to carry out, make it possible to observe the behaviour of building materials in contact with water 🗀15. Although simple, they are limited by the necessity to work on samples of a precise geometrical shape and size (e.g. cubes, cylinders, etc.). It is therefore seldom possible to take samples of this nature from a historic structure. Furthermore, several samples must be analysed to obtain a statistically viable result.

A) WATER ABSORPTION TEST BY TOTAL IMMERSION

This test measures the water absorption rate and the maximum water absorption capacity. The total quantity of water absorbed is related to the total open porosity, while the kinetics of the process depend principally on the distribution of the pore sizes.

B) WATER DESORPTION TEST

This measures the evaporation rate of saturated samples at room temperature and pressure. This is an extremely useful test that indicates the drying properties of the materials (i.e. whether they will dry quickly or remain wet for a long time). The presence of ink bottle pores, for example, has an adverse effect on the drying process due to their particular geometry.

C) WATER ABSORPTION BY CAPILLARITY

This test measures the capillary rise of water, the most common form of liquid water migration in building materials. It is inversely proportional to the diameter of the pores; the smaller the diameter, the greater the capillary absorption. Certain building materials, because of their low capillary absorption, are selected for specific uses, for example, as a barrier where masonry is in contact with the soil or as a base for wood fixtures to protect the structure from rising damp. *(photo 5)*

5 Inadequate rising damp barrier

All the above tests may be correlated to the behaviour of masonry in contact with liquid water.

D) WATER VAPOUR PERMEABILITY

The permeability test is very important to predict the water vapour transmission capacity of added materials, especially plasters. It measures the quantity of water vapour that passes through a given thickness of material, limited by parallel surfaces, as a result of the partial difference in pressure of the water vapour between the two sides. The test is also a useful method to evaluate the suitability of paints as finishing layers which provide protection without reducing water vapour transmission.

Although all these measurements provide information relating to porosity, they are often used to make comparisons between quarried, weathered or treated stone materials.

PRACTICAL 1

MEASURING APPARENT VOLUME AND OPEN PORE VOLUME OF A STONE SAMPLE

Aim

The aim is to become familiar with a measuring procedure to obtain % open porosity, using basic equipment.

Equipment and chemicals

- Oven
- Technical balance
- Desiccator
- Beakers or plastic containers
- Soft cloth
- Glass rods
- Silica gel
- Deionized water

① A cylinder of suitable size should be chosen for the sample with a scale that makes it easy to read the change in volume.

Procedure

A) APPARENT VOLUME

- If the sample has a *regular* form (i.e. cube, cylinder), it is sufficient to measure the size and calculate the geometrical volume which, in this case, corresponds to the *apparent volume* of the sample.

In the case of small samples of *irregular* shapes and sizes :

- Wash the sample in deionized water before beginning this test to eliminate powdered material from the surface.
- Dry the sample in the oven for 24 hours at 60°C and then place it in a desiccator with dry silica gel to cool off.
- Weigh the sample. Then, repeat the drying process until the mass of the sample is *constant* (i.e. until the difference between 2 successive measurements, at an interval of 24 hours, is not more than 0.1% of the mass of the sample).
- Once the sample has been completely dried and the *constant mass* recorded (m_c), place it in a container or beaker on a base of glass rods and slowly cover with deionized water until the sample is totally immersed with about 2 cm of water above it.
- Take the sample out of the container 8 hours later, blot it quickly with a damp cloth to remove surface water and record its weight.
- Re-immerse the sample in the water and repeat the measurement until the difference in weight between 2 successive measurements at 24-hour intervals is less than 1% of the amount of water absorbed.
- Record the mass of the wet samples (m_s) and the time of measurement on the data sheet.
- Put the saturated sample in a graduated cylinder① filled with deionized water and measure the increase in volume indicated on the cylinder.

Calculation

Apparent volume V_a (cm^3) corresponds to the observed increase in the volume of water measured on the graduated cylinder.

Procedure

B) OPEN PORE VOLUME

- Use the values recorded (m_c and m_s) to calculate open pore volume and % open porosity.

Calculation

a) The open pore volume V_{op} (cm^3) corresponds to the volume of water absorbed by the sample. Since the density of water is 1 g/cm^3 at 4 °C, the difference in weight (g) of the sample before and after being saturated corresponds to the open pore volume:

$$\boxed{V_{op} = m_s - m_c}$$

where

m_s = the mass of the saturated sample (g)

m_c = the dry mass of the sample (g)

V_{op} = open pore volume (cm^3)

b) To calculate the % open porosity, use the following formula:

$$\boxed{\%\text{ open porosity} = 100 \times (V_{op}/V_a)}$$

where

V_{op} = calculated open pore volume (cm^3)

V_a = calculated apparent volume (cm^3)

PRACTICAL 2

WATER ABSORPTION BY TOTAL IMMERSION

Equipment and chemicals

- Oven
- Technical balance
- Chronometer
- Desiccator
- Beakers or plastic containers
- Soft cloth
- Glass rods
- Silica gel
- Deionized water

Definitions

Water Absorption by Total Immersion: the quantity of water absorbed by a material immersed in deionized water at room temperature and pressure at successive time intervals (i.e. the rate of water absorption), expressed as a percentage of the dry mass of the sample.

Water Absorption Capacity: the maximum quantity of water absorbed by a material at room temperature and pressure under conditions of saturation, again expressed as a percentage of the dry mass of the sample.

Aim

The measurement of water absorption is a useful laboratory test to characterize porous building materials, evaluate the degree of deterioration, and monitor the effects of conservation treatments.

Here is a simple method for such measurement that gives reliable results without the use of sophisticated equipment.

Procedure

Samples should be of a regular shape (cubes, cylinders, or prisms). In the case of cubes, the side should neither be less than 3 cm nor greater than 5 cm, so that the value of the ratio S/V (total surface to apparent volume) is between 2 and 1.2 cm^{-1}.

The number of samples required depends on the heterogeneity of the material being tested. In general a series of at least three samples is recommended. These should be as similar as possible in terms of physical properties and condition.

- Wash the samples in the deionized water before beginning this test in order to eliminate powdered material from the surface.
- Dry the samples in the oven for 24 hours at 60°C (this relatively low drying temperature will prevent the deterioration of organic substances in the case of treated samples). Then place the samples in a desiccator with dry silica gel to cool off.
- Weigh the samples. Repeat the drying process until the mass of the each sample is constant, that is, until the difference between 2 successive measurements, at an interval of 24 hours, is no more than 0.1% of the mass of the sample.
- Once the samples have been completely dried and the *constant mass* recorded (m_o), place them in a container or beaker, on a base of glass rods and slowly cover with deionized water until they are totally immersed with about 2 cm of water above them.
- At programmed intervals of time①, take each sample out of the container, blot it quickly with a damp cloth to remove surface water, then record the mass of the wet samples (m_i) and the time of measurement on the data sheet.
- Re-immerse the samples in water and continue measuring until the difference in weight between 2 successive measurements at 24-hour intervals is less than 1% of the amount of water absorbed.
- At this point, take the samples out of the water and dry them again in an oven at 60°C until they have reached *constant mass* (as above). Record this value (m_d) on the data sheet. Proceed with the calculations.

Calculation

a) At each interval, the quantity of water absorbed with respect to the mass of the dry sample is expressed as:

$$\boxed{M_i\% = 100 \times (m_i - m_o)/m_o}$$

where

m_i = weight (g) of the wet sample at time t_i

m_o = weight (g) of the dry sample

b) Record these values on a data sheet and on a graph as a function of time.

c) Again, using the figures from the data sheet calculate the water absorption capacity (WAC) with the following formula:

$$\boxed{WAC = 100 \times (m_{max} - m_d)/m_d}$$

where

m_{max} = the mass (g) of the sample at maximum water absorption

m_d = the mass (g) of the sample after re-drying at the end of the test

As an example, a generic series of samples are recorded in Fig.1 and Table 1.

① The length of the intervals during the first 24 hours depends on the absorption characteristics of the materials:

a) Stone and brick should be weighed after the first 5 minutes of immersion and then every hour for the first 3 hours.

b) Mortar samples should be weighed a few minutes after immersion, and then at increasing intervals (15 min, 30 min, 1 hour, etc.) for the first 3 hours.

All samples should then be weighed 8 hours after the beginning of the test and then at 24-hour intervals until the quantity of water absorbed in two successive measurements is not more than 1% of the total mass.

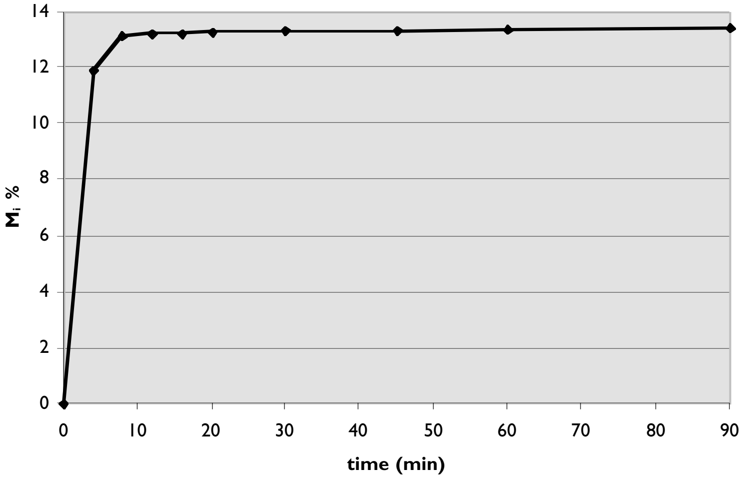


Fig. 1 - Water absorption by total immersion

MEASUREMENT INTERVALS	SAMPLE 1 m_o = 124.70 g		SAMPLE 2 m_o = 113.88 g		SAMPLE 3 m_o = 122.03 g		MEAN VALUES
t_i (min)	**m_i (g)**	**M_i (%)**	**m_i (g)**	**M_i (%)**	**m_i (g)**	**M_i (%)**	**$\bar{M}_i$ (%)**
0	124,70	0,00	113,88	0,00	122,03	0,00	0,00
4	138,28	10,88	127,78	12,21	137,44	12,62	11,90
8	140,97	13,05	128,97	13,25	137,93	13,03	13,11
12	141,08	13,14	129,12	13,38	138,01	13,09	13,20
16	141,12	13,16	129,15	13,41	138,06	13,13	13,23
20	141,19	13,22	129,22	13,47	138,11	13,18	13,29
30	141,21	13,24	129,21	13,46	138,15	13,21	13,30
45	141,23	13,25	129,29	13,53	138,19	13,24	13,34
60	141,25	13,27	129,30	13,54	138,23	13,27	13,36
90	141,27	13,29	129,35	13,59	138,29	13,32	13,40
1440	141,35	13,35	129,42	13,65	138,31	13,34	13,45
2880	141,95	13,83	129,74	13,93	138,75	13,70	13,82

Table 1 - Water absorption by total immersion

where

m_o = weight of dry sample

m_i = weight of the wet sample at time t_i

M_i = $100 \times (m_i - m_o)/m_o$ calculated for each interval time and for each sample

6 Measuring equipment

PRACTICAL 3

WATER DESORPTION

Equipment and chemicals

- Oven
- Balance
- Chronometer
- Desiccator
- Soft cloth
- Glass rods
- Silica gel

Definition

The variation in water content of the material, expressed as a percentage of the dry mass of the sample at a constant temperature and under fixed conditions of humidity, is measured over a period of time.

Aim

The aim is to indicate the drying capacity of porous materials.

Procedure

Samples should be of a regular shape (cubes, cylinders, or prisms). In the case of cubes, the side should neither be less than 3 cm nor greater than 5 cm, so that the value of the ratio S/V (total surface to apparent volume) is between 2 and 1.2 cm^{-1}.

The number of samples required depends on the heterogeneity of the material being tested. In general a series of at least three samples is recommended. These should be as similar as possible in terms of physical properties and condition.

- Soak the samples in water to the point of saturation *(see Practical 1)*. Blot them with a damp cloth to remove surface water and weigh them (m_o).
- Place each sample inside the desiccator containing anhydrous silica gel with a cobalt chloride indicator. Store at a constant room temperature of 20 ± 1°C.

  The size of the desiccator and the number of samples for each desiccator must be determined, through preliminary tests, by the nature of the material, so that the relative humidity corresponding to the equilibrium of the silica gel is maintained within the desiccator during the whole testing phase. Check the relative humidity by placing a cobalt chloride strip indicator on the wall of the desiccator. The indicator must always remain blue throughout the test. If not, quickly replace the silica gel at the bottom of the desiccator.
- Remove samples periodically from the desiccator and weigh them. During the first 24 hours the length of interval will depend on the evaporation characteristics of the material, which is determined by a preliminary test to identify the initial evaporation rate.

Procedure continued

- Repeat weighing at 24-hour intervals, until the following formula has been verified:

$$\boxed{1.0 \geq (m_o - m_{i-1}) / (m_o - m_i) \geq 0.90}$$

where

m_0 = mass (g) of sample at time t_0 (hrs)
m_{i-1} = mass (g) of sample at time t_{i-1} (hrs)
m_i = mass (g) of sample at time t_i (hrs)

- Proceed with the desiccation of the samples in an oven at 60 ± 5°C, until constant mass is reached. Mass is considered constant when the difference between two successive measurements at 24-hour intervals is less than or equal to 0.01% of the mass of the dry sample.
- Plot the experimental values to obtain a "drying curve" (water content as a function of time) *(Fig. 1)*.

Calculation

The residual water content Q_i of the sample at time t_i is calculated with the following formula:

$$\boxed{Q_i = 100 \times (m_i - m_{of}) / m_{of}}$$

where

Q_i = water content at t_i expressed as a percentage of the final dry mass
m_i = mass (g) of sample at t_i (hrs)
m_{of} = mass (g) of the desiccated sample at the end of the drying test

Record the values of Q_i in a graph versus time t_i and draw the relative curve①.

① The initial water content corresponds to the value of the absorption capacity WAC determined during the process of total immersion.

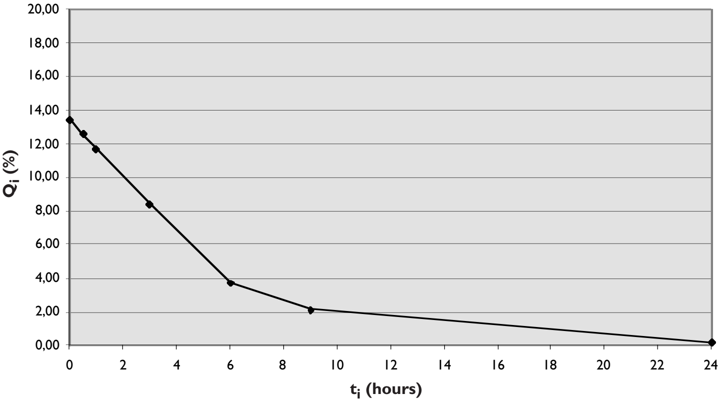


Fig. 1 - Water content versus time

8 CASE STUDY

PRELIMINARY SURVEY FOR THE CONSERVATION OF THE NORTH FAÇADE IN THE CHURCH OF S. MARIA FORMOSA-VENICE

(The author acknowledges the kind contribution of W. Schmid, ICCROM)

Background

This survey was organized in 1997, as part of the XII International ICCROM/UNESCO Course on the Technology of Stone Conservation (SC97). It was undertaken by a multidisciplinary group of conservation architects, conservator-restorers and engineers supervised by experts in the field.

(N.B. Only the part of the survey referring to the porosimetry analysis is reported here).

Aim

The aim was to develop a proposal for conservation treatment by assessing the conditions of the north façade, integrating *in situ* observations, historical data and scientific investigations and carrying out treatment trials.

A program of laboratory analysis was carried out in order to:

- assess the façade's existing condition and possible decay mechanisms,
- identify altered materials,
- better understand the original material.

Fig. 1 - S. Maria Formosa

Description

S. Maria Formosa *(Fig. 1)* is considered one of the earliest Venetian churches (7th century). However, over the centuries it has undergone so many modifications that it now appears in typical Renaissance style. It has a Latin cross plan with three aisles, deep side chapels, a presbytery, a semicircular apse and a central dome over the transept. The chapel on the right-hand side borders the canal whereas the north façade, to which the case study refers, overlooks Campo S. Maria Formosa.

The façade is divided into five parts by pilasters with four semicircular windows in the first order. Three busts are located in the upper part of the façade. The central bust stands at the base of an oculum at the centre of an open arch with volutes. Five statues are symmetrically positioned above the upper cornice.

① *Porosity ≅ 0,2 - 0,5 %*
② *Porosity ≅ 0,5 - 1 %*
③ *Porosity ≅ 25 - 28 %*

Survey: materials, previous treatments and state of conservation of north façade

The façade of the church is made up of *Istrian limestone*① blocks; the three busts of *Carrara marble*②, while the five statues may have been originally carved out of *Vicenza limestone*③.

Attention was mainly concentrated on the structural condition of the church although there was also significant decay and physical change of the stone surface: areas of black crusts, rainwashing and pigeon excrement as well as *biological growth*. Flaking and scaling was evident on all the stone surfaces. *Disaggregation* was apparent on the three marble busts and the upper right sculptures and *blistering* on the top central sculpture. *Erosion* was present mainly below the cornices, on the corners near the pilasters where there is rainwater washing.

There were quite a few small and medium sized broken or loose pieces on corners and projecting architectural elements. *Cracks, fissures* and *fractures* were related either to differential decay and bedding of the stone or to structural problems. Furthermore, many of the joints between the stone blocks were devoid of mortar, especially on the right side of the façade and in places where considerable water erosion had taken place.

Experimental

The scientific investigations focused on the essential problems of the façade due to limited time and funds. Apart from soluble salts analysis, biological identification, and petrography analysis, research concentrated on the porosimetry of Vicenza limestone in order to assess the degree of deterioration of the uppermost sculptures.

Sampling

Fig. 2 shows sampling locations with indications of relevant analyses.

POROSIMETRIC ANALYSIS

Using a mercury porosimeter the total porosity and open pore size distribution was calculated for sample n. 110 from a sculpture at the uppermost part of the façade and on a quarry sample of unweathered Vicenza limestone.

The total porosity of the quarried stone was **18.24%** compared to the **27.29%** of the statue (*Fig. 3*). This sharp increase of about 50% in total porosity is due to the extreme weathered condition of the stone.

The open pore size distribution of the two samples was determined because it plays an important role in the chemical and physical behaviour of porous materials.

A comparison of the pore size distributions of the two samples shows a marked difference (*Fig. 4 and 5*). The *quarried* limestone shows a bell-shaped curve with a maximum amount of pores in the range

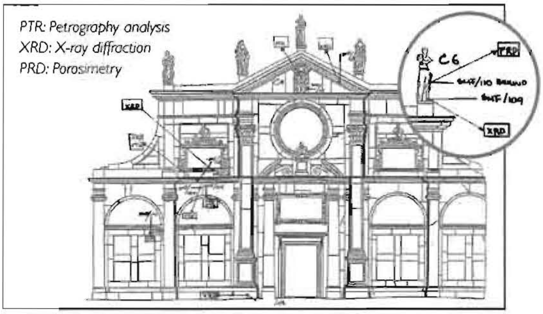


Fig. 2 - Sampling plan

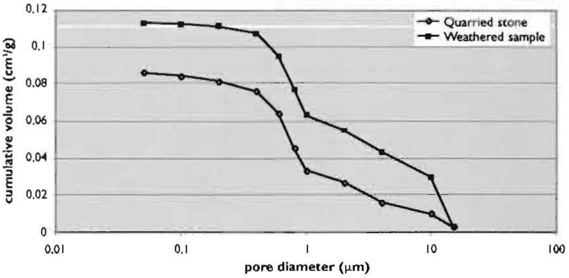


Fig. 3 - Mercury porosimetry analysis

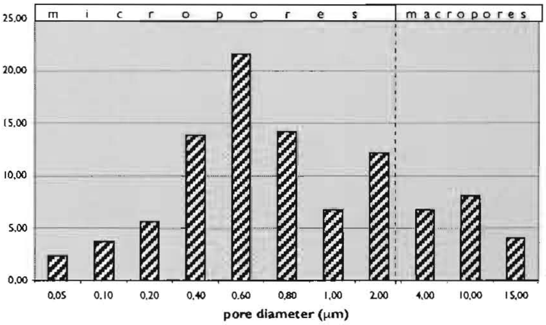


Fig. 4 - Quarried stone sample (Pore size distribution)

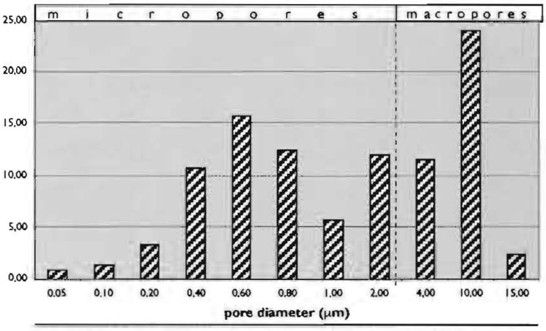


Fig. 5 - Weathered sample from the sculpture (Pore size distribution)

of **0.4 - 0.8 μm**. The *weathered* sample from the sculpture shows a bi-modal curve: the first part of the pore size distribution curve is similar to that of the quarried sample **(0.4 - 0.6 μm)**, while the second part of the curve indicates higher open porosity in the range of **4 -10 μm**.

Conclusions

It must be noted that all the statues require some form of consolidation to re-establish the cohesion of the material. The increase in the amount of larger open pores reflects the severe deterioration of the sculpture which may be due to several factors. For example, soluble salt crystallization cycles would greatly affect the pores due to the expansion and pressure caused by salt crystals. There are cement fills in the sculpture from where these salts probably originate. Other sources of salts may be from air pollution.

The severe weathering of these sculptures is visible to the eye, but the analysis made it possible to qualify and quantify the deterioration.

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STANDARDS

ASTM standards (American Society for Testing and Materials)

- Designation: C 121-90. Standard test method for water absorption of slate
- Designation: D 4404-84 (reappr. 1992). Standard test method for determination of pore volume distribution of soil and rock by mercury intrusion porosimetry
- Designation: D 4959-89. Standard test method for determination of water (moisture) content of soil by direct heating method
- Designation: D 4525-90. Permeability of rocks by flowing air
- Designation: D 653-90. Terminology relating to soil, rock and contained fluids
- Designation: C 566-89. Test method for total moisture content of aggregate by drying
- Designation: E 12-70 (reappr. 1991). Density and specific gravity of solids, liquids and gases

RILEM tests (Réunion Internationale des Laboratoires d'Essais des Matériaux)

- Test n. I.1: Porosity accessible to water
- Test n. I.2: Bulk and real densities
- Test n. I.3: Air-permeability
- Test n. I.4: Pore-size distribution (suction)
- Test n. I.5: Pore-size distribution (mercury porosimeter)
- Test n. II.1: Saturation coefficient
- Test n. II.2: Coefficient of water vapour conductivity
- Test n. II.3: Water absorption under low pressure (box method)
- Test n. II.4: Water absorption under low pressure (pipe method)
- Test n. II.5: Evaporation curve
- Test n. II.6: Water absorption coefficient (capillarity)
- Test n. II.8a: Water drop absorption

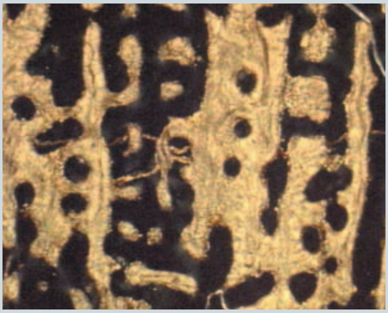
NORMAL documents (Commissione Normativa Manufatti Lapidei)

- NORMAL 4/ 80: Distribuzione del volume dei pori in funzione del loro diametro
- NORMAL 7 /81: Assorbimento d'acqua per immersione totale – Capacità di Imbibizione
- NORMAL 11/ 85: Assorbimento d'acqua per capillarità – Coefficiente di assorbimento capillare
- NORMAL 21/ 85: Permeabilità al vapor d'acqua
- NORMAL 29/ 88: Misura dell'indice di asciugamento (Drying index)
- NORMAL 33/ 89: Misura dell'angolo di contatto
- NORMAL 44/ 93: Assorbimento d'acqua a bassa pressione

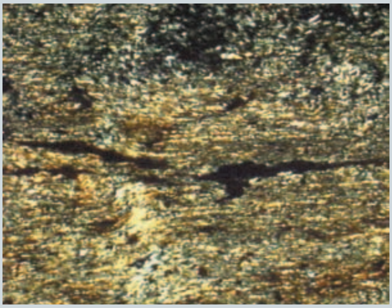
MICROPHOTOGRAPHS OF THIN SECTIONS

Examples of macroporosity

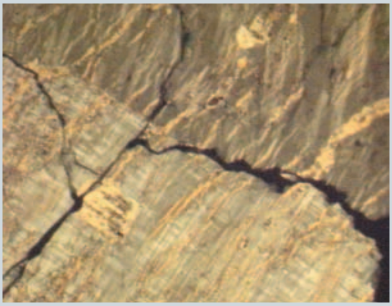
1
Coral stone



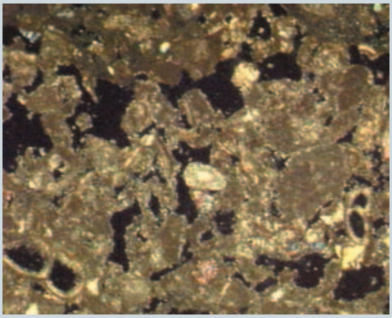
2
Slate



3
Granite



4
Organogenic limestone



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CONSERVATION OF ARCHITECTURAL HERITAGE,
HISTORIC STRUCTURES AND MATERIALS

Salts

SALTS

ARC
LABORATORY HANDBOOK

VOLUME 3/99

Ernesto Borrelli

The ICCROM ARC Laboratory Handbook is intended to assist professionals working in the field of conservation of architectural heritage and historic structures. It has been prepared mainly for architects and engineers, but may also be relevant for conservator-restorers or archaeologists.
It aims to:

- ***offer an overview of each problem area combined with laboratory practicals and case studies;***
- ***describe some of the most widely used practices and illustrate the various approaches to the analysis of materials and their deterioration;***
- ***facilitate interdisciplinary teamwork among scientists and other professionals involved in the conservation process.***

The Handbook has evolved from lecture and laboratory handouts that have been developed for the ICCROM training programmes. It has been devised within the framework of the current courses, principally the International Refresher Course on Conservation of Architectural Heritage and Historic Structures (ARC).

The general layout of each volume is as follows: introductory information, explanations of scientific terminology, the most common problems met, types of analysis, laboratory tests, case studies and bibliography.

The concept behind the Handbook is modular and it has been purposely structured as a series of independent volumes to allow:

- ***authors** to periodically update the texts;*
- ***users** to work selectively with the volume relating to the particular problem they are facing*
- ***new volumes** to be gradually added in line with developing needs.*

1998 - 99 volumes:
*(1) Introduction, (2) Porosity, **(3) Salts,** (4) Binders, (5) Colour specification and measurement*

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CONSERVATION OF ARCHITECTURAL HERITAGE,
HISTORIC STRUCTURES AND MATERIALS

ARC
Laboratory Handbook

Salts

Ernesto Borrelli

ICCROM

Rome, 1999

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① : Footnotes
🗁 : Bibliographic references

SALTS

1 INTRODUCTION

The presence of water-soluble salts in porous building materials is one of the principal conservation problems. Their crystallization is in fact the cause of those phenomena of deterioration that so often appear on surfaces: lack of cohesion, scaling, flaking and bulging *(photo 1)*.

Sources of salts can be the building materials themselves (sand, bricks, mortar) or external sources (soil, materials used for conservation treatment, pollutants in the atmosphere, sea spray, de-icing salts scattered on roads in winter, products generated by the metabolism of micro-organisms). Salts are transported into porous materials by rainwater, rising damp, infiltration or condensation 🗀**1**.

Almost all masonry contains soluble salts, principally ***sulphates, nitrates, chlorides and carbonates of sodium, potassium, calcium, magnesium and ammonium*** and so all liquid water present in walls is more or less a diluted salt solution 🗀**2**.

But not all salts generate decay. This depends on their solubility, hygroscopicity, mobility and the hydration level of their crystalline form.

When the water transporting the salts through porous materials evaporates, due, for example, to changing climatic conditions, the solution becomes more concentrated. As soon as it becomes supersaturated, the salts crystallize giving rise to both efflorescences on the surface and/or sub-efflorescences below the surface layer 🗀**3**.

It is very important to know the salt content of deteriorated surfaces both to understand the causes of decay and plan conservation strategies. The nature of the salt provides us with information about its origin and therefore indicates the possible conservation treatment to adopt 🗀**4**. For example, the presence of nitrates is generally attributed to the infiltration of sewage water or to the proximity of burial sites while sulphates are often due to the effect of atmospheric pollution particularly in urban areas.

1 Marble deterioration due to sulphates

colour print on inside back cover

2 BASIC SALTS CHEMISTRY

Ions

When a salt is dissolved in water, it is dissociated into ions.

e.g. $\underset{\text{sodium chloride crystals}}{NaCl} + H_2O \longrightarrow Na^+ + Cl^-$

Ions are electrically charged atoms or groups of atoms. If positive, they are called <u>cations</u>:

e.g. Li^+ *(lithium)*, Na^+ *(sodium)*, K^+ *(potassium)*, NH_4^+ *(ammonium)*, Ca^{++} *(calcium)*, Mg^{++} *(magnesium)*, Fe^{+++} *(iron)* ....

If negative, they are called <u>anions</u>:

e.g. F^- *(fluoride)*, Cl^- *(chloride)*, NO_2^- *(nitrite)*, NO_3^- *(nitrate)*, SO_4^{--} *(sulphate)*, CO_3^{--} *(oxalate)*, PO_4^{---} *(phosphate)* ....

Salts

Compounds formed by the crystallization of a solution deriving from the reaction of an acid (e.g. HCl) with a base (e.g. NaOH).

$$\underset{\text{hydrochloric acid + sodium hydroxide}}{HCl + NaOH} \longrightarrow \underset{\text{water + sodium chloride solution}}{H_2O + Na^+ + Cl^-}$$

$$Na^+ + Cl^- + H_2O \xrightarrow{\text{evaporation}} NaCl \text{ (crystals)}$$

Solubility

The maximum amount of solute (salt) that will dissolve in a given amount of water. It is usually expressed in g/l or g/100 ml at a given temperature. Solubility is constant at a constant temperature and generally rises with an increase in temperature. *(Table 1)*

SALTS	FORMULA	SOLUBILITY (g/l)	
Calcite	$CaCO_3$	0.015	(25 °C)
Magnesite	$MgCO_3$	0.106	(20 °C)
Gypsum	$CaSO_4 \cdot 2H_2O$	2.58	(20 °C)
Halite	NaCl	264.0	(20 °C)
Mirabilite	$Na_2SO_4 \cdot 10H_2O$	363.4	(20 °C)
Natrite	$Na_2CO3 \cdot 10H_2O$	486.5	(20 °C)
Hydrophilite	$CaCl_2$	595.0	(0 °C)
Nitronatrite	$NaNO_3$	921,0	(25 °C)
Nitrocalcite	$Ca(NO_3)_2 \cdot 4H_2O$	2660,0	(0 °C)

Table 1: Examples of the solubility of a number of salts

Saturated solution

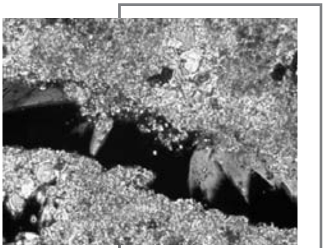
A solution containing the maximum equilibrium amount of solute at a given temperature. In a saturated solution, the dissolved substance is in equilibrium with the undissolved substance. In other words, the rate at which solute particles crystallize is exactly balanced by the rate at which they dissolve. A solution containing more than the equilibrium amount of solute is said to be supersaturated (and can be formed by slowly cooling a saturated solution). Such solutions are metastable; if a small crystal seed is added, the excess solute crystallizes out of solution.

Crystallization *(photo 2)*

This takes place when conditions for a salt to remain in solution no longer exist: at this point the solution is supersaturated.

On porous building materials crystallization can take place 🗀5:

- WITHIN THE PORES of materials if the solution becomes supersaturated, that is, if the concentration of salts exceeds solubility.
- ON SURFACES of materials in relation to the humidity level of the environment. It is very important to know the **temperature** and **relative humidity** conditions that induce phase transformations of the solutions, particularly for indoor environments where it is easier to control climatic conditions 🗀6.



2 Gypsum crystals
colour print on inside back cover

Within the masonry, each saturated solution of a given salt at a given temperature corresponds to the "equilibrium relative humidity"①. When the ambient relative humidity becomes lower than the equilibrium relative humidity of the saturated solution, evaporation from the walls takes place, the solution becomes supersaturated and the condition for crystallization is reached②. This is what happens, for example, when a room is heated or ventilated. To avoid crystallization, it is always necessary to maintain the **ambient relative humidity** at a higher level than the **equilibrium relative humidity** of the salts inside the masonry *(Fig. 1)*.

① *This means that the humid air in contact with the surface influences the equilibrium between salt, solution and vapour and therefore conditions crystallization and dissolution*

② *However we are generally dealing with systems containing a mixture of salts and so both "solubility" and "relative humidity" of pure salts cannot be applied, as they only represent indicative values 🗀4. For example, salt efflorescences on walls containing complex salt mixtures have been observed at considerably lower relative humidity levels than would have been expected from those of pure salts.*

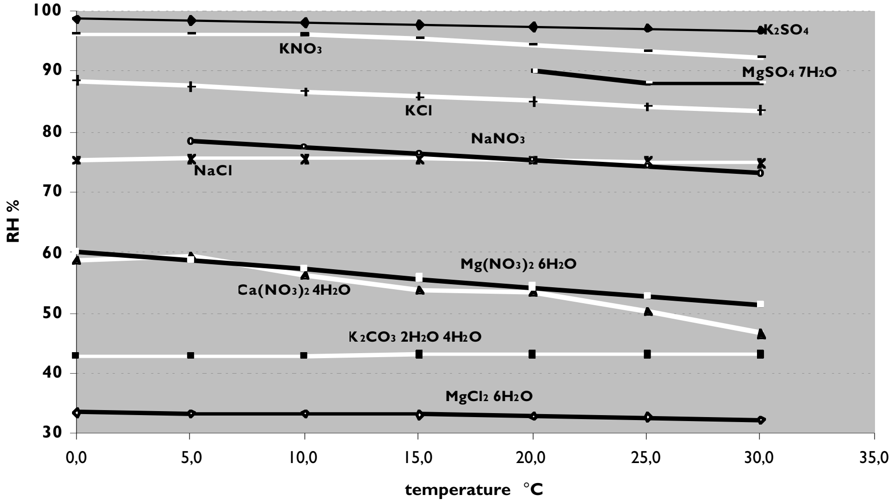


Fig 1. Equilibrium relative humidities of salts commonly found in walls 🗀**7.**

3 DETERIORATION

There is a relationship between the **solubility** of salts and their **disruptive action** on materials 🗀8:

- **Practically insoluble** salts do not produce phenomena of dangerous crystallization. Even though their poor solubility enables them to reach saturation inside materials, the concentrations at saturation are minimal and insufficient to cause conspicuous damage.
- **Slightly soluble** salts are generally more dangerous. Due to their low solubility, they often crystallize just below the surface layer and cause bulging, detachment and loss of fragments. Among these, *gypsum* is the predominant salt ($CaSO_4 \cdot 2H_2O$), which crystallizes even in humid climates③ , becoming the principal cause of deterioration.
- **Highly soluble** salts (principally chlorides and nitrates, e.g. sodium chloride NaCl, sodium nitrate $NaNO_3$, potassium nitrate KNO_3), can accumulate and reach very high concentrations of highly hygroscopic salts which therefore remain in solution in humid environments producing dark patches. In drier conditions (e.g. inside heated buildings), when crystallization occurs, efflorescences appear. However due to the high solubility, crystallization requires strong evaporation that takes place especially on surfaces causing limited damage. Sometimes the crystallization is so abundant that it spreads below the surface layer affecting cohesion.

Another parameter for evaluating the danger of salts is their hydration properties. $Na_2SO_4 \cdot 10H_2O$ *(mirabilite)* is a particular example as it is highly soluble and therefore, according to the above explanation, should not be dangerous when in fact it is. Mirabilite, deriving from the hydration④ of Na_2SO_4 *(thenardite)*, increases in volume by about 400% causing considerable stress within the pore structure.

The presence of soluble salts in walls can cause their deterioration in at least three ways:

- soluble salts attract water and produce phenomena of osmosis⑤ and hygroscopicity, causing an increase in the moisture content which always leaves the masonry damp;
- due to microclimatic variations, the saline solutions present in walls give rise to dissolution and crystallization cycles. If they are frequent, even daily, they produce mechanical stress and consequent crumbling of the material;
- when salts crystallize close to the surface, they form efflorescences and sub-efflorescences.

③ *Gypsum has a very high deliquescence humidity (>99%) which diminishes considerably in the presence of other salts (it increases its solubility). We can therefore find efflorescences of sulphates also in moderately humid climates (e.g. relative humidity of 70-80%).*

④ *This phenomenon is caused by a change in temperature. At <24.3 °C mirabilite is the stable form, while at t >32.4 °C thenardite represents the equilibrium. This range in temperature is normal on surfaces in temperate climates.*

⑤ *Osmosis is a physical phenomenon: in this case it happens when water (solvent) flows through the porous material from a weaker to a stronger solution increasing the moisture content of the wall.*

4 MAIN CHARACTERISTICS OF SOME SALTS

Sulphates SO4^{--}

Origin 🗀9

They are generally found in walls in the form of dihydrate calcium sulphate ($CaSO_4 \cdot 2H_2O$ *gypsum*), sodium sulphate ($Na_2SO_4 \cdot 10H_2O$ *mirabilite*) and more rarely as magnesium sulphate ($MgSO_4 \cdot 7H_2O$ *epsomite*).

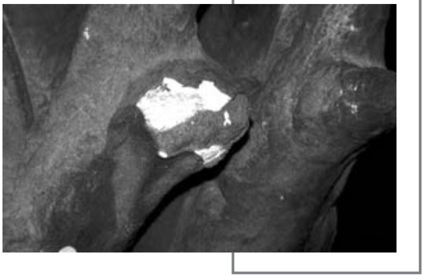
The most important source of sulphates is **atmospheric pollution**. Wet acid deposition from sulphur dioxide and humidity in the air attacks calcium carbonate in masonry to form calcium sulphate, but according to some authors sulphates can also be deposited on the surface from particulate matter existing in the air (dry deposition) 🗀10.

Other sources include

- AGRICULTURAL LAND: (ammonium sulphate) from which sulphates can penetrate masonry through capillary action;
- ORIGINAL OR ADDED MATERIALS: inorganic binders like cement contain sulphates which can be mobilized by water. Portland cement normally contains about 4% of calcium sulphate and certain grouting binders contain sodium sulphate as an impurity when plasticizers are added;
- SEA SPRAY: which contains low concentrations of magnesium sulphate that can be found mainly on surfaces;
- MICRO-ORGANISMS: sometimes present in calcareous materials, able to metabolize compounds containing reduced forms of sulphur and oxidize them to sulphates 🗀11.

The most common forms of deterioration

Black crusts *(photo 3)* are generally found on the calcareous material of buildings sheltered from the rain but exposed to the attack of atmospheric pollutants. Their composition is essentially gypsum and the black colour is due to the accumulation of carbon particulate matter present in polluted air. Apart from disturbing the aesthetic appearance of the surface, they can also conceal damage extending well below the surface layer 🗀12.



3 Black crusts
on marble
colour print on
inside back cover

Efflorescences are particularly evident on mural paintings and generally appear in three forms:

- GYPSUM DUST: a whitish deposit (from a few micrometers to 0.1 mm) mixed with small fragments of the paint layer and lightly attached to it.
- WHITE DOTS: between 0.1 and 1 mm in size, they are well attached to the surface and are usually found close to small imperfections (e.g. cracks); they are made up of clusters of gypsum aggregate.
- WHITENING: whitish or transparent layers which can detach themselves from the surface in flakes; they are typical of areas with increased humidity and can become gypsum dust if humidity decreases.

Pitting: gypsum is easily adsorbed in the macro-porosity of mortars forming minute sub-efflorescences and consequently detaching microfragments from the surface.

Chlorides Cl^-

Origin 🗀13

The most common source is **sea spray** (above all NaCl *halite*). Chlorides can also originate from impurities present in building materials used, for example, from sand for preparation of mortars; from de-icing salts spread on roads in winter and from emissions into the atmosphere of hydrochloric acid coming from certain types of industrial activity.

The most common forms of deterioration

Chlorides are highly soluble salts and this enables them to even penetrate very deeply into materials inducing alterations. Since they are highly hygroscopic (especially calcium chloride $CaCl_2$), their presence in a material induces a higher moisture content at equilibrium compared to one where they are absent. The high water content in the walls, following the freeze-thaw cycles, leads to the formation of **cracks** and **crumbling**.

Corrosion of steel reinforcement in concrete can occur if cracks allow chlorides to penetrate the structure. Calcium cloride ($CaCl_2$) is particularly dangerous 🗀14.

Nitrites and Nitrates NO_2^- NO_3^-

Origin 🗀15

Nitrites are produced by the **organic decomposition** of nitrogen-containing products and may therefore be found where there is infiltration of sewage water or proximity to burial sites. The tendency for nitrites (NO_2^-) to oxidize to nitrates (NO_3^-) makes it difficult to find them in masonry.

Nitrates can have the same origin but can also come from **agricultural land** (fertilizers) or from the **photochemical smog** typical of highly polluted areas with long periods of sunshine. Nitric acid (from nitrogen oxides in the air) attacks calcium carbonate in masonry to form calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$ *nitrocalcite*).

Another source of both nitrites and nitrates is **microbiological**: nitrous and nitrobacteria can transform nitrogen compounds into nitrites and nitrates in metabolic processes 🗀16.

The most common forms of deterioration

Nitrates, like chlorides, are highly soluble. The most serious damage is due to high moisture content in the masonry caused by the hygroscopicity of the nitrates. This leads to **decay phenomena** that generally occur in masonry with permanent high moisture content.

The other alteration is from nitric acid formed under particular atmospheric conditions: **corrosive action** attacks the mortar and causes loss of material in calcareous stone.

Carbonates CO_3^{--}

Origin 🗀17

Calcium carbonate ($CaCO_3$ *calcite*) is a constituent of both calcareous stone and mortars, and though being practically insoluble in water, can be transformed into the **more soluble bicarbonate** $Ca(HCO_3)_2$. If there is a higher than normal quantity of carbon dioxide (CO_2) in the atmosphere (as a result of industrial activity or due to the presence of a large number of people in a closed space), carbonic acid (H_2CO_3) can be formed in the presence of water and reacts with calcium carbonate to form calcium bicarbonate.

Equilibrium exists between these two compounds:

$$\boxed{2\,CaCO_3 + H_2O + CO_2 \leftrightarrow Ca(HCO_3)_2}$$

The soluble bicarbonate comes to the surface where evaporation shifts the equilibrium to the left again forming insoluble $CaCO_3$ which is deposited on the surface.

Another source can be the soluble alkali content of cement in masonry from which the highly soluble $Na_2CO_3 \cdot 10H_2O$ (*natron*) can be formed. Sodium carbonate (Na_2CO_3) can then be transformed into sodium bicarbonate ($NaHCO_3$), again due to the presence of a high quantity of CO_2 in the atmosphere. Both can be found as $Na_2CO_3\ NaHCO_3 \cdot 2H_2O$ *(trona)*.

The most common forms of deterioration

Accumulation of calcareous material in the form of encrustations and concretions mainly on protruding parts of buildings (where crystallization occurs) *(photo 4)*.

A mixture of $Na_2CO_3 \cdot 10H_2O$ and $NaHCO_3$ has a very disruptive effect on building materials.

4 Calcareous concretions
colour print on inside back cover

Oxalates $C_2O_4^{--}$

Origin 🗀18

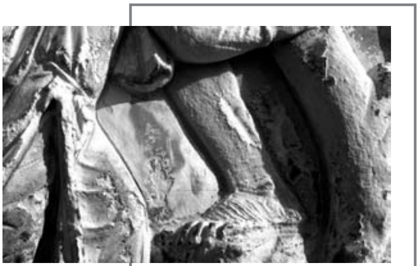
Among the various suggested mechanisms for the formation of these salts, the following two are usually cited:

- the biodestruction by certain micro-organisms of complex proteins (such as casein and egg white) sometimes applied in conservation treatments of the past.
- the presence of oxalic acid ($H_2C_2O_4$) secreted by lichens, reacting with the calcite ($CaCO_3$) on the surface, generates calcium oxalates (CaC_2O_4) with different hydration states like *whewellite* ($CaC_2O_4 \cdot H_2O$) and *weddellite* ($CaC_2O_4 \cdot 2H_2O$). These are both highly insoluble, unlike most of the other salts so far taken into consideration.

There are, however, other interpretations about the formation of oxalates, the most recent involving the presence of carbon monoxide in the air as a pollutant 🗀19.

The most common forms of deterioration

The presence of oxalates appears as chromatic modifications: generally a yellowish, reddish or brownish patina depending on the impurities it contains *(photo 5)*. They are usually well attached to the surface of the stone. Some authors suggest that they may even protect the stone surface.



5 Oxalate patina
colour print on inside back cover

Phosphates PO_4^{---}

Origin 🗀20

Bird excrement contains phosphate salts. The accumulation of excrement permits phosphates, which are soluble, to migrate over large surface areas under damp conditions. Another source of phosphates is fertilizers (ammonium phosphates).

The most common forms of deterioration

Dark black deposits and white patches which are rich in organic matter providing nutrient for microbiological growth and therefore increasing decay 🗀21.

5 SURVEYING AND SAMPLING

The first considerations regarding masonry damaged by salts must be made on site through an overall visual inspection and annotation of the following:

- type of masonry (brick, stone)
- orientation (north, south, etc.) and exposure (sun, shade) of the external surfaces
- indoor climate, existence of air-conditioning and/or heating systems, movement of air;
- identification of humid areas, rising damp and possible infiltration of water from roof or drainage system;
- visible deterioration caused by salts.

The result of this first inspection must be recorded on a plan of the building indicating the phenomena observed as a guide to planning sampling and future analysis relating to the presence of soluble salts.

Having completed a survey of the overall situation, photographic and/or graphic documentation must be carried out and if sampling is needed, a plan must be decided on.

6 ANALYSIS

With the exception of X-ray diffraction (XRD), the following types of analysis require the ground sample to be shaken in pure water to dissolve the soluble salt content and the analysis to be done only on the solution. They provide us with information about the ions and only indirectly about the salts.

This is often insufficient. For example, if dihydrate calcium sulphate ($CaSO_4 \cdot 2H_2O$) and decahydrate sodium sulphate ($Na_2SO_4 \cdot 10H_2O$) are present in a sample, the result with these methods will only show a certain amount of both calcium and sodium cations and sulphate anions. X-ray diffraction, instead makes it possible to identify the exact mineralogical composition of the compound so the result, in the above case, would show *gypsum* and *thenardite*. Furthermore, if $MgSO_4 \cdot 6H_2O$ *(hexadrite)* and $MgSO_4 \cdot 7H_2O$ *(epsomite)* are both present at the same time, only XRD can identify the two phases.

Simple tests

There are several very simple tests for the analysis of salts which require very little chemical know-how. Their cost is minimal and they provide semi-quantitative results in a few minutes. But there are no simple methods available for testing the presence of all the salts we may want to analyse (e.g. phosphates, oxalates) and the tests currently available are often not accurate enough for our purpose. If this is the case, it is better to resort to instrumental analysis (e.g. ion chromatography) at a specialized laboratory.

6 Microchemical tests

A) MICROCHEMICAL TESTS *(photo 6)*

These are laboratory tests that, through simple chemical reactions, make it possible to identify the type of anion (negative ion deriving from the dissociation of the salts, i.e. sulphate, chloride, nitrate, etc.) present in a solution. Even though they do not give quantitative information, they enable us to distinguish when there are negligible or massive quantities of the various anions and give a preliminary indication of the observed decay.

B) STRIP TESTS *(photo 7)*

These are plasticized strips with specific zones of reaction which are immersed in the solution to identify a specific ion⑥. If an ion is present, the strip changes colour at varying degrees according to the quantity.

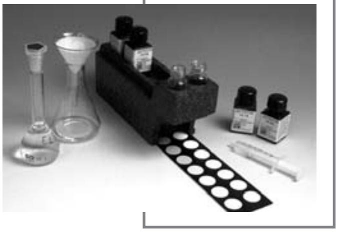
7 Strip test kit
colour print on inside back cover

Each type of strip test is sensitive to only one type of ion and they are available in boxes of 25 and 100 strips and cost approximately half a US dollar per strip.

The sensitivity varies according to the type of ion; there is a marked variation in range between one ion and another (e.g. sulphates 200-1600 ppm⑦(mg/l); nitrates 10 - 500).

C) COLORIMETRIC KITS *(photo 8)*

These are based on reactions that lead to the formation of coloured compounds formed by each ion and its specific reagent. All the reagents and equipment necessary for analysis are inside the kit together with the instructions for their use.



8 Colorimetric test kit
colour print on inside back cover

As in the previous case, the intensity of the colour indicates the amount of ions present in the solution and the kit provides a colour card against which to measure the sample.

Each kit is sensitive to only one type of ion (and sensitivity varies according to the type of ion) and is sufficient to carry out at least 100 tests. One kit costs about 100 US dollars.

Instrumental analysis

A) MEASURING CONDUCTIVITY *(photo 9)*

Chemical compounds that in solution are totally dissociated into ions are called electrolytes. A characteristic of electrolytic solutions is that they conduct electricity through the ions. This property increases with the concentration of the ions in solution, and also depends on their charge, mobility and the temperature of the solution.

9 Conductivity measurements

For diluted salt solutions there is a linear dependence between ion concentration and specific conductivity (χ)⑧ *(Fig. 2)*.

We can therefore use measurements of conductivity to provide us with information on the total content of ionic species and therefore of soluble salts even though we know nothing of the quality of these salts. The measurements can be effectively used both to give preliminary indications and to monitor trial treatment for the removal of salts from building surfaces 🗀**22**.

The measurements are expressed in microSiemens/cm (distilled water: about 7-8 μS/cm, tap water 300-400 μS/cm).

⑥ *They can also be used on site by placing a wetted reagent strip directly against an efflorescence. Obviously the result in this case is only qualitative and only regards the outer surface in contact with the strip.*

⑦ *Parts per million: yet another very much adopted way of expressing the concentration that for aqueous solutions is equivalent to mg/l.*

⑧ *Specific conductivity (χ) is the reverse of its specific resistance (ρ)*
$\chi = 1/\rho = \mathbf{1/R \times l/s}$
Where: **R** *= resistance of conductor expressed in ohm (Ω)*
1/R *expressed in Siemens (S);*
l *= length of conductor (cm);*
s *= cross section of conductor (cm^2);*

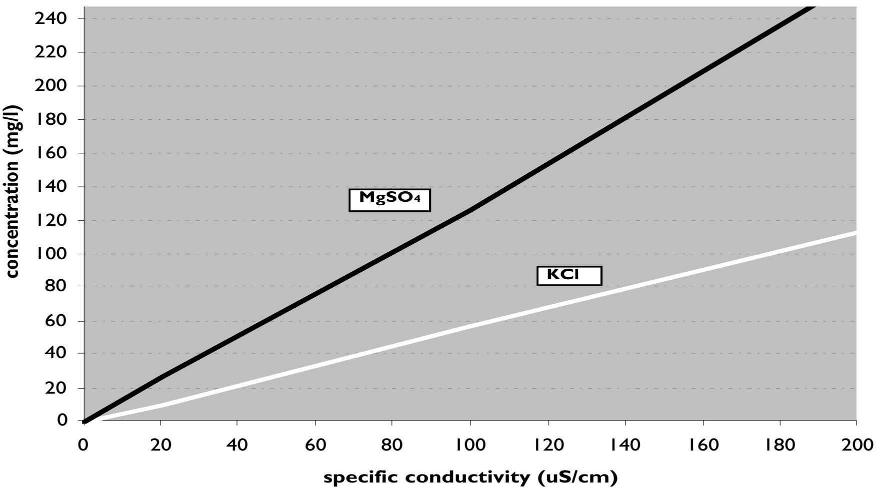


Fig 2. Specific conductivity curves

B) IONIC CHROMATOGRAPHY

Whenever diagnosis demands a more precise knowledge not only of the type but also the quantity of cations and anions present in the solution it is necessary to resort to more sophisticated technology.

Chromatography is used in chemical analysis to separate complex mixtures into single components based on the different velocities of migration (retention time) of the various components through a chromatographic column filled with a specific stationary phase.

From the retention time we can then recognize the anions and cations present in the solution and, calibrating the instrument with the standard solutions⑨ of anions and cations, we can calculate their precise concentration⑩.

The advantage is that the instrument is highly sensitive and can reveal ionic species in concentrations below 1 ppm in a short time but analysis must be done at a specialised laboratory at a cost of about 90 US dollars.

C) X-RAY DIFFRACTION

X-rays provide information on the exact nature of the crystalline⑪ substances and not only on the ions, identifying the mineralogical composition of the compound.The minimum amount needed for the analysis ranges from 10 to 100 mg and the minimum percentage of crystalline compound detectable is about 3% of the mass of the sample, this limit depending upon the crystallinity of the compound.

One of the advantages of XRD is that the analysis must be done directly on the powdered sample without putting it in solution and therefore the sample after the analysis can also be used again for additional investigations.The analysis costs about 130 US dollars.

D) INFRARED SPECTROSCOPY

Fourier-transform infrared spectroscopy (FTIR) can be used with organic and inorganic compounds. Although inorganic compounds sometimes do not give clear readings, depending on the complexity of the mixture, FTIR has been widely used to analyse efflorescences, crusts and patinas on stone materials and is able to identify constituent materials and deterioration products. This technique is usually chosen because it only requires a tiny sample (1-2 mg). It costs about 90 US dollars in a specialized laboratory.

The relatively high cost of the last three types of analysis is obviously due to the high initial capital investment for equipment and the technical expertise necessary for their application.

⑨ *Solutions with known concentrations.*

⑩ *In practice, as in any other measurement, there is always a margin of error.*

⑪ *Non-crystalline phases (amorphous) cannot be identified and in fact cause an increase in background noise and consequently a reduction in the sensitivity of the instrument.*

PRACTICAL 1

PREPARATION OF SOLUTIONS WITH VARYING CONCENTRATIONS OF SODIUM SULPHATE

Aim

The aim is to gain confidence working with soluble salts and appreciate the forces in play. The prepared solutions will be needed for the second experiment which will involve observation of the damage caused by soluble salts on stone samples.

Equipment and chemicals

- 600 ml beaker
- 1 litre flask
- Deionized water
- Sodium sulphate decahydrate ($Na_2SO_4 \cdot 10H_2O$)
- Technical balance

Procedure

A) SATURATED SOLUTION AT ROOM TEMPERATURE.

Fill the beaker with 500 ml of deionized water and add the sodium sulphate decahydrate a little at a time, shaking gently, until it no longer dissolves (about 180 grams are necessary).

B) 10% SOLUTION W/V①.

Weigh 100 g of $Na_2SO_4 \cdot 10H_2O$, place it in the flask, bring it up to the volume of 1000 ml with deionized water and shake the solution.

①The percentage composition is a way of expressing the concentration. There is generally an indication as to whether it is expressed as weight per volume (w/v) or weight per weight (w/w).

PRACTICAL 2

CRYSTALLIZATION CYCLES②

Aim

The aim is to directly observe how salts can be transported inside materials, for example by capillary action, and how, over a period of time, the repetition of dissolution and crystallization cycles can lead to aesthetic and structural damage *(photos 10 and 11)*.

Equipment and chemicals

- Oven
- Glass or plastic tray
- 10% sodium sulphate solution
- Unaltered stone sample (preferably cube-shaped 5 x 5 x 5 cm)
- Stereomicroscope

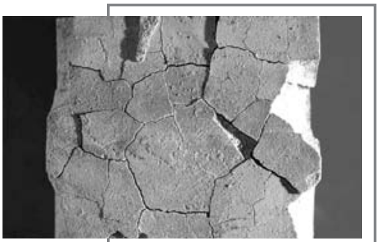
Procedure

- Dry the stone sample in the oven at 110°C for 24 hours.
- Leave it to cool.
- Put the sample in the tray totally filled with the solution of 10% sodium sulphate in deionized water.
- After 24 hours, remove the sample, blot excess water and dry it in the oven for 24 hours.
- Immerse the sample again in the sodium sulphate solution and repeat the cycle at least three times or until some evident alteration is visible.

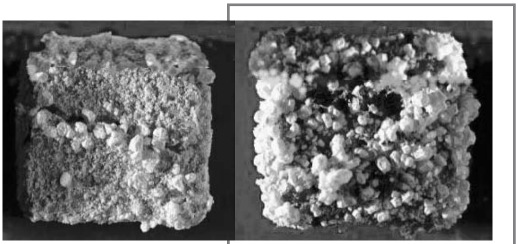
The number of cycles necessary to achieve physical change varies according to the type of stone material.

Naturally, the experiment can be done under more drastic conditions so as to heighten its effect, for example, by using solutions with higher concentrations.

It is very useful to study the macroscopic variations of the sample with a stereomicroscope and learn to recognize the macroscopic effects typical of the crystallization of the various salts.



10 Disruptive action of 10% sodium sulphate solution on mortar sample
colour print on inside back cover



11 Two phases of prolonged disruptive action of saturated solution of sodium sulphate
colour print on inside back cover

②Movement of salts in porous materials and observation of their deterioration.

PRACTICAL 3

SAMPLING

Aim

The aim is to learn correct sampling procedure and technique.

Equipment

- Scalpel
- Paper pulp
- Plastic bags and small containers for samples
- Identification cards for samples
- Adhesive tags
- Camera

12 Sampling kit

Procedure

- Once the overall situation has been assessed and the need for sampling verified, photographs must be taken and a sampling plan decided upon.
- Before taking any samples, photograph the sample point (indicating it with the scalpel and putting a label on it specifying the identification number of the sample).
- It is advisable to take at least two photos for each sample: a general one that gives an overall view of the area and a close-up of the precise sampling location.
- Each sample taken with the scalpel (about 100 mg are sufficient③) is recorded on its data sheet with all relevant data (position, aspect, reason for taking sample, assumptions, analysis to be carried out); the sample container must be marked to avoid mixing up samples.
- Whenever the taking of samples is not possible, as in the case of mural paintings, the alternative is to use pulp poultices④ (suggested size: 10 cm^2, thickness approximately 5 mm, ratio of pulp to water about 1/6 or 1/8 in weight soaked in deionized water and applied to the wall so that it sticks to the surface *(photo 13)* 🗀*23*.
- After a certain time (a day, for example) the pulp poultice is removed and analysed in the laboratory. It must be remembered that, depending on the solubility of the salts, the efficiency of the extraction can vary. To ensure reliable results, more than one extraction may be necessary.

13 Sampling salts using pulp poultice
colour print on inside back cover

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③ *In the specific case of pure salt efflorescence the amount can be even smaller, the sample being constituted only of salt.*

④ *These must be carefully chosen preferably with the assistance of a conservator as they must guarantee adherence to the surface even after the water has evaporated. They must neither contain impurities nor leave visible traces of fibre on the paint layer.*

PRACTICAL 4

QUALITATIVE ANALYSIS OF SULPHATES, CHLORIDES, NITRITES, NITRATES AND CARBONATES (microchemical tests)

Aim

The identification of salts present in masonry, though it may only be qualitative, provides information that assists us in understanding phenomena of deterioration and may be the only instrument available in field laboratories, such as those on conservation worksites.

Equipment and chemicals

- Mortar and pestle
- Test tubes
- Filter paper and a small glass funnel
- Diluted hydrochloric acid (HCl 2M)⑤
- Diluted nitric acid (HNO_3 2M)
- Diluted acetic acid (CH_3COOH)
- Sulphamic acid (HSO_3NH_2)
- 10% solution of barium chloride ($BaCl_2$) in deionized water
- 0.1M solution of silver nitrate ($AgNO_3$)
- Zinc powder
- Griess-Ilosvay's reagent

14 Microchemical analysis: glassware

Procedure

PREPARATION OF SAMPLE TAKEN FROM WALLS

- Grind part of the sample (0.1 gram is more than enough) to a fine homogeneous powder.
- Put half⑥ of the ground sample in a test tube and add about 5 ml of deionized water and shake it gently to dissolve the material.
- Wait a few minutes so that the insoluble residue is deposited at the bottom of the tube. The solution must be clear. If not, filter it using filter paper and a small funnel.
- Keep the test tube containing the insoluble part for the analysis of carbonates and divide the clear solution above into another 4 small test tubes to use for testing for sulphates, chlorides, nitrites and nitrates.

PREPARATION OF PULP POULTICE SAMPLE

If indirect sampling with pulp poultices must be carried out:

- Take a small piece (about 1 cm^2) of the detached poultice and shake it in a beaker with deionized water. Wait till the cellulose fibres have sunk to the bottom and use the clear solution to do the tests on the next page.

Safety precautions

When working with these reagents always wear safety gloves and observe the safety precautions recommended for dealing with *corrosive* materials

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⑤ *M indicates the molarity, frequently used in chemistry to express the concentration of a solution. It signifies the quantity of moles of a certain substance in a litre of water. The mole of a compound corresponds to the quantity in grams equal to its molecular weight, for example, in a 1M solution of NaCl (molecular weight 58.44), there will be 58.44 grams of NaCl dissolved in 1 litre of water.*

⑥ *The other half can be used to repeat the analysis in case of doubt or error.*

For each of the following tests a simultaneous test should be carried out on approximately 1ml of deionized water so as to compare these so-called "blank" results with those of the sample.

Analysis of sulphates (SO_4^{--})

Add 1 or 2 drops of **HCl 2M** and 1 or 2 drops of a 10% solution of **barium chloride** to the first test tube.

The appearance of a white precipitate of barium sulphate, insoluble in nitric acid, indicates the presence of sulphates. Gently stroking the walls of the test tube with a glass rod helps the nucleation of the crystals, and therefore the formation of the precipitate.

The reaction can be
summarized as follows:

$$(SO_4^{--}) + BaCl_2 \rightarrow BaSO_4\ \textit{(prec.)} + 2\ Cl^-$$

The sulphate present in the solution precipitates as it reacts with barium chloride forming the insoluble salt barium sulphate.

Analysis of nitrites (NO_2^-)

Add 1 or 2 drops of **CH_3COOH 2M** and 1 or 2 drops of **Griess-Ilosvay's reagent** to the third test tube.

The appearance of a more or less intense **pink colour** indicates the presence of nitrites.

Analysis of chlorides (Cl^-) *(photo 15)*

Add 1 or 2 drops of **$HNO_3$2M** and 1 or 2 drops of a 0.1M solution of **silver nitrate** to the second test tube.

The appearance of a whitish-blue gelatinous precipitate of silver chloride indicates the presence of chlorides.

The reaction can be
summarized as follows:

$$Cl^- + AgNO_3 \rightarrow AgCl\ \textit{(prec.)} + NO_3^-$$

The chloride present in the solution precipitates as it reacts with silver nitrate forming the insoluble salt silver chloride.

15
Microchemical
test for chloride
identification.

Analysis of nitrates (NO_3^-)

A) If the test for nitrites was negative add a small quantity of **zinc powder** to the same solution. In this way, if there are nitrates, they will be reduced to nitrites which, reacting with the Griess-Ilosvay's reagent already in the solution, will give rise to a more or less intense pink colour.

B) If the test for nitrites was positive add a small quantity (1 or 2 crystals) of **sulphamic acid** to the fourth test tube to eliminate the nitrites (make sure you have eliminated all the nitrites by carrying out the test for nitrites on a small portion of the solution).

Add 1 or 2 drops of **CH_3COOH 2M**, 1 or 2 drops of **Griess-Ilosvay's reagent** and a small quantity of **zinc powder**.

The appearance of a more or less intense pink colour indicates the presence of nitrates.

Analysis of carbonates (CO_3^{--})

Add 1 or 2 drops of **HCl** to the test tube with the insoluble residue. Bubbles of gas (CO_2) indicate the presence of carbonates.

The reaction can be summarized as follows:

$$CaCO_3 + 2\,HCl \rightarrow CaCl_{2\,(sol.)} + H_2O + CO_{2\,(gas)}$$

The insoluble calcium carbonate is attacked by the chloride acid forming a soluble salt (calcium chloride) and developing carbon dioxide.

Recording results

As this analysis is only qualitative it is not necessary to weigh a fixed amount of the sample and add a precise volume of water. The results are therefore recorded on a table expressing the different intensities of the reaction observed in the tests through the use of symbols:

–	indicates the absence of an ion
±	indicates the presence of an ion at the limit of perceptibility
+	indicates the presence of an ion
++	indicates the presence of an ion in relative abundance

PRACTICAL 5

SEMI-QUANTITATIVE ANALYSIS

The remaining powdered sample can be used to prepare another solution for the analysis with the strip test⑧.

Equipment

Strip test	Deionized water
Kit test	Analytical balance
100 ml flask	

⑧ *If salt content in the sample is very low, use the more sensitive kit test.*

⑨ *Check the instructions which vary slightly for the different strip tests.*

⑩ *If the dilution volume (Vd) is different, apply the formula:*

$$A^- \% = \frac{A^- (mg/l) \times Vd (ml)}{1000} \times \frac{100}{\text{sample mass } (mg)}$$

⑪ *If the dilution volume (Vd) is different, apply the formula:*

$$A^- (mg/100\ cm^2) = \frac{A^- (mg/l) \times Vd (ml)}{1000} \times \frac{100}{\text{sample size } (cm^2)}$$

Procedure

A) PROCEDURE FOR POWDERED SAMPLE TAKEN FROM WALLS

Weigh 100 mg of sample and put it into a small 100 ml flask. Bring it up to the indicated volume with deionized water and shake it for 10 minutes.

Briefly immerse the reaction zone of the test strip in the solution and after about one minute⑨ compare the reaction zones with the colour scale or use an ion kit test *(see section 6 c - p. 10)*.

CALCULATION

Since in this case you are dealing with semi-quantitative analysis it is advisable to express results in a precise way. In fact, in this practical the amount of the sample is weighed and the water volume added is precise.

The ion content ($A^-\%$) is expressed in percentage weight of the initial dry mass of the sample:

$$A^- \% = \text{recorded } A^- \text{ concentration } (mg/l) \times 0.1$$

where A^- is a generic anion (*sulphate, chloride, etc.*)⑩.

B) PROCEDURE FOR PULP POULTICE SAMPLE

Use a section of pulp poultice of 5 x 10 cm^2 in size (see Sampling Practicals) and immerse it in a beaker with 200 ml of deionized water *(photo 16)*.

Wait until the cellulose fibres have sunk to the bottom and do the measurement on the clear solution.

16 Dried pulp poultice

CALCULATION

The ion content A^- is expressed in milligrams of ions per 100 square centimetres of pulp poultice.

$A^- (mg/100cm^2) = \text{recorded } A^- \text{ concentration } (mg/l) \times 0.4$

where A^- is a generic anion *(sulphate, chloride, etc.)* ⑪.

DISCUSSION PROPOSALS

Depending on the data obtained, sum up the results of the analysis carried out, and proceed as follows:

- Draw a map of the distribution of soluble salts at different heights on the walls.
- From the information obtained about the composition of salts found in the wall, try to indicate the provenance of the salts.
- On the basis of the analysis results and broader considerations, come up with a diagnosis.
- Propose how to remedy the actual deterioration of the materials and how to intervene in order to limit the infiltration of salts.

8 CASE STUDY

SALT AND MOISTURE SURVEY ON MASONRY AND MURAL PAINTINGS IN THE CHURCH OF S. ELIGIO DEGLI OREFICI – ROME

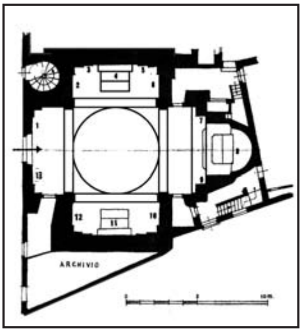
(The author acknowledges the kind contribution of W. Schmid, ICCROM)

Background

This survey was organized in May 1998, as part of the International ICCROM Course on the Conservation of Mural Paintings and Related Architectural Surfaces (MPC 98). The limited time frame of the course did not allow for the collection of further historical data, the monitoring of the microclimatic parameters over a longer period and an overall building analysis. Only the integration of these elements would have made it possible to draw effective conclusions.

Description

Fig 1



"S. Eligio degli Orefici" is a small church, in Greek cross plan *(Fig. 1)*, whose design has been attributed to Raphael. It is situated between Via Giulia and the River Tiber in Rome.

The building material is brick covered with plaster. In the apse of the central chapel and in the two lateral altars there are mural paintings (16th century) mainly done in fresco technique: "Madonna con Santi" attributed to Matteo da Lecce, "Adorazione dei Magi" by Francesco Romanelli and "Nativita' di Gesu' Cristo" by Giovanni De Vecchi.

Survey

The church is close to the river and has adjoining civil buildings on both sides that show a uniform level of rising damp up to about 1.5 m. This probably dates back to when the water table in this area of the town was much higher before the construction of the Tiber embankment in 1870.

The plaster indoors shows isolated patches of decay in all the lower parts of the church. A white veil covers the paintings up to 4 metres from ground level.

The case study refers mainly to the fresco "Nativita' di Gesu' Cristo" on the left of the altar whose alteration (a patchy white veil) suggests the presence of crystallized salts. Traces of infiltration are visible on the ceiling to the right of the altar. The interior of the church, although repainted in 1983, appears to have deteriorated in many areas, due to lack of roof maintenance.

17 Church of St. Eligio: Salts analysis on mural painting

colour print on inside back cover

Sampling

Three types of samples were taken to provide information about moisture and water-soluble salt content.

1. Six powdered samples of the plaster and/or masonry were collected by drilling gently into the pilaster strip to the left of the painting at heights of 1, 2 and 3 metres and at a depth of between 0-3 cm (samples "a") and 15-18 cm (samples "b").
2. Pulp poultices were applied, on two successive occasions, on the right side of the mural painting at three different heights *(photo 17)* and removed after drying was complete. In this way, soluble salts were extracted from the surface for a total of six samples.
3. One sample was obtained by gently scratching the whitish surface veil on the painting.

Experimental

A) SALTS ANALYSIS

The **salt content** of the samples described in points 1 and 2 was measured by ionic chromatography according to the Italian standard "UNI Normal U84000050. Beni culturali. Materiali lapidei naturali ed artificiali. Determinazione del contenuto di sali totali".

The **moisture content** of the powdered samples (point 1) was measured by weighing them before and after drying at 60°C in an oven until constant weight was reached. The weight loss corresponds to the moisture content and is expressed as a percentage of the dry mass of the sample.

The surface sample *(point 3)* was analysed by X-ray diffraction to determine its **mineralogical composition**.

B) MICROCLIMATE MONITORING

The **microclimate** (relative humidity and air temperature) was monitored both inside and outside the church by using two thermohygrographs.

The first one was on a shelf *(photo 18)* very close to the fresco, and the second, in the church courtyard but protected from direct sunlight. A data logger ⑫ inside the church was also used to measure air temperature, relative humidity and surface temperature of the walls. The measurements were carried out over a period of two weeks between April and May 1998.

⑫ *A portable instrument for the collection and processing of environmental data*

18 Church of St. Eligio:
Climate monitoring
colour print on inside back cover

Results

• *Salts and moisture analysis*

A) POWDERED SAMPLES

Data relative to the moisture and anion content of the samples taken close to the surface (depth 0-3 cm) and samples taken inside the wall (depth 15-18 cm) are summarized in Fig. 2 and Tables 1, 2, 3.

If we take nitrates, the most abundant salts, as an example, two trends can be observed:

1. In the "a" samples (depth 0-3 cm), the salt concentration is related to the moisture content and diminishes with height; the higher the sample, the lower the concentration.
2. In the "b" samples (15-18 cm inside the wall) where the moisture content is constant, the trend is vice versa; the higher the sample, the higher the concentration, according to their mobility.

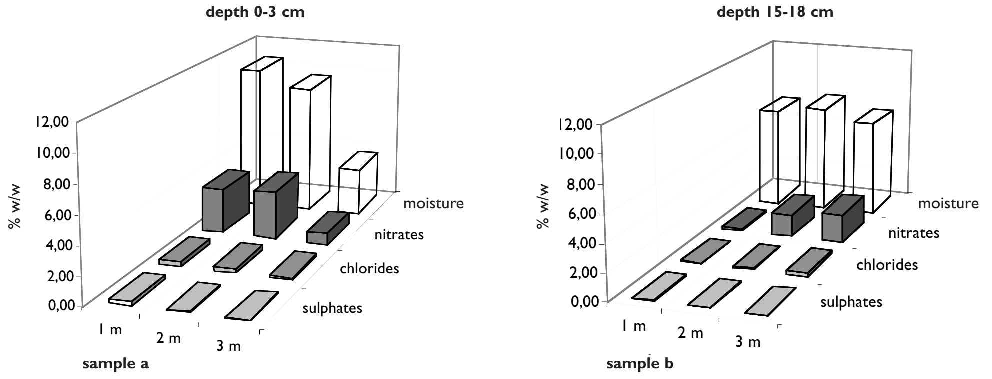


Fig 2. Church of St. Eligio - Rome. Powdered samples taken at different depths

B) Pulp poultice samples

Data for the salts extracted with poultices are summarized in Fig. 3 and Tables 4, 5. These also indicate that nitrates are the most abundant anions (followed by chlorides and, in much lower concentrations, sulphates and phosphates) and that there is a general decrease in concentration between the first and second extraction except for the sample at 3 metres that shows the opposite trend. The corresponding cations are principally calcium and sodium with a much lower quantity of potassium and magnesium.

C) Efflorescence sample

The XRD analysis indicates that it is made up of a significant amount of gypsum ($CaSO_4 \cdot 2H_2O$) together with some traces of calcite ($CaCO_3$).

- ***Microclimate monitoring***

Relative humidity and temperature showed normal daily fluctuations outside the church while inside there was no variation. The inside temperature was constant at 14°C during the first week of rainy weather and increased from 14 to 17°C during the second week of sunny weather. Inside relative humidity increased from 75% to 95% during the first week and was constantly higher than 90% during the second week.

The surface temperature of the wall was generally in equilibrium with the air temperature and also remained stable during sudden indoor climatic fluctuations, for example, when the church was opened for worship on Sundays.

Sample		Height (m)	Depth (cm)	Moisture content (% w/w)
1	a	1	0-3	10.62
	b	1	15-18	7.64
2	a	2	0-3	9.43
	b	2	15-18	8.12
3	a	3	0-3	3.49
	b	3	15-18	7.27

Table 1 - Moisture content of powdered samples

Sample		Height (m)	Depth (cm)	NO_3^{--}	Cl^{--}	SO_4^{--}
1	a	1	0-3	3.30	0.33	0.23
	b	1	15-18	0.12	0.03	0.04
2	a	2	0-3	3.50	0.33	0.07
	b	2	15-18	1.70	0.1	0.05
3	a	3	0-3	0.86	0.12	0.02
	b	3	15-18	2.11	0.23	0.01

Table 2 - Anion content (% w/w) of powdered sample

Sample		Height (m)	Depth (cm)	Na^{+}	K^{+}	Mg^{++} b	Ca^{++} 3
1	a	1	0-3	1.45	0.82	0.10	1.46
	b	1	15-18	0.34	0.32	0.04	0.66
2	a	2	0-3	0.49	0.87	0.09	1.81
	b	2	15-18	1.00	0.95	0.09	0.9
3	a	3	0-3	0.10	0.38	0.07	0.98
	b	3	15-18	0.35	0.79	0.14	1.47

Table 3 Cation content (% w/w) of powdered samples

a = plaster
b = masonry

Fig 3. Church of St. Eligio - Rome. Salts extraction by wet pulp poultice application

Sample		Height (m)	Extraction	Cl^-	NO_3^-	SO_4^{--}
1	a	1 m	first	68	719	3
	b	""	second	48	44	2,6
2	a	2 m	first	61	420	2
	b	""	second	34	250	1
3	a	3 m	first	25	150	1
	b	""	second	35	200	3

Table 4 - Anion content (mg/100cm^2) in wet pulp poultice samples (paint layer)

Sample		Height (m)	Extraction	Na^+	$NH4^+$	K^+	Mg^{++}	Ca^{++}
1	a	1	first	59.7	21.7	34.7	27.9	142.4
	b	1	second	59.3	n.d.	32.0	25.4	110.5
2	a	2	first	40.7	7.4	36.9	18.6	132.9
	b	2	second	21.8	4.4	21.5	14.7	89.7
3	a	3	first	17.0	n.d.	14.5	7.5	62.8
	b	3	second	22.9	n.d.	17.6	10.0	74.2

Table 5 - Cation content (mg/100cm^2) in wet pulp poultice samples (paint layer)

Conclusions

1. Soluble salts.

   These are concentrated mainly inside the first 3 cm. Therefore it is advisable not to plan to extract salts from this wall because there is no serious danger of crystallization due to the high levels of indoor relative humidity.

2. Humidity in the wall.

   This is attributed mainly to the high hygroscopicity of the deliquescent salts (mainly nitrates) within the wall. Capillary action, which was considerable in the past, is now present only at a lower level.

3. Condensation on the mural painting.

   If this occurs, it could be very dangerous due to the presence of gypsum on the paint layer (whitish veil) which could become partially dissolved, penetrate the plaster and begin the crystallization cycle. In this case study, there was no risk of condensation as the monitored surface temperature was the same as the air temperature.

Proposals

First of all, constant monitoring throughout the whole year is recommended in order to obtain data relating to all seasonal variations.

As salts are above all present inside walls in the form of highly soluble salts (mainly nitrates due to the fact that the area was inhabited in ancient times), there is no reason to desalinate the walls.

In order to avoid condensation principally on the paint layer, it is necessary to reduce the relative humidity inside the church. Levels of 85-90% are obviously too high but also a drastic reduction is dangerous because it could activate the crystallization of soluble salts inside the wall. The optimum level of relative humidity should be studied further.

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STANDARDS

RILEM tests (Réunion Internationale des Laboratoires d'Essais des Matériaux)

Test n.V.1a: Crystallization test by total immersion (for untreated stone)

Test n.V.1b: Crystallization test by total immersion (for treated stone)

Test n.V.2: Crystallization test by partial immersion

Test n.VI.4: Electrical conductivity

NORMAL documents (Commissione Normativa Manufatti Lapidei)

UNI NORMAL U84000050: Determinazione del contenuto di sali solubili totali

NORMAL 1/88 : Alterazioni macroscopiche dei materiali lapidei: Lessico

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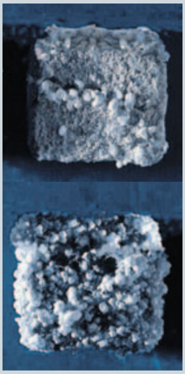
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ICCROM

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CONSERVATION OF ARCHITECTURAL HERITAGE,
HISTORIC STRUCTURES AND MATERIALS

Binders

BINDERS

ARC
LABORATORY HANDBOOK

VOLUME 4/99

Ernesto Borrelli

The ICCROM ARC Laboratory Handbook is intended to assist professionals working in the field of conservation of architectural heritage and historic structures. It has been prepared mainly for architects and engineers, but may also be relevant for conservator-restorers or archaeologists.
It aims to:

- ***offer an overview of each problem area combined with laboratory practicals and case studies;***
- ***describe some of the most widely used practices and illustrate the various approaches to the analysis of materials and their deterioration;***
- ***facilitate interdisciplinary teamwork among scientists and other professionals involved in the conservation process.***

The Handbook has evolved from lecture and laboratory handouts that have been developed for the ICCROM training programmes. It has been devised within the framework of the current courses, principally the International Refresher Course on Conservation of Architectural Heritage and Historic Structures (ARC).

The general layout of each volume is as follows: introductory information, explanations of scientific terminology, the most common problems met, types of analysis, laboratory tests, case studies and bibliography.

The concept behind the Handbook is modular and it has been purposely structured as a series of independent volumes to allow:

- ***authors** to periodically update the texts;*
- ***users** to work selectively with the volume relating to the particular problem they are facing*
- ***new volumes** to be gradually added in line with developing needs.*

1998 - 99 volumes:
*(1) Introduction, (2) Porosity, (3) Salts, **(4) Binders**, (5) Colour specification and measurement*

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CONSERVATION OF ARCHITECTURAL HERITAGE,
HISTORIC STRUCTURES AND MATERIALS

ARC
Laboratory Handbook

Binders

Ernesto Borrelli

ICCROM

Rome, 1999

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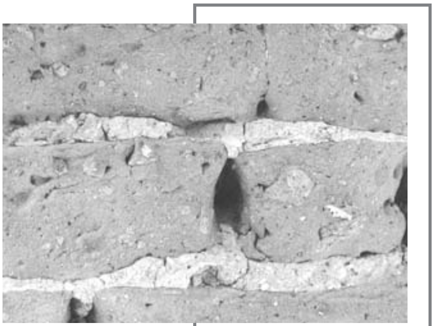
① : Footnotes

🗁 : Bibliographic references

1. INTRODUCTION



1. Mud blocks

For thousands of years the availability of raw materials has been the main factor influencing building traditions. In the past, building tradition was always strictly linked to the geographical and geological nature of the different areas of civilisation.

The use of *clay*, *gypsum* and various types of *lime* as binder material are the traditional expression of certain ancient cultures.

It is well-known that solid mud constructions such as the Egyptian mastaba tombs *(photo 1)* reflect the presence of alluvial material from the Nile, and the use of gypsum as the principal binder again in Egypt is the result of the wide distribution of gypsum rocks in the region. The development of lime technology and the natural presence of materials such as pozzolana in the Mediterranean Basin were the main reasons for the excellence of Roman architecture.

From the fall of the Roman Empire until the 18th century, there were very few innovations in the use of materials and construction techniques. Gypsum, lime mixed with sand, with pozzolana or with brick dust, had been used for centuries, following almost identically the ancient methods handed down in architectural treatises from Vitruvius① to those of the 15th and 16th centuries.

John Smeaton② (1750) was the first to experiment in the production of a new type of lime. The 18th century saw the beginning of a new phase in the development of new binders ranging from hydraulic lime to modern-day cement.

2. BASE TERMS

Binders

Natural (inorganic) and/or artificial materials that, if mixed with water, permit the preparation of a plastic mixture that hardens to form a solid mass.

Materials which bind sand particles or crushed stones together to obtain mortars (i.e. gypsum, lime, cement, etc.)

Mortar

A combination of binder and other components such as sand, crushed stones and water to form a paste.

Mortars are used because of their capacity to fill all the gaps between masonry material and for their quality of adhering strongly and hardening to form a whole with the stone or bricks to which they have been applied③.

Aggregate

Materials added to binders to prepare mortars. They can either be natural such as sand and crushed stones④ or artificial such as crushed bricks or pottery shards. In the majority of cases the aggregate is an inert material (e.g. sand); in other cases, it can be chemically reactive (e.g.

① *The ten books of architecture 10 B.C.*

② *J. Smeaton. A Narrative of the Building and a Description of the Construction of the Edystone Lighthouse, London 1791.*

③ *Further classification and types will be presented in the volume on "Mortars"*

④ *Usually defined as fine aggregate*

crushed bricks or natural materials such as pozzolana⑤). Occasionally fibrous material may be added as reinforcement (i.e. vegetable fibres, straw, etc.).

Admixtures (additives)

Added substances which modify properties such as the workability of the mortar mixture that cannot be obtained using basic binders (i.e. casein, oils, or synthetic resins, water reducers and setting time retarders).

(Both aggregates and additives will be further described in the volume on "Mortars")

3. CLASSIFICATION

The most common binders used in the past and still recommended today for restoration purposes can be classified

either according to their **origin** as *natural* or *artificial* (modified inorganic materials)

or according to their **setting process** as *dehydration/hydration-setting*, *air-setting* or *hydraulic-setting*.

4. MAIN BINDERS

A) CLAY

Natural origin

Clay is a natural binding material and was the first used for building not only in the preparation of hand-made mud bricks but also as a binder of the masonry.

Clay is the finest fraction of the soil. It has a significant content of clay minerals of the aluminosilicate group with a sheeted layer crystal structure and micrometric dimensions⑥.The minerals give plastic properties to the soil when mixed with the right amount of water.

B) GYPSUM 🗀 1

Artificial origin

Gypsum is a mineral primarily consisting of hydrated calcium sulphate (or calcium sulphate dihydrate) commonly found in the form of selenite⑦, alabaster⑧ or compact gypsum stones.

$$\boxed{CaSO_4 \cdot 2\ H_2O}$$

gypsum

When heated gypsum loses water at a moderate temperature (130-150 °C) passing from the dihydrate ($CaSO_4 \cdot 2\ H_2O$) to the hemihydrate:

$$\boxed{CaSO_4 \cdot 0.5\ H_2O}$$

the dry powder better known as plaster of Paris.

Setting process

The hardening of gypsum is due to a process of *hydration*. The hemihydrate (plaster of Paris) when mixed with water, sets rapidly to form hardened gypsum:

---

⑤ Of volcanic origin, used by the Romans and still in use in the South of Italy (pulvis puteolanus). Trass in Germany and gaize in France are the same class of substance.

⑥ This will be further illustrated in the volume on "Earthen Building Materials".

⑦ Macrocrystalline - a variety of gypsum occurring as colourless and transparent crystals or large crystalline masses.

⑧ Microcrystalline – fine-grained massive gypsum, normally white and often translucent.

$$\text{CaSO}_4 \cdot 0.5\,\text{H}_2\text{O} \quad + \quad \text{water} \longrightarrow \underset{\text{hardened gypsum}}{\text{CaSO}_4 \cdot 2\,\text{H}_2\text{O}} \quad + \quad \text{heat}$$

$$\text{plaster of Paris} \quad + \quad \text{water} \xrightarrow[\text{set}]{} \text{hardened gypsum} \quad + \quad \text{heat}$$

It neither shrinks nor requires aggregates. As calcium sulphate is slightly soluble in water (2.5 g/l), gypsum is not used normally on exposed surfaces in damp climates. It is not very hard⑨, and in the presence of water it has a slightly acid reaction so that any iron imbedded in it is easily corroded.

c) LIME 🗀2

Artificial origin

Lime is obtained through the decomposition of natural stone material *(photo 2)*: limestone (calcareous deposits of calcium carbonate $CaCO_3$).

If limestone is heated at ~900 °C, it decomposes into calcium oxide (CaO) which, when slaked with water, forms hydrated lime $Ca(OH)_2$.


2. Limestone stockpile

Lime is a general term which includes the various chemical and physical forms of

Quicklime *Hydrated lime* *Hydraulic lime*

Quicklime (calcium oxide) is obtained by heating limestone, which is composed essentially of calcium carbonate, in a suitable kiln at 850 ~900 °C.

$$\text{Limestone} \xrightarrow{850 \sim 900\ ^{\circ}\text{C}} \text{Quicklime}^{⑩} \quad + \quad \text{gas CO}_2 \nearrow$$

$$\underset{\text{calcium carbonate}}{\text{CaCO}_3} \longrightarrow \underset{\text{calcium oxide}}{\text{CaO}} \quad + \quad \underset{\text{carbon dioxide}}{\text{CO}_2}$$

~**12** kg of charcoal are necessary to decompose *(burn)* **100** kg of limestone, from which **56** kg of quicklime are obtained.

The use of lime for building has a very ancient history⑪, and so the type of kiln used to produce quicklime has become more and more refined, improving with the building tradition and developing technology.

Today *rotary kilns*, *(photo 3)* which allow continuous production of quicklime are widely used, but more traditional kilns such as *flare kilns (photo 4)* and *open* or *batch kilns (photo 5)* are still quite common. 🗀3

Some problems still arise when using traditional kilns, as they do not generate the required heat uniformly within the whole mass of limestone


3. Rotary kiln


4. Flare kiln


5. Batch kiln

⑨ Mohs scale 2

⑩ Due to the high reactivity of quicklime this product is an irritant and special safety measures must be adopted when handling it (i.e. protect skin and eyes from accidental contact).

⑪ The earliest use of lime dates back to 1700 B.C. in Mycenaean and Minoan civilizations; in Egypt, it was adopted much later in the Ptolemaic period (300 B.C.)

and part of the material may not burn especially if the stones are too large. On the other hand, overburned limestone produce nodules of sintered quicklime that react very slowly with water. They may hydrate at a later stage causing the mortar to expand and crack. In the past these problems were solved by sieving the slaked lime.
Slaking is the process of adding water to quicklime to obtain lime putty *(photo 6)*:

$$\underset{\text{quicklime}}{CaO} + \underset{\text{excess water}}{H_2O} \longrightarrow \underset{\text{slaked lime}}{Ca(OH)_2} + \text{heat}$$

This reaction also creates heat and must be carried out with care. Like quicklime, slaked lime is also caustic and strict safety precautions must be taken when handling it.

Lime putty is slaked quicklime stored in a pit *(photo 7)* and covered with an excess of water. Longer slaking encourages the formation of a soft, greasy mass and improves the plasticity and workability of the lime paste.

Most of the problems relating to inappropriate lime slaking procedures are linked to insufficient hydration and lumps of unslaked lime which can have a negative effect on the performance of the material when applied.

Slaking problems also arise if the original limestone, used to produce quicklime⑫, contains more than 5% magnesium carbonate ($MgCO_3$) as an impurity⑬ . This leads to the formation, together with the calcium oxide (CaO), of magnesium oxide (MgO) which requires much longer to pass to the hydrated form $Mg(OH)_2$. The latter has a reduced capacity to develop into a greasy mass.

⑫ *It can be high-calcium, magnesium or dolomitic depending on the type of limestone used.*

⑬ *Good lime can be produced from magnesian limestone if the material is well understood and enough time is allowed for slaking.*

⑭ *Portlandite.*

6. Slaking lime

Vitruvius recommends storing the lime in a pit for at least two years and this is still considered the accepted method to follow when working in conservation:

aged lime putty → *growth of flat lime crystals*⑭

Hydrated lime $Ca(OH)_2$ is a dry powder obtained by treating quicklime (CaO) with enough water to combine chemically to form calcium hydroxide.

$$\underset{\text{quicklime}}{CaO} + \underset{\text{right amount of water}}{H_2O} \longrightarrow \underset{\text{hydrated lime}}{Ca(OH)_2}$$

In this process the dry calcium hydroxide powder is formed.

Limewash is obtained by adding a large amount of water to slaked quicklime or hydrated lime and is used as a paint-like coating.

Setting process

Lime sets by a process called carbonation.
Slaked lime is also called *air-setting* lime due to its hardening process.
The hardening of slaked lime takes place by reaction with carbon dioxide (CO_2) from the air and evaporation of water.

$$\underset{\text{hydrated lime}}{Ca(OH)_2} + \underset{\text{from air}}{CO_2} \longrightarrow \underset{\text{hardening}}{CaCO_3} + H_2O$$

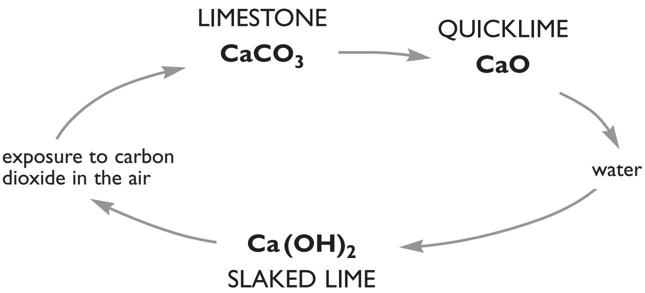
[a]

The *carbonation process* is rather delicate and varies according to the water evaporation rate and the presence of CO_2. The pore structure as well as the thickness of the mortar play an important role. 🗀4

7. Lime putty pits

In a lime mortar, hydrated lime is present during the setting process both in the form of solid particles and as a saturated solution. The carbon dioxide (CO_2) from the air reacts directly and exclusively with the saturated solution of calcium hydroxide $Ca(OH)_2$, working gradually from the exposed surface towards the internal layers and forming a thin crystalline surface layer of calcium carbonate ($CaCO_3$) .
The subsequent shrinkage due to the evaporation of the mixing water normally leads to the formation of microfractures providing access routes to the carbon dioxide from the air and consequently restarting the cycle. As long as there is evaporation of water, carbonation takes place⑮ and the lime mortar becomes harder and harder as carbonation progresses gradually towards the inner layers. 🗀5

The lime cycle



Use of pozzolana or other "pozzolanic" materials

When hydrated lime is used in combination with volcanic earth (i.e. pozzolana) a different setting process takes place:

pozzolana⑯ contains a certain amount of silica (SiO_2) and alumina compounds (Al_2O_3) in a reactive state (glass). These react with calcium hydroxide and water to produce new compounds: **calcium silicate hydrate** and **calcium aluminate hydrate** which are responsible for the chemical setting of this type of mortar. 🗀6

$$Ca(OH)_2 + H_2O + \text{pozzolana} \longrightarrow CSH + CAH$$

where:

CSH stands for calcium silicate hydrate
CAH stands for calcium alluminate hydrate⑰
The speed with which this reaction occurs is certainly greater than that of the carbonation process when hydrated lime is mixed with inert sand (calcite, quartz, rock fragments, etc.). That is why a pozzolanic mortar hardens more rapidly. This process of hardening defined as hydraulic in principle⑱ does not require the presence of air and therefore of CO_2.

The capacity of lime-based mortars and pozzolana to harden within a formwork with scarcely any contact with the air even under extremely wet conditions was well known to the Romans. It was in fact the discovery of the special properties of aggregates such as volcanic earth (pozzolana), ground tiles or pumice⑲ that permitted them to construct hydraulic works.

slaked lime + pozzolana + cleaved tuff stone = Roman concrete

Reactive aggregates coming from other geographic areas such as trass (from the Rhine region), volcanic earth (from Santorino in the Aegean), gaize (from France) containing silica (SiO_2) and alumina

---

⑮ *It must be emphasized that the carbonation reaction frees a water molecule that considerably aids the solubilization of further calcium hydroxide which is gradually exposed to the action of the CO_2.*

⑯ *The name derives from the town of Pozzuoli, near Naples.*

⑰ *CSH and CAH are cement chemistry abbreviations for more complex formulas.*

⑱ *The reaction between lime and alumino silicates does not exclude the simultaneous carbonation process as in the reaction [a] p.6*

⑲ *A light-coloured cellular glassy rock of volcanic origin which is highly porous.*

(Al_2O_3) in a reactive form are classified as hydraulic aggregates or pozzolanic additives. These are still in use today though modern technology also uses silica fumes and blast furnace slag from industrial processes. 🗀7

D) HYDRAULIC LIME

Hydraulic lime is a dry product obtained by burning limestone containing silica and alumina (marl●) at a temperature above 900 °C.

Origin

As a product obtained through the transformation of another, its origin can be classified as *artificial*, but if hydraulic limes are made from limestone containing natural clay minerals (e.g. attapulgite, kaolinite, montmorillonite) in varying quantities, they are commonly known as *natural hydraulic limes*.

It was already known in the 16th century that impure limestone from some quarries would produce quicklime, which when mixed with water, hardened quite rapidly●. It was in 1756, however, that John Smeaton, experimenting with lime and additives obtained a new lime by burning limestone containing about 11% clay impurities.

In 1796, Parker obtained a hydraulic lime, patented as Roman cement, produced by heating limestone with a high clay impurity content at ~1100 °C.

Only later, in 1818, did Vicat● first demonstrate the possibility of producing hydraulic limes **"artificially"** by burning limestone with clay added purposely to improve the hydraulic performance of the final product.

Hydraulic lime production is the result of complex thermal and chemical processes 🗀8 with the direct formation in the kiln of calcium silicates and aluminates as shown below, in simplified steps that take place at around 500 °C, 850 °C and 1000 °C.

Thermal decomposition of the clay material starts when the limestone and clay mixture is heated gradually up to 500 °C:

$$\text{CLAY} \xrightarrow[500\ °\text{C}]{} \underset{SiO_2}{\text{SILICA}} + \underset{Al_2O_3}{\text{ALUMINA}} + H_2O$$

Limestone starts to decompose at around 850 °C:

$$\text{LIMESTONE} \xrightarrow[850\ °\text{C}]{} \text{QUICKLIME} + CO_2$$

At 1000°C

$$\begin{aligned} &\text{QUICKLIME} + \text{SILICA} \longrightarrow \textit{di-calcium silicates} \\ &\text{QUICKLIME} + \text{ALUMINA} \longrightarrow \textit{calcium aluminates} \end{aligned}$$

In cement chemistry the above-mentioned compounds are often represented in an abbreviated form:

CS for calcium silicates and **CA** for calcium aluminates.

Limestone Clay impurities	
Kiln 1000 ÷ 1100 °C	
calcium oxide	(CaO)
di-calcium silicate	(C_2S)
calcium aluminate	(CA)

● *A sedimentary rock consisting mainly of a mixture of clay and calcium carbonate in varying proportions.*

● *Palladio mentions this limestone.*

● *J.L.Vicat, Recherches experimentales sur les chaux hydrauliques, les bétons et les mortier ordinaries, 1818.*

Setting process

The setting process, in this case, is due to the hydration of both calcium silicate and calcium aluminate to form a network of fibrous crystals of calcium silicate hydrate **CSH** and calcium aluminate hydrate **CAH** which are mainly responsible for the hardening (without excluding the carbonation of the calcium hydroxide formed by the hydration of the existing CaO).

Based on the work carried out by Vicat in 1837, varying degrees of setting and strength are usually defined as:

Feebly hydraulic lime (produced from limestone containing under 12% clay)

Moderately hydraulic lime (produced from limestone containing 12% to 18% clay)

Eminently hydraulic lime (produced from limestone containing 18% to 25% clay). [9]

E) PORTLAND CEMENT

A hydraulic cement produced by pulverizing a clinker obtained by firing clay and limestone at temperatures above 1400 °C. It consists essentially of hydraulic calcium silicates and aluminates, and contains a small amount of calcium sulphate added to reduce the setting rate. [10]

Portland cement has only been briefly mentioned in this volume as it is considered unsuitable for repairs in historic buildings and monuments. It is almost incompatible with old masonry, its main disadvantages being its high mechanical resistance, its soluble salts content and its low porosity .

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- Designation: C 5-79 (reappr. 1992). Standard specification for quicklime for structural purposes
- Designation: C 51-90. Standard terminology relating to lime and limestone
- Designation: C 110-95. Standard test methods for physical testing of quicklime, hydrated lime and limestone
- Designation: C 141-85 (reappr. 1994). Standard specification for hydraulic hydrated lime for structural purposes

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- NORMAL 36/92: Glossario per l'edilizia storica nei trattati dal XV al XIX secolo

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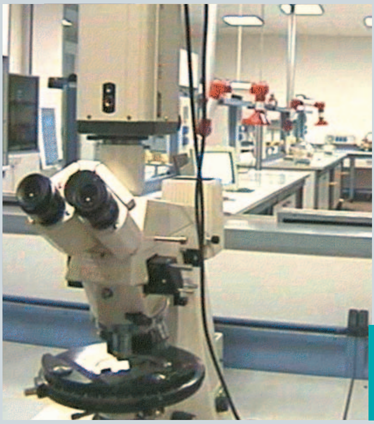
CONSERVATION OF ARCHITECTURAL HERITAGE,
HISTORIC STRUCTURES AND MATERIALS

Colour

Specification and measurement



COLOUR

ARC
LABORATORY HANDBOOK

VOLUME 5/99

Andrea Urland

The ICCROM ARC Laboratory Handbook is intended to assist professionals working in the field of conservation of architectural heritage and historic structures. It has been prepared mainly for architects and engineers, but may also be relevant for conservator-restorers or archaeologists.
It aims to:

- ***offer an overview of each problem area combined with laboratory practicals and case studies;***
- ***describe some of the most widely used practices and illustrate the various approaches to the analysis of materials and their deterioration;***
- ***facilitate interdisciplinary teamwork among scientists and other professionals involved in the conservation process.***

The Handbook has evolved from lecture and laboratory handouts that have been developed for the ICCROM training programmes. It has been devised within the framework of the current courses, principally the International Refresher Course on Conservation of Architectural Heritage and Historic Structures (ARC).

The general layout of each volume is as follows: introductory information, explanations of scientific terminology, the most common problems met, types of analysis, laboratory tests, case studies and bibliography.

The concept behind the Handbook is modular and it has been purposely structured as a series of independent volumes to allow:

- ***authors** to periodically update the texts;*
- ***users** to work selectively with the volume relating to the particular problem they are facing*
- ***new volumes** to be gradually added in line with developing needs.*

1998 - 99 volumes:
*(1) Introduction, (2) Porosity, (3) Salts, (4) Binders, **(5) Colour specification and measurement***

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CONSERVATION OF ARCHITECTURAL HERITAGE,
HISTORIC STRUCTURES AND MATERIALS

ARC
Laboratory Handbook

Colour
specification
and measurement

Andrea Urland

ICCROM

Rome, 1999

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① : Footnotes
🗁 : Bibliographic references

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COLOUR

1 INTRODUCTION

In recent years, the use of applied colour science in conservation and restoration practice has steadily increased.

In particular, colour specification and measurement have become essential tools for interdisciplinary teams of professionals dealing with architecture and works of art. When conventional methods of visual colour assessment are combined with instrumental methods, visual and aesthetic judgements are enriched with physical data that complement the capacities of the experienced eye.

Among the main fields of application of colour specification and measurement are:

- Survey and documentation:
  architectural and decorative surfaces, stratigraphy or chromo-chronology.
  Visual and instrumental methods
- Monitoring:
  colour changes as an indicator of alterations, such as natural ageing due to environmental influences, effects and performance of treatments over time (e.g., assessment of light-induced fading, cleaning or protective treatments exposed to atmospheric pollution and climatic risk factors).
  Mainly instrumental methods
- Data banks and reference archives:
  reference colour measurements for monitoring future changes, as lasting records of historic colour schemes, surfaces before cleaning or treatment.
  Visual and instrumental methods
- Colour schemes, urban colour plans:
  environmental colour assessment, restoration of historic colour schemes.
  Mainly visual methods

Other examples:

Study of painting techniques (*Mainly instrumental methods*), Study of colour scales of traditional pigments for external painting 🗀1 (*Mainly visual methods*), Study of variations of the perceived colour of buildings depending on the observation situation. 🗀2 🗀3 (*Mainly visual methods*)

This Volume outlines basic concepts and information helpful for the application of colour science, colour specification and measurement to conservation and restoration practice. Some of the most commonly used systems and techniques are explained and illustrated by examples and a case study.

Further practical information applied to conservation and restoration of architectural surface finishes will eventually be covered in a separate volume.

1.1 Colour concepts

The definition of colour still remains a subject of debate among colour scientists.

There are basically two schools of thought:

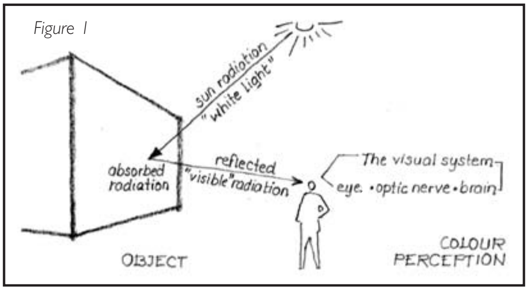
- The first claims to explain colour "objectively" as a physical phenomenon, i.e., electromagnetic waves. According to this interpretation,
  Colour is physics
- The second claims to explain colour "subjectively" as a response to a physical stimulus①; the stimulus itself is not considered the subject of study. According to this interpretation,
  Colour is psychology

physical stimulus (electromagnetic radiation / light②) ---------→ *sensation / perception* (colour)

The relation between the physical stimulus (radiation) and the sensation (colour) is not direct. A one-dimensional change in the radiant flux may cause a multi-dimensional change in the colour perceived.

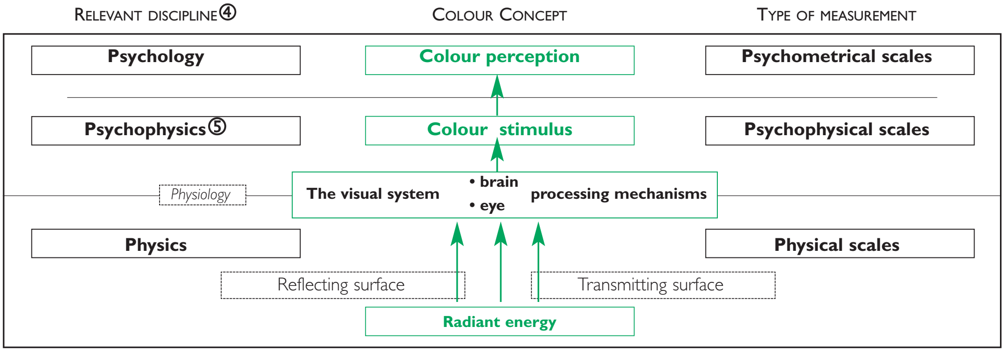
① *The physical (colour) stimulus is an electromagnetic radiation entering the eye and triggering a sensation of colour, either chromatic or achromatic (Commission Internationale de l'Eclairage, CIE, 1987)*

② *The word "light" has been used for the physical stimulus for a long time. Reviewers of lighting vocabulary of the CIE are reaching agreement to adopt the more correct wording "electromagnetic radiation," which should replace the current usage. The wording "visible radiation" will most probably remain, although considered inappropriate as we cannot see radiations. (O. Da Pos)*



This volume deals with *surface colours,*③ also referred to as opaque object colours.

An overview of colour concepts (based on similar representations 🗀4) is given in the diagram below, which should be read from the bottom up.



Respectively, the corresponding terminology 🗀5 is:

PHYSICS	PSYCHOPHYSICS		PSYCHOLOGY	
(Radiant energy)	(Stimulus)		(Colour perception)	
Wavelength	Dominant wavelength	Chromaticity	Hue	Chromaticness
Wavelength-composition	Purity		Saturation	
Intensity	Luminance (light sources)		Brightness	
	Reflectance (objects)		Lightness	

1.2 BASIC TERMINOLOGY⑥ AND ACRONYMS

This section provides generally accepted definitions; the terms and related concepts are expained gradually in the course of the text that follows.

HUE: attribute of a visual sensation according to which an area appears to be similar to one of the perceived colours red, yellow, green and blue, or to a combination of two of them. (CIE, 1987)⑦

SATURATION: colourfulness of an area judged in proportion to its brightness. (CIE, 1987) It is the attribute of a colour perception determining the degree of its difference from the achromatic colour perception most resembling it.

BRIGHTNESS; LUMINOSITY: attribute of a visual sensation according to which an area appears to emit more or less light.

③ Colour perceived as belonging to a surface from which the light appears to be diffusely reflected or radiated. (CIE, 1987) Object colour is defined as the colour perceived as belonging to the object. It is not the property of the physical object itself, but rather depends on the combination of its reflecting or absorbing power and its illumination as assessed by an observer.

④ Colour can be studied from the perspective of several disciplines, mainly chemistry, physics, physiology, psychology and aesthetics.

⑤ Psychophysics is a branch of psychology that studies the quantitative relations between psychological events and physical events, or more specifically between stimuli and the corresponding sensations. 🗀6

⑥ Terminology is currently under revision by the CIE.

⑦ CIE 1987 indicates definitions of colour terms based on the International Lighting Vocabulary. 🗀7

PSYCHOLOGY

LIGHTNESS: the brightness of an area judged relative to the brightness of a similarly illuminated area that appears to be white or highly transmitting. (CIE,1987)

CHROMATICNESS; colourfulness: attribute of a visual sensation according to which the perceived colour of an area appears to be more or less chromatic. (Formerly chromaticness denoted the combined perceptions of hue and saturation, i.e., the perceptual correlate of chromaticity). (CIE, 1987)

CHROMA: colourfulness of an area judged in proportion to the brightness of a similarly illuminated area that appears white or highly transmitting.

PSYCHOPHYSICS

CHROMATICITY: property of a colour stimulus defined by its chromaticity coordinates, or by its dominant or complementary wavelength and purity taken together. (CIE, 1987)

LUMINANCE/REFLECTANCE: a measurable physical quantity (intensity of radiation in a given direction) subjectively appreciated as brightness.

DOMINANT WAVELENGTH: wavelength of the monochromatic stimulus that, when additively mixed in suitable proportions with the specified achromatic stimulus, matches the colour stimulus considered. In the case of purple stimuli, the dominant wavelength is replaced by the complementary wavelength. (CIE, 1987)

COMPLEMENTARY WAVELENGTH: wavelength of the monochromatic stimulus (spectrum colour) that when additively mixed with the given colour in suitable proportions matches with a specified achromatic colour.

EXCITATION PURITY: simply stated, it can be defined as an expression of the degree of complexity of a colour stimulus with respect to its spectral composition. Monochromatic radiation consisting of only one wavelength has the highest spectral purity. 🗀8

CIE: *Commission Internationale de l'Eclairage* (International Committee on Illumination).
ASTM: American Society for Testing and Materials
ISO: International Standards Organization
OSA/UCS: Optical Society of America Uniform Colour Scales
NCS: Natural Colour System

⑧ *The sensation of white corresponds to a radiation having a continuous spectrum containing all the components of various wavelengths in equal intensity.*

⑨ *Spectrum colour is the colour perceived when the retina is stimulated by a monochromatic radiation of a single frequency wavelength.*

2 BASIC PRINCIPLES

2.1 BASIC PHYSICS

There is no colour without an observer, just as there is no colour without light. *Light* is the perceptual correlate of a form of radiant energy, which acts as a stimulus to the eyes and causes the observer to see. 🗀9 It comprises only a small portion of the total electromagnetic spectrum of radiant energy *(Figure 2)*. We perceive noon sunlight as white light, a neutral reference for normal colour vision. Sun radiation is composed of many wavelengths; a beam of white light (an equal energy beam)⑧ passed through a prism will form a continuous *spectrum of wavelengths*⑨ from about 700 nm (corresponding to red) to about 400 nm (corresponding to violet).

When white light strikes an *opaque surface*, some wavelengths are absorbed, others reflected. As a result we perceive the colour of an object.

Perception of white light can also be triggered by mixtures of *long* (*l*), *medium* (*m*) and *short* (*s*) wavelengths in suitable proportions. These radiations are called *additive primaries*, because in appropriate mixtures they can match lights of any hue.

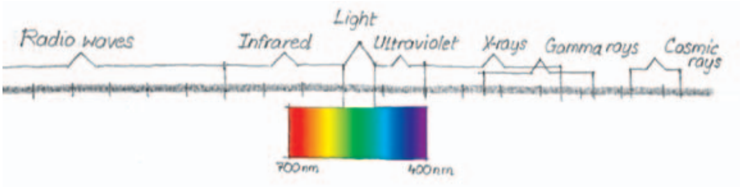
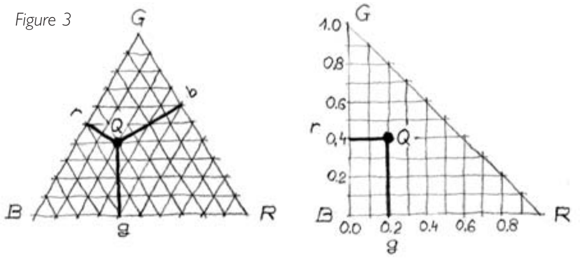


Figure 2

THE ELECTROMAGNETIC SPECTRUM – *schematic drawing with image of "visible" radiation*

Figure 3



THE MAXWELL TRIANGLE

Transformed to rectangular coordinates

The Maxwell triangle⑩ shows the mixture of additive primaries graphically. The colour corresponding to any mixture of the primaries can be represented by a point in the triangle. The point at the centre of the triangle represents white. The *chromaticity* of a particular primary mixture can be expressed by the sum: $l + m + s = 100\%$, often quoted as r (red) + b (blue) + g (green) = 100% because of the colours perceived when each single primary stimulates the eye. This means that the percentages of only two primaries are sufficient to define chromaticity, which corresponds in a general way to the colour of a light without regard to its *brightness.*

2.2 COLOUR VISION

Vision is one of our five senses, and has both practical and aesthetic functions.

It is the response to a *physical stimulus* acting on our *visual system*: the eyes, optic nerve, brain. We see and perceive the world around us through colour (chromatic and achromatic⑪). Through colour differences we are able to perceive forms.

Under optimum conditions, an average person with normal colour vision distinguishes about 1000 *hues* and about 200 *saturation* degrees in certain hues. The number of distinguishable colours is estimated as 7.5 to 10 million.

⑩ *James Clark Maxwell first used this triangle. Transformed to rectangular coordinates, it later became the basis for the chromaticity diagram (see page 13).*

⑪ *Chromatic colour perception is defined as having a hue; achromatic colour does not possess a hue.*

⑫ *The example of metameric pairs: two objects with different spectral reflectances match under one illumination, but may not do so under a second illumination.*

2.3 COLOUR PERCEPTION

Studying visual perception means explaining why we see and how we see.

At times, the same perception can be triggered by physically different stimuli or a physically constant stimulus can correspond to various perceptions in different situations. The relationship between physical stimulus and colour sensation is not constant.

A number of scientists have long stressed the need to distinguish between colours as visual qualities and the physical conditions or reasons for these phenomena, maintaining that the study of physics is unlikely to provide any information about the structure of the world of perception (also called *phenomenal* world), as one stimulus can give rise to two or more fundamentally different colour perceptions.⑫ 🗀**10**

Some of the physiological factors that influence the perception of colour are:

ADAPTATION: the adjustment of the visual system to the intensity or quality of the light stimulus. When the eye is exposed to a given illumination level for sufficient time, it accepts this level as normal and all other intensities are processed relative to it.

COLOUR CONSTANCY: a process that tends to make the colours of objects look the same despite relatively great changes in the stimulations.

COLOUR CONTRASTS: e.g., simultaneous colour contrast: the tendency of the eye to intensify the difference between different colours placed next to each other.

MEMORY COLOUR: the colour perception that a familiar object under normal illumination would arouse in the judgement of the observer. 🗀11

AREA EFFECT: change in apparent colour caused by the size of the colour sample.

2.4 COLOUR APPEARANCE

Colour appearance means the colour that an object appears to be. Colours are in constant change and transformation.

A recently proposed system 🗀12 which helps to describe all the visual perceptions produced by light stimuli distinguishes:

- *spatial perceptions* (size, shape, location)
- *temporal changes in the intensity of light* (flicker, sparkle)
- *attributes of colour sensation* (brightness, hue and saturation)
- *cesia* ⑬ (includes glossiness, opacity, mattness, diffusivity, transparency, absorption, etc.).

⑬ *The term "cesia" is being used for that aspect of appearance which deals with the perceptions aroused by transformation in quantity and spatial distribution of the light that reaches the eye after being either partially absorbed and/or re-emitted by an object.* 🗀13 *Like colour, it is not an intrinsic property or attribute of materials and surfaces.*

⑭ *Colour space is a frame of reference in which a point representing a colour may be located in such a way that each of its attributes corresponds to a dimension in that space.* 🗀16

The apparent colour of an object depends on 🗀14:

1. THE LIGHT STRIKING THE OBJECT (= RADIATION, ITS SPECTRAL ENERGY DISTRIBUTION)
   The spectral distribution of a light source is its relative energy at each wavelength of the visible spectrum.
2. THE OBJECT ITSELF (ITS SPECTRAL REFLECTANCE)
   The spectral reflectance of an object is the fraction of the incident light reflected by it at each wavelength.
3. THE OBSERVER (HER/HIS SPECTRAL RESPONSE)
   An observer's spectral response is determined by his relative response to light at each wavelength. Assuming that the observer has normal colour vision, the ability to discriminate colours depends on training, experience, mental attitude, age, etc. Visual receptor response is governed by an individual's inherited and acquired capacities. 🗀15

In other words, various factors influence the observed colour of a surface: the spectral quality of the illumination, the direction of the illumination and of viewing, the distance of viewing, the surround/background, the nature of the light reflected from the surface, surface material, texture, surface area and the state of adaptation of the eyes of the observer.

3 COLOUR ORDER SYSTEMS

Colour order systems are systems for categorizing colours.

3.1 PURPOSE, FEATURES AND TYPES

PURPOSE AND FUNCTIONS

The existing colour order systems were developed for various purposes, mainly because of the practical need to *describe* colours accurately and to be able to *communicate* about them easily over long distances and periods of time. Colour order systems make it possible to:

- *identify, determine* a single colour, or
- *analyze and define the (aesthetic) relationship* among colours
- *choose, produce and control* colours unambiguously.

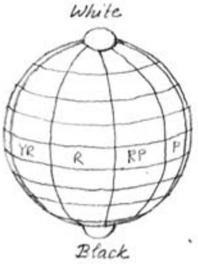
CHARACTERISTIC FEATURES

These systems organize all existing colours in a *3-dimensional colour order*. Their own *colour spaces,* ⑭ however, can be restricted, depending on the concepts of "colour" on which they are based:

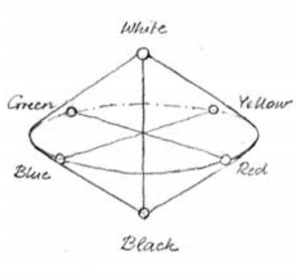
- colorant ⑮
- primary lights
- perceived colour – subjective visual sensation.

⑮ *Colorants are substances used to modify the colour of a material or an object; they mainly include pigments and dyes.*

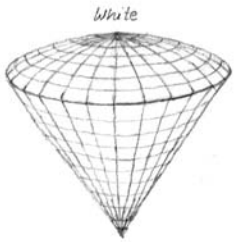
The 3-dimensional nature of the colour order as a framework is illustrated by a *color solid*, most often based on a sphere, a cylinder or a double cone. The systems sample the world of colour according to 3 basic *variables* or *colour attributes* that constitute the coordinate axes of the colour system.



Munsell (1905)



NCS



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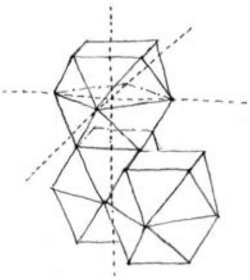

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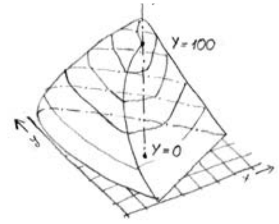


CIE (Rösch)

EXAMPLES OF COLOUR SOLIDS

(Adapted from Gerritsen and Derefeldt)

Further differences between colour order systems lie in the principles they are built on, the number of primary colours ⑯ used, the types of variables or attributes by which they describe colours, the spacing of colours, etc.

In order to be a useful tool, they must meet two main requirements: uniqueness of description and replicability.

Colour order systems can be exemplified in the form of colour atlases and other colour sample collections.

Type	**1**	**2**
Systems based on	Systematic variation of the amounts of colorants, or amounts of the primary radiations (in an additive colour mixture)	Colour appearance (systems described and classified according to perception)
Type of use	Useful for restricted application in printing, dyeing, television, illumination	For general use

TABLE 1 🗀18

TYPES

Recent studies 🗀17 divide colour systems into two major groups *(Table 1)*:

1. *Colour-stimulus systems*, also called psychophysical colour systems, are mainly centered on the characteristics of the stimuli suitably measured.
2. *Colour-appearance systems*, also called psychological or perceptive colour systems, are based on appearance parameters psychometrically measured.

TABLE 2 🗀19

3.3.a Descriptive systems		**3.3.b Equi-spaced systems**
NCS (as descriptive Method) ISCC-NBS ⑰	NCS colour atlas	Munsell DIN Coloroid OSA-UCS
Perceptively defined	Colorimetrically defined	

---

⑯ *Primary or basic colours are those from which all the other colours can be mixed, but which cannot themselves be mixed from other colours (e.g., for light: red, green, blue; for perception: yellow, red, blue, green, white, black).*

⑰ *Inter-Society Color Council and National Bureau of Standards = Method of Designating Colour and Dictionary of Color Names, 1939. This is a system of colour names, in which colour limits for each name were defined in Munsell terms.*

3.2 COLOUR-STIMULUS SYSTEMS

The CIE colorimetric system (1931) belongs to this first group. The 1976 CIELAB and CIELUV are widely used in science and industry as approximate colour appearance systems. They offer the possibility of unambiguous colour stimulus specification and colour difference measurements *(see page 15)*.

3.3 COLOUR-APPEARANCE SYSTEMS *(Table 2)*

Current colour appearance systems have been developed for surface colours. They follow the following principles 🗀20:

a. PERCEPTUAL COORDINATES OR SCALES: the description of colour appearance in relation to easily recognizable reference colours. Prevailing consensus is that of 6 reference colours. Colour samples are helpful, but not required. *(Descriptive systems)*.

b. UNIFORM OR EQUAL VISUAL SPACING ⑱ of colours according to the scales, where steps in colour notation should represent equal differences in appearance. These systems rely on description of colour appearance by physical colour samples, which are usually necessary for reference. *(Equi-spaced systems)*.

The following are examples of modern colour appearance systems that are among the most commonly used nationally or internationally:

- Munsell system (country of origin: USA)
- Natural Colour System (NCS) (Sweden)
- DIN-Farbsystem 6164 (*Deutsches Institut für Normung*, Germany)
- Optical Society of America Uniform Color Scales (OSA/UCS)
- Coloroid system (Hungary)

In many applications, the CIELAB and the CIELUV colour spaces are used as approximations to colour appearance systems.

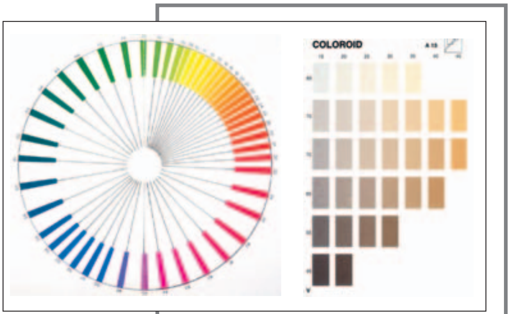
⑱ *Concept of perceptually uniform colour space: uniformity depends on the colour-difference perception ability of the human visual system. The scales of the colour space are defined using perception-threshold measurements.*

⑲ *Country of origin: Germany.*

3.4 COLOUR ATLASES

Colour atlases are physical exemplifications illustrating colour order systems in a systematic and quite complete form. The function and importance of atlases depends on the respective colour order system.

- *Descriptive colour systems*, by concept do not rely on atlases. If they are accompanied by an atlas, its samples show the appearance corresponding to perceptively defined notations. The colorimetric specifications serve mainly to ensure the reproducibility of the samples, they do not define the system itself. 🗀21
- The *equi-spaced systems* usually do rely on colour atlases.
- There are now also colour atlases (e.g., Eurocolor, RAL-system ⑲) based *directly on colorimetric coordinates*, illustrating the CIE colour space. 🗀22



Example of a hue circle and a section through the vertical axis of a colour solid (The Coloroid system exemplified by the Coloroid Atlas)

CHARACTERISTIC FEATURES

Atlases sample the system's colour space according to 3 basic (perceptual) colour attributes that constitute the coordinate axes of the colour system. These usually are the hue, the achromatic and the chromatic colour dimensions. The hue circle is visualized by horizontal sections of the colour solid, and the other two colour dimension ranges are represented in vertical sections through the vertical axis.

USE INSTRUCTIONS AND RESTRICTIONS

Each colour atlas provides guidance to proper use. Given the influence of the surrounding factors, the effects of illumination and the influence of the viewing conditions, various restrictions have to be taken into account when working with colour atlases:

- colour samples are to be viewed under conditions of standard illumination. The CIE recommends average daylight, represented by illuminant D_{65} or CIE illuminant C *(see page 14)*.
- colour samples are to be viewed against a homogeneous background – usually gray or white
- colour samples are to be illuminated and viewed at a certain angle.

A change in these conditions may cause a change in the sample's appearance. In colorimetrically defined colour systems and atlases, the definitions are valid only so long as the viewing conditions remain constant. Changes in appearance are, however, partly counteracted by the phenomenon of colour constancy.

3.5 GENERAL CONSIDERATIONS

Several countries have adopted specific colour order systems as national standards, e.g.:

Munsell: USA, Japan, Italy; *NCS:* Sweden, Norway, Spain; *Coloroid:* Hungary; *DIN:* Germany. Given the wide variety of established colour order systems, it has not been possible to issue a single international standard.

The advantages and disadvantages of a system's colour space structure and variables, density of sampling, etc., emerge in practical use and should therefore be tested in advance. It is important to choose the right system with regard to **the conditions and final aim of the work**.

4 COLOUR SPECIFICATION AND MEASUREMENT

4.1 COLOUR SPECIFICATION - GENERAL ASPECT AND METHODS

Colour specification is a description of colours, which varies in accuracy depending on the particular situation.

Object colours (surface colours) were first recorded by names, followed by more elaborate methods of designation. Although name identification is still widely practiced, it is of limited accuracy.

Knowledge of other more precise methods can therefore be very useful. An illustration of six levels of increasing accuracy is provided by Kenneth Kelly's *Universal Colour Language*: 🗀**23**

Level	Description / Method	Examples
1.	13 names (10 hues, 3 neutral)	Yellow
2.	29 names, including intermediate hue names	Reddish yellow
3.	267 names (colour name blocks of the ISCC-NBS)	Light reddish yellow
4.	About 1000 names (colour samples in the Munsell Book of Color)	Munsell notation 10 YR 6/4
5.	Interpolated Munsell notation (100,000 divisions of the colour solid)	9.5 YR 6.4/4.25
6.	CIE method, chromaticity coordinates x, y, Y	x=0.395, y=0.382, Y=35.6%

Colour measurement can be either *visual or instrumental*. For architectural surfaces and surface finishes it can be done *in situ* or in laboratories or studios if working with collected samples. In most measurement procedures, clear documentation of the position of the measurement points is important for future reference.

It is essential to bear in mind the actual purpose of measuring when choosing a certain method or level of accuracy. ⑳

⑳ Example: In visual assessment, the human eye might record colour differently than instrumental measurements (e.g., variations of colour within weathered samples, where the eye tends to exclude the dirt).

How to obtain accurate visual or instrumental measurements of colour appearance is still a largely unsolved problem of colour science, especially when dealing with complex scenes with a number of colours of different surface areas.

4.2 VISUAL COLOUR SPECIFICATION AND MEASUREMENT

Visual measurements are generally considered easier to carry out than instrumental ones. Although less precise, they give us information on the appearance of the colour, which instrumental measurements do not.

Visual colour asssessment – colour identification, description or designation – is done by observation, using the following types of methods:

4.2.1 METHODS WITHOUT REFERENCE SAMPLES

These methods refer to descriptive colour appearance systems as a conceptual tool that can be used without reference samples. Chromatic surveys of architecture or urban spaces can be performed this way using the NCS system, for example.

4.2.2 METHODS WITH COLOUR SAMPLES THROUGH VISUAL COMPARISON (COLOUR MATCHING)

Colour matching is specification of object colour by visual comparison to colours whose specification is known, looking for equality or the closest similarity.

It is a visual procedure performed to decide whether or not two colours differ perceptually. Colour matching can be used for determining whether the two colours are identical (not distinguishable under all three variables) or it can focus on one aspect of the two colours, judging whether, e.g., the hue, or the saturation is the same.

Colour matching is useful in both identification of colours and their reproduction. It is done by direct observation of the *test* and the *reference samples*; more rarely an instrument (visual colorimeter) is used to compare the samples.

a. USING SKETCHES

In practice, sketches with matching colours are often produced directly on site, using colour pencils and/or paints to reproduce the colour of the test sample.

b. USING REFERENCE SAMPLES

Another approach is to use various colour charts for quickly recording the colour of the test sample. These can be paint chips of various manufacturers, or the reference sample collections of colour order systems. In the first case there is generally no systematic ordering of the colours; this may not be important in the recording phase, but can be a major drawback as soon as any further study and communication are required. Therefore colour order systems, especially the standardized ones, are always preferable.

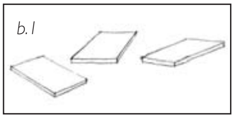
Tools:

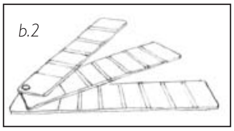
Reference sample collections are all lightweight and easily transported for field use. They can take the following forms:

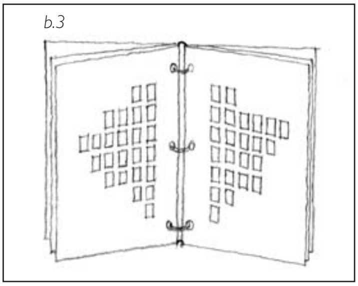
b.1 single paint chips
b.2 colour scales (colour samples of one-dimensional variation), indexes
b.3 atlases (collections of colour samples intended to represent a considerable fraction of all colours in a 3-dimensional variation).

Reference samples of the b.1 and b.2 type can be placed directly on the test sample surface for comparison.

In the case of colour atlases, b.3, there are two possibilities. Usually the reference samples are fixed, and visual comparison is made at a distance. *Masks* (white or gray) can be helpful to place on the reference samples in order to limit the area of comparison for finding the closest match. Some atlases have removable reference samples which permit the same use as b.1 and b.2, i.e., direct contact


b.1


b.2


b.3

between test and reference samples, which often facilitates making a judgement.

If the colours of the reference sample collection are spaced sufficiently closely, the nearest match can be found by direct visual comparison; if not, an intermediate value can be estimated by *visual interpolation*.

As a rather small number of specimens has to cover the range of all possible colours, it is of great importance to choose the most appropriate tool (system and its companion reference samples) to work with, as each system is built in a different way.

Criteria to consider for the choice of tools can be:

- density of reference sample spacing in the colour area of the range of test samples (for architectural surfaces and surface finishes, certain hue, saturation and lightness ranges prevail);
- relationship of the reference samples to standards and to colour order systems;
- appropriateness of the variables on which the system is built, evaluated in relation to the purpose of the work (intended data elaboration and interpretation possibilities);
- compatibility and comparability of the colour measurement data with other related studies;
- cost of the reference sample collection with regard to the character of the work, its continuity, context, conditions, etc.

Rules

Matching to a colour chart or reference sample must follow certain rules; in the case of atlases, these are precisely described, and sometimes there are separate standard methods to apply, e.g., ASTM Standard Method of specifying colour by the Munsell system.

Typical precautions are: lay the samples flat and view them directly from above; have the illumination fall on the samples at an angle of approximately 45 degrees, etc. The standard practice is to view specimens illuminated by daylight from a slightly overcast sky or the equivalent of this illumination.

Reference samples should be stored and used with care (avoid direct touching, etc.), as they are also subject to ageing.

4.3 INSTRUMENTAL COLOUR MEASUREMENT

Instrumental colour measurement consists of the analysis and description of colour directly by *colorimeters* or indirectly from data based on measurements using a *spectrophotometer*.

Instrumental measurement focuses on the physical stimulus, i.e., electromagnetic radiation (light) and is based on the CIE colour system.

Instrumental colour measurement has basically gone through three main **development phases**.

The first two phases were limited to two stimuli under identical conditions:
MATCHING: concerns whether or not two stimuli match each other;
DIFFERENCE: attempts to quantify colour differences;
APPEARANCE, the third phase, compares stimuli under different viewing conditions. The first models for predicting colour appearance ㉑ date to the early 1980s.

㉑ *Experimental research has shown that colorimetric matches do not necessarily produce a satisfactory visual match when the viewing conditions differ, i.e., colours having the same CIE coordinates need not appear identical if the material and the viewing conditions are not the same. For this reason, models that are capable of predicting the perceived change in the appearance under different viewing conditions are being developed and tested.*

4.3.1 COLORIMETRY AND SPECTROPHOTOMETRY

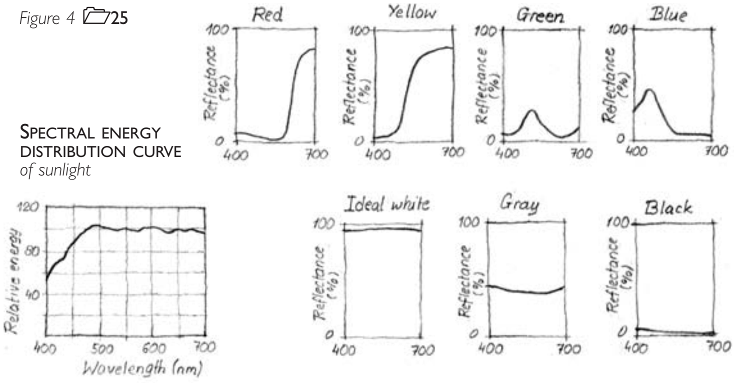
Spectrophotometry or "measurement of the spectrum" allows us to determine the relative way in which the total energy in a beam of light is divided among the wavelengths it contains.

The spectrophotometer breaks down the radiation reflected or transmitted by the measured object surface into its component wavelengths from short waves (about 400 nm) to long (about 700 nm). By a series of prisms, lenses and a mirror, a beam is directed at the object, wavelength by wavelength. The ray reflected from the object surface is then compared with the ray reflected from a virtually perfect diffusing surface㉒ in the spectrophotometer. 🗁**24** The differences in their relative reflectances across the spectrum are recorded and visualized as a curve *(examples in Figure 4)*. By computation the spectrophotometric curve can be translated into colorimetric terms, such as CIE, that can be plotted on a chromaticity diagram. The instruments are usually also capable of converting the measurements into the notations of some colour order system, such as the Munsell.

Colorimetry works with the three additive primaries, corresponding to the physiological aspects conditioning colour perception, mainly the trichromatic nature of the normal eye. Results measured are expressed as the quantities of these radiations reflected from the object surface (tristimulus specification of colours).

Colorimetric data allow further study and evaluation of colour characteristics and differences. They are indispensable in any production (such as colour atlases) where exact colour reproduction must be guaranteed.

Figure 4 🗁**25**



SPECTRAL ENERGY DISTRIBUTION CURVE *of sunlight*

SPECTRAL REFLECTANCE *of opaque materials of different colours*

4.3.2 THE CIE SYSTEM

CIE XYZ, CIE (x, y, Y)

The CIE colorimetric system was defined in 1931 as a standard system, enabling the specification of all colours as points within a 3-dimensional colour space. It is a system for colour stimulus specification. The spacing of the colour stimuli is not uniform, and as the system is not based on perceptual scaling of colours, it does not give appearance characteristics of colours. 🗁**26** There are three defined real primaries: long waves (corresponding to a red perception, R), medium waves (corresponding to a green perception, G), short waves (corresponding to a blue perception, B), and three imaginary *mathematical primaries* X, Y, Z, also called *tristimulus values*.㉓

The main use of the system is in science and industry.

CIE Chromaticity diagram㉔

The chromaticity diagram is based on the method of colour specification known as the CIE Standard Observer㉕ and Coordinate System recommended by the CIE. 🗁**27** It shows the colours of the

---

㉒ *White, such as magnesium oxide.*

㉓ *Tristimulus values are the amounts of the three reference lights (matching stimuli, primary colours) required to give a match with the test colour (light) by additive mixture.*

㉔ *Chromaticity diagram: a plane diagram in which points specified by chromaticity coordinates represent the chromaticness of colour stimuli. (CIE, 1987)*

㉕ *The Standard Observer is a theoretical average of human observers with a visual response mechanism possessing the colorimetric properties defined by the CIE and a known spectral response.*

spectrum and all their possible mixtures. Pure spectrum colours with the corresponding wavelengths are located along the partly curved boundary line *(spectrum locus)*. Violet (approx. 400 nm) and red (approx. 700 nm) are connected by a straight line, representing their mixture into purple, which does not appear in the spectrum.

Any point within the boundary line can be located by *chromaticity coordinates*,㉖ x and y.

The chromaticity diagram is based on the Maxwell triangle used to show graphically the mixture of additive primaries. The x values on the horizontal scale and the y values on the vertical scale represent the proportions of the theoretical X (red) and Y (green) primaries㉗ respectively required to produce all possible colours; the partly curved boundary line represents the proportions of primaries needed to match all single wavelengths. The colour of any light can be fully specified by its chromaticity coordinates x, y and its *luminance/reflectance* Y, i.e., if we know both the proportion of the three primaries in the matching mixture and its luminous intensity.

The CIE chromaticity diagram indicates the chromaticity of a light without regard to its luminance, Y. A 3-dimensional solid showing the limits within which all real colours lie when viewed in daylight can be constructed, having for its base the chromaticity diagram with the luminance indicated as a vertical dimension *(page 8)*. The diagram provides no impression of the colour appearance of the object measured; nor is there a regular series of reference samples to represent the system.

From the chromaticity coordinates x and y, the *dominant wavelength* can be computed, as well as the *purity*.㉘ These, together with Y (luminance/reflectance) are referred to as *Helmholtz coordinates* *(Figure 5)*.

Standard light sources are defined for the CIE system, with their temperature correlates in Kelvin degrees. Most often used are:

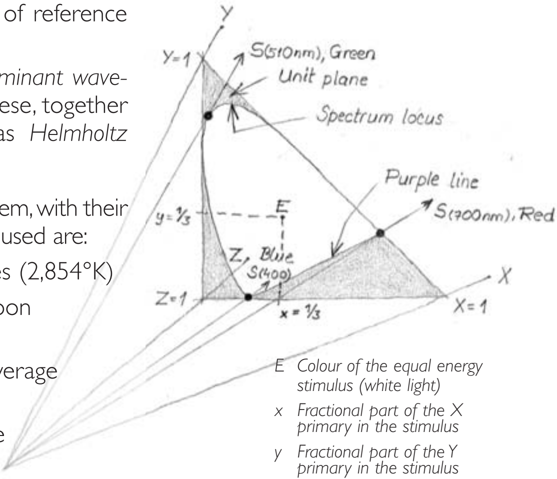
A, which represents common tungsten light sources (2,854°K)

B, with a spectral distribution that approximates noon sunlight (4,870°K)

C, with a spectral distribution that approximates average daylight (sunlight and skylight, 6,740°K)

D_{65}: spectral distribution that approximates average daylight㉙ (6,500°K).

TRISTIMULUS COLOUR SPACE *(based on the CIE 1931 primaries X,Y,Z) and*
THE CHROMATICITY DIAGRAM.
(Adapted from Judd, Wyszecki)

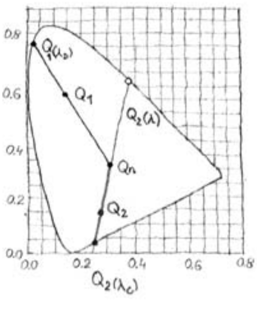


E *Colour of the equal energy stimulus (white light)*

x *Fractional part of the X primary in the stimulus*

y *Fractional part of the Y primary in the stimulus*

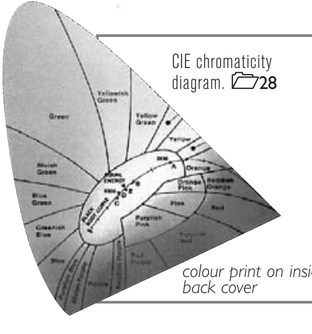
Figure 5 - DEFINING THE DOMINANT WAVELENGTH AND THE EXCITATION PURITY *on the CIE 1931 Chromaticity diagram* 🗀**29**



Q_1, Q_2	*given stimulus (colour Q_1, Q_2)*
$Q_1(\lambda_D)$	*dominant wavelength corresponding to the given stimulus*
$Q_2(\lambda_C)$	*complementary wavelength (in case of purple colours)*
Qn	*achromatic stimulus (white light)*

$$\text{Excitation purity } p_e = \underset{\text{for stimulus } Q_1}{\frac{|\,Q_nQ_1\,|}{|\,Q_nQ_{1(\lambda_D)}\,|}}\ \text{, or } p_e = \underset{\text{for stimulus } Q_2}{\frac{|\,Q_nQ_2\,|}{|\,Q_nQ_{2(\lambda_C)}\,|}}$$

$0 < p_e \leq 1$;
$p_e = 0$ for achromatic stimuli



CIE chromaticity diagram. 🗀**28**

colour print on inside back cover

㉖ *Ratio of each of a set of three tristimulus values to their sum: (CIE, 1987)*

$$x = \frac{X}{X+Y+Z} \quad y = \frac{Y}{X+Y+Z} \quad z = \frac{Z}{X+Y+Z}$$

㉗ ***Of course in the additive mixture there is also the theoretical Z primary in the z proportion.***

㉘ ***Monochromatic radiation consisting of only one wavelength has the highest spectral purity and is located at the border of the diagram. The achromatic mixture has the lowest purity and is located at about the centre of the diagram: its actual place depends on the illuminant, being exactly at the centre for the illuminant EE (equal energy source).***

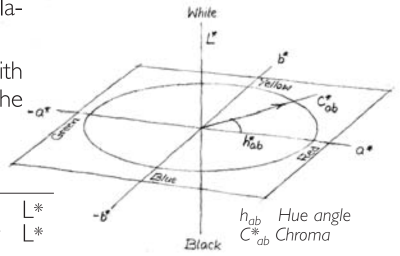
㉙ ***Illuminant D_{65} is based on numerous spectrophotometric measurements of daylight at different locations in the USA, Canada and Great Britain.*** 🗀**30** ***The Munsell, NCS, DIN and OSA/UCS systems are based on average daylight, represented by D_{65} or CIE illuminant C.***

CIELAB, CIELUV

Responding to a generally felt need, efforts have been made since 1931 to make the spacing of colour stimuli on the CIE (x,y) chromaticity diagram more uniform with the purpose of computing colour differences corresponding to perceived differences, and to relate the system more closely to colour appearance. The *CIE 1976 uniform colour spaces* - CIELUV and CIELAB - were introduced as an improved coordinate system, based on mathematical transformations of the CIE 1931. 🗁**31**

Both systems were developed for the three main purposes of tristimulus specification of colour: to provide a means for recording colour stimuli, as a medium for specifying colours and colour tolerances, and for making it possible to quantify and visualize the relationships of colours.

In the CIELAB colour space the L*,a*,b* coordinates correlate with lightness, redness-greenness, and yellowness-blueness, even though the chromatic axes only approximately correspond to the unique hues.



h_{ab} Hue angle
C^*_{ab} Chroma

CIE 1931, 1964			
Tristimulus values	X	Y	Z
Chromaticity coordinates	x	y	Y
Helmholtz coordinates	λ_D	p_e	Y

CIELAB 1976			
Cartesian coordinates	a*	b*	L*
Cylindrical coordinates	H°	C*	L*

4.4 COLOUR DIFFERENCES

The calculation of colour differences is necessary for quantification of colour changes (e.g., for monitoring, in connection with cleaning of surfaces). Changes in colour are precisely and objectively recorded and analyzed. These measurements allow one to quantify and analyze which parameters or colour variables and characteristics have changed and to what extent (e.g., in cleaning, the exact deviations in hue, saturation and lightness, comparing the data of before and after the process). Interpretation of the data leading to the explanation of observed phenomena is important.
Depending on the precise needs and purpose of measuring colour differences, these can be quantified for one or more colour variables. Mostly instrumental methods are used.

Instrumental measurement of colour differences is practical especially for subtle colour differences and for cases when measurement (as in monitoring) of colour changes must be performed over a longer period of time and by various people.

Colorimetric practice often makes use of the CIELAB colour spaces for the measurement of colour differences; a colour difference is computed in a simple way as the Euclidean distance between two points representing the colour stimuli in the colour space. Therefore it is expressed by a single number independently of where the two colours are located in the colour space. The difference of two stimuli (L^*_1, a^*_1, b^*_1) and (L^*_2, a^*_2, b^*_2) can be calculated using the formula 🗁**32**:

$$\Delta E^*_{ab} = [(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2]^{1/2} =$$

$=[(\Delta L^*)^2 + (\Delta C^*_{ab})^2 + (\Delta H^*_{ab})^2]^{1/2}$, in cylindric coordinates (L^*, C^*_{ab}, H_{ab})

In CIE (x,y,Y) the colour differences are calculated as differences in the chromaticity coordinates, and the difference in luminance.

Visual measurements rely on colour appearance systems to measure colour differences. They are useful when judging perceived colour differences on larger surface areas, at certain distances, and of colours in the context of neighbouring colours. They are particularly useful for the analysis of phenomena connected to the chromatic characteristics of a site, the urban and natural environment, traditions of colour combinations, etc.
Given the notations of two colours, the differences in variables can be expressed in figures and/or graphically using the tools described in the section on visual colour measurement.

Perceived or instrumentally measured colour differences must be evaluated and elaborated and be judged acceptable or not, according to criteria defined with regard to the problem under study.

PRACTICAL 1

VISUAL COLOUR MEASUREMENT

Aim

Specify the colour of a given sample by colour matching, using the NCS and/or the Munsell systems.

Tools

Munsell Book of Color and/or NCS Colour Atlas or Index, white or gray masks with rectangular openings.

Principle

The colour of the test sample is compared to the colour(s) of the reference samples of the atlas or index, in order to find an equal or closest match. The notation of the reference sample describes the colour appearance of the test sample.

Procedure

- Place the test sample in natural daylight (close to a window, or outdoors) on a neutral background (white), having the light come preferably from the left side. Avoid direct sunlight.
- Follow the instructions in the respective atlas as to how to observe the sample (viewing distance, angle, etc.).
- Find the reference sample that is a closest match to the test sample.
- If a single matching reference sample cannot be found, find the most similar colours (2 to 4 samples).
- Read the notation of the reference sample and write it down in your table as the notation of the test sample. In the case of 2 or more similar samples, interpolate the readings of their variables/attributes.

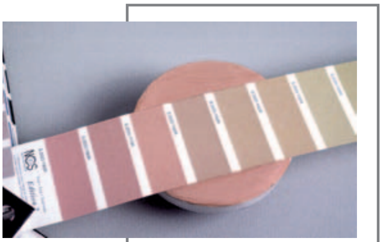
Example

For the given test sample:

- USING THE NCS SYSTEM

  In the NCS Index Edition 2, no single reference sample corresponded to the colour of the test sample. Three reference samples were identified as most similar to the test sample: S2020-Y50R, S2020-Y60R and S2010-Y50R.

  By interpolation of these notations, the notation of the test sample was calculated as S2015-Y55R.



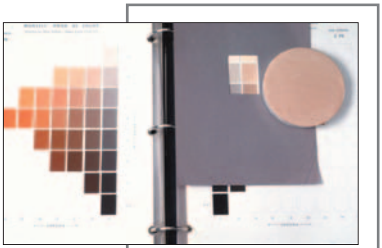
Colour matching using the NCS Index, Edition 2

- USING THE MUNSELL SYSTEM

  In the Munsell Book of Color, the closest match was represented by four samples lying in close proximity to each other:

  5YR 7/2, 5YR 8/2, 5YR 7/4, 5YR 8/4.

  By interpolation of these notations, the notation of the test sample was determined as 5YR 7.5/3.



Colour matching using the Munsell Book of Color

PRACTICAL 2

INSTRUMENTAL COLOUR MEASUREMENT

Aim

Measure the colour of a given sample instrumentally using the CIELAB system. Find the spectral distribution curve and the Munsell notation of the test sample.

Equipment

Portable colorimeter.

Principle

The colorimeter quantifies the light reflected from the surface of the test sample under the pre-selected standard illuminant. The spectral reflectance curve can be visualized (e.g., by connecting the instrument to a computer). As a rule, more than one measurement is taken of each sample; three are usually recommended to have a good average.

Procedure

- Calibrate the colorimeter, following the instructions given with the instrument.
- Adjust the size of the opening for measurement to the size of the sample.
- Choose the illuminant; this depends on the purpose of the measurement. Usually D_{65} is recommended.
- Place the colorimeter on the test sample surface and activate the measuring procedure.
- Read the notation in the pre-selected systems on the colorimeter or computer.
- Calculate the average of three measurements to obtain the final data.

Compare the results of the instrumental measurements to the visual ones. Evaluate the differences, if any, and try to give reasons for them.

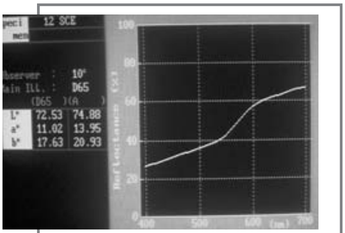
Example

In the example shown, the illuminant D_{65} was used, and data were requested in the CIELAB system, plus the Munsell notation. The following measurements corresponding to the spectral reflectance curve visualized on the computer screen could be read from the instrument:

A portable colorimeter and test sample

colour print on inside back cover

Colour measurement using a portable colorimeter; the results are plotted
on a computer screen



```
(D65  )(A    )
L*  72.53  74.88
a*  11.02  13.95
b*  17.63  20.93
```

The spectral reflectance curve of the test sample colour and the L*,a*,b* readings

colour print on inside back cover

Visual measurements		**Instrumental measurements**	
NCS	Munsell	CIELAB	Munsell
S2015-Y55	R 5YR 7.5/3	L*=73,40 a*=10,52 b*=17,08	5.1YR 7.3/3.5

When compared, the results of visual and instrumental measurements are rarely identical. Some difference between the visually and instrumentally obtained Munsell notations in this example can be observed for hue, value and chroma. They are, however, very small (especially for hue and value). The reasons could be inaccurate interpolation, effect of illumination, etc. Also, it could be recommended to do several instrumental measurements in various parts of the sample and consider the calculated average.

RESTORATION OF COLOUR SCHEMES IN HISTORIC TOWNS – experience of applied colour specification and measurement at BANSKÁ ŠTIAVNICA ㉚

Restoration of historic colour schemes within urban colour plans is one of the areas where applied colour science is used. Many successful examples exist and useful methodologies have been developed, yet each particular case requires its own approach.

㉚ Banská Štiavnica, a town in Central Slovakia, is inscribed on the World Heritage List.

Context and purpose

This pilot project was developed for the local authorities, especially for the town administration and the local office of the National Institute for Protection of Monuments, as a conceptual model to meet urgent needs of practice. There was no systematic study of the complex problem of historical colour schemes in their broader context, which could serve as the basis for day-to-day practice, coordination and control of the conservation and restoration process. The project involved the development of a working methodology and the elaboration of a colour master plan to achieve a visually coherent, functional environment that would correspond to the historical findings and enhance the values of the town's architectural and urban heritage. The project attempted to combine sound conservation and restoration principles with applied colour science. The work was carried out by a multidisciplinary team in less than 9 months of part-time work.

Problems and specific features of the project

The study focused on the existing façades in their current form (each had a complicated building history).

There were some limiting factors, such as the degree of knowledge regarding individual façades at the time of the study, the incomplete character of the available documentation and the limited time frame. The project included 130 buildings, located in 19 streets in the historic centre.

Colour specification and measurement aspects of the project; working method and phases

Preparatory phase:

- Archival research;
- Feasibility studies regarding the possibility of colour mapping of the façades, based on available tools and instruments.

  A survey was made to identify:
  1. what methods and techniques of colour specification and measurement had been used in local practice concerning the relevant buildings;
  2. what equipment was available and how familiar with its use were the professionals involved.
  The survey found that the general practice was the use of description of colour by name, more rarely in combination with a chip (mostly taken from a paint manufacturer's catalogue or sample collections to identify or indicate colours). The standardized colour appearance systems were neither known nor available.
- Experimental research attempting to define the objective factors underlying subjective aesthetic evaluations of architectural colour schemes. 🗀33

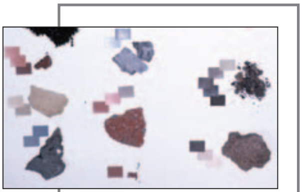
  This was a complementary, quite independent study involving analyses of colour schemes to comprehend people's present-day preferences.

Photodocumentation of the façades

colour print on inside back cover

Survey *in situ:*

- **Façades**: surveys for determining the art-historical development and building history, state of conservation, historical colour schemes. Assessment of the currently prevailing architectural expression of each façade and corresponding colour schemes. ㉛ Earlier phases were also assessed where possible, by stratigraphic surveys ㉜ in selected points of the façades, 5-15 per façade, depending on its complexity. Site sketches, notes on plans, maps and elevations, and photographic documentation were used. On the basis of an overall analysis and evaluation of the character of the architectural surfaces of the buildings, as well as the character of the project itself, it was decided to work with visual colour assessment, or colour matching. The ACC system (see below) was chosen after prior testing of its appropriateness for the purpose. This system, exemplified in the Sikkens Colour Collection 2021, had a very good density of reference samples in the colour ranges concerned, whereas the standardized colour systems were of limited accessibility and costly for general use in the context. In studio and research work, Munsell and NCS systems were also employed.



Survey of the typical colours of elements of the environment

- **Environment:** colour survey and assessment of permanent built elements (roads, pavements, supporting walls, etc.) as well as natural elements. This provided data for analysis of the typical colour features of the site, i.e., the landscape and the town with their characteristic permanent and changing colours.

Analyses

The collected data were analyzed to determine:

-The colour typology of the stylistic periods (from Gothic to present-day) with specified colour characteristics such as: prevailing hues, saturations, lightnesses; characteristic colour combinations, qualitative and quantitative relations between colours of wall and façade elements, types and levels of contrasts.

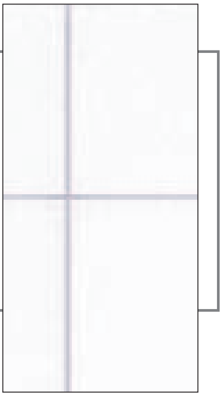
-The environmental colour palette with quantified ranges of the colour variables.

Synthesis

The synthesis of all information obtained in the previous phases of the project and its comparison with established criteria permitted the elaboration of colour schemes. Either one scheme was proposed, or alternatives within a defined range of colours.

In the final catalogue, the following were provided: a photo and a form for the street façade of each building with information on the façade's stylistic character, its technical characteristics, the colour scheme findings corresponding to the prevailing architectural style of the façade (described in words, shown by a sample and specified in the ACC system), recommendations for further research, indications on conservation and restoration interventions, recommended colour scheme. Graphic documentation consisted of plans 1:1000 of the present state, analyses and proposals.

Illustration of façade colour typology studies for stylistic periods. Example: classicism, last third of 19th century



A system for organizing all relevant information on colour schemes into data banks was set up.

Discussion of results

- This experience confirmed that for each case and situation there is a need to develop an appropriate condition-specific working method. Other successful cases and well-established methodologies ㉝ can be of great help.
- The use of a colour notation based on a colour order system for data assessment proved to be very important, as it conditions the further analysis and elaboration of the data, including the possibility of creating

The final catalogue; example of the photo and related table for a façade

㉛ *Façades of the individual buildings and the historical surroundings were studied: style of the street façades, their dating; categories of façades with respect to their stylistic-architectural values; state of research on the individual façades; state of conservation, restorations of the façades.*

㉜ *All were plastered façades. Gradual scraping to reveal colour layers was done for chromo-chronology; samples for cross-sections were not necessary for these buildings.*

㉝ *Some of the most useful ones have been developed by G. Brino, A. Nemcsics and J.P. Lenclos.*

computerized data banks. Notation by colour names only (as is still often the practice) limits the usefulness of the information.

- Colour surveys and their elaboration should be carried out by experienced interdisciplinary teams, with at least one team member having practical experience with the characterization and measurement of colour.

Not all countries have an official standard colour system, and in many cases institutes and individual professionals are not equipped with colorimeters, colour atlases, indexes or other relevant material from any recognized colour order system. It is not always possible to have a collaborating colorist, or persons familiar with such systems and working methods, so compromises still have to be sought.


Banská Štiavnica, 1996.
Example of implementation
of the colour plan

THE ACC SYSTEM 🗀34

The Akzo Nobel Coatings Colour Codification System (ACC System) is a colour ordering method that has been in use since 1974 by Sikkens Akzo Nobel Coatings (Holland). In 1978, the company introduced the Sikkens Colour Collection 2021, recently followed by the Collection 3031. These collections, developed by industry for façade and space design, are among those most widely used today.

Guiding principles:

The system is based on colorimetric measurements of three basic colour variables (colours are coded according to hue, saturation and lightness) as well as on their perceptual evaluation by the human visual system. Its application of colour to architecture is expressed in the ordering of the reference samples and density intervals. The system's space is cylindrical.

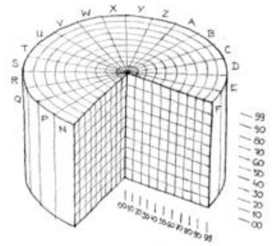
Variables:

Hue, H: HC = Hue Codification. The hue circle is divided into 24 parts (letters A to Z, excluding I and O); each part is subdivided in 10 sections numbered 0-9.

Saturation, S: SC = Saturation Codification. Saturation is expressed by the distance between the central axis and the outer perimeter of the cylinder by a scale from 00 (for achromatic) to 99 (for highest saturation). Colours with a saturation lower than 03 are marked N.

Lightness, L : LC = Lightness Codification. Lightness on the vertical axis of the cylindrical colour space is numbered from 00 (minimum, ideal black) to 99 (theoretical maximum, ideal white).

ACC Colour Notation: HC. SC. LC Example: E4.10.60



THE ACC COLOUR SOLID

Special features

From the total amount of colours that the ACC System can describe, the collections 2021 and 3031 select 635 and 1243 colours respectively, based on response to trends and demand. Although they are meant for selecting colours and products for practice, they are equally useful for specification of existing colours, because of the very good representation of reference samples in those ranges into which façade colours most often fall.

Work with the collection is easy, developed on a logical basis and scientifically supported by the codification system (further analysis and study of the measured data are quite possible). The system and in particular the collections are widely known and therefore allow for good colour communication.


Sikkens Colour Collection
3031

7 APPENDIX

7.1 THE MUNSELL SYSTEM

The MUNSELL SYSTEM is a U.S. standard and has been recognized in other countries as well. (The standard method of specifying colour by the Munsell System is ASTM D 1535).

General characteristics and use:

The Munsell system is the oldest colour appearance system in worldwide use. The colour notation system was developed by Albert H. Munsell, artist and art teacher, with the aim of providing an aid in teaching colour, particularly to children.

History and development: 🗀35

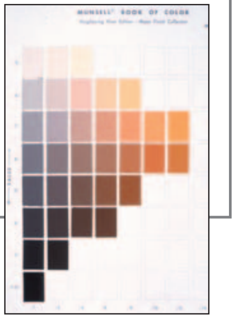
1905: **A COLOR NOTATION** (conceptual structure of the system, published by Munsell)

1915: **MUNSELL ATLAS OF COLOR** published (first complete version for 10 hues)

1929: **MUNSELL BOOK OF COLOR**, improved scales as result of subsequent studies at the National Bureau of Standards and in the Munsell laboratory. The system was defined by the spectral reflectance functions of the colour chips. The spacing of the samples was based on visual scaling experiments of value, hue and chroma (20 hues).

1943: **MUNSELL RENOTATION SYSTEM** ㉞ published. New scaling experiments were carried out; based on these data, new Munsell notations were specified for the 1931 CIE standard observer, standard illuminant C.

1976: **MUNSELL BOOK OF COLOR** is the atlas with physical exemplification of the renotation system



Example of a Munsell Book of Color constant hue chart (section of the colour solid through the vertical axis)

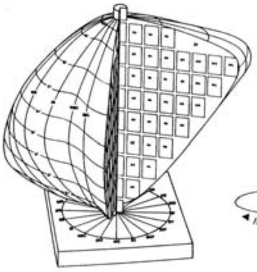
Guiding principles:

Munsell worked on having the system empirically anchored in both psychophysical scaling methods and physical measurement techniques. ㉟ Within each of the individual hue, value and chroma scales, the spacing is approximately uniform but not identical.

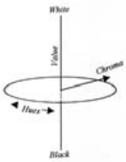
Variables: 🗀37

HUE (H): The hue notation of a colour indicates its relation to a visually equally-spaced scale of 100 hues. The Munsell hue circuit is based on 10 *major hues* R, YR, Y, GY, G, BG, B, PB, P, RP (five *principal* and five *intermediate*). For each of the 10 major hues there are 10 hue steps, and the most representative hue is located in the middle of the interval: therefore the best red is 5R, the best yellow is 5Y, etc.

This form of hue notation – based on a combination of numerals with the hue initials – is considered the most descriptive. It has been used in the **MUNSELL BOOK OF COLOR** on the 40 constant hue charts.

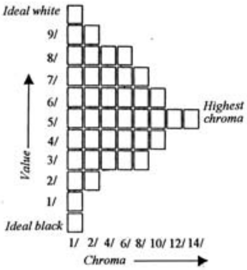


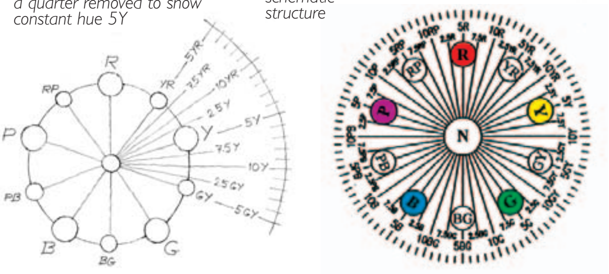
THE MUNSELL COLOUR SOLID
a quarter removed to show constant hue 5Y



The solid's schematic structure

Vertical section through the solid





Diagrams showing the structure of the hue circuit based on 5 principal hues and 5 intermediate hues. 🗀38

㉞ *The Munsell Renotation was standardized by the ASTM in D 1535 Standard Test Method for Specifying Color by the Munsell System. The Standard system of colour specification is standard Z138.2 of the American National Standards Institute, as well as the Japanese Industrial Standard for Color JIS Z 8721; the German Standard Colour System DIN6164 includes Munsell notations for each of its colours. Several British National Standards are also expressed in Munsell terms (www.munsell.com).*

㉟ *His "photometer" was the Maxwell disc.* 🗀36

Value (V): The value notation indicates the lightness of a colour in relation to a neutral gray scale, which extends from absolute black to absolute white. Values are indicated by figures from 0 (absolute black) to 10 (absolute white).

Chroma (C): The chroma notation indicates the degree of departure of a given hue from a neutral gray of the same value. The scales of chroma extend in equal steps from 0 for neutral gray to 10,12,14 or farther.

Munsell colour notation㊱ : H V / C Example: 7.5Y 6/4.

When a finer division is needed, decimals are used for any of the attributes.

Tools, Munsell Color Communication Products㊲:

The tools most commonly used for colour assessment are:

- The **Munsell book of color**, Matte Collection (about 1270 colour chips).
- The **Munsell book of color**, Glossy Collection (about 1564 colour chips). Two-volume glossy edition with removable free chips.
- The **Munsell book of color** Nearly Neutrals Collection (about 1100 pastel colours).

Costs vary from product to product.

7.2 THE NATURAL COLOUR SYSTEM (NCS)

The NCS colour notation system, the relationship between NCS notations and instrumental measurements, and the Colour Atlases have been Swedish Standards since 1979 and have also been introduced in several other countries.

General characteristics and use: 🗀39

- The Natural Colour System is a way to describe and order, by means of psychometric methods, the characteristic relationship between all possible colour percepts of surface colours.
- The NCS colour notation system is said to be general: it makes it possible to describe object colours as they appear in any given viewing and illumination situation. It is based exclusively on the possibilities and restrictions of human colour vision, and its use does not require any knowledge of physical or physiological attributes of colour stimuli.
- The psychophysical relationship between the experimentally derived psychometric colour scales in the NCS space and the corresponding physical parameters in the CIE-system has been determined.
- The NCS system is widely used in environmental colour design, and it is also being increasingly used in colour research (studies of colour combinations, people's perceptions and evaluations of colours in the environment, of aesthetic colour relationships, etc.).

History and development: 🗀40

The origins of the system go back to the six primaries of Leonardo da Vinci and Ewald Hering's theory about the "natural order system" of the percepts of colour (1874). The modern colour system is based on the work of Johansson and Hesselgren. Hesselgren published his Colour Atlas in 1952, with 507 colour samples, as a first attempt at physical exemplification of the variables of hue, saturation and lightness (not instrumentally measured). NCS research and development began in 1964, with the following key phases:

- 1964: The Swedish Colour Center Foundation was created. Its first task was the revision of Hesselgren's Colour Atlas using new psychophysical experiments, spectrophotometric measurements, collaboration of phenomenologists, physicists and pigment chemists.
- 1972-73: Swedish Standard for Colour Notation, SS 01 91 00.
- 1979: Swedish Standard Colour Atlas, SS 01 91 02 (1412 samples), developed by A. Hard and L. Sivik.
- 1995: Major revisons of the NCS Colour Atlas 🗀41 were made. The most important changes were: exclusion of toxic and environmentally harmful pigments; addition of 261 completely new samples (46 old ones withdrawn, about 1000 former samples changed slightly in colour, about 400 given a new notation). NCS Edition 2 has a total of 1741 colours, allowing closer colour selection and greater precision. Three quality levels㊳ of products have been introduced.

㊱ *This is a system of letters or numbers, or both, by which the colour of any opaque object may be specified with respect to Munsell hue, value and chroma, written in the form H V/C (ASTM).*

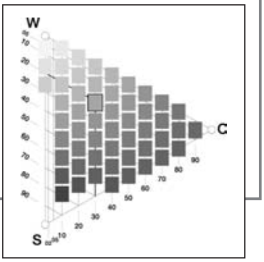
㊲ *GretagMacbeth, New Windsor, New York, USA. (www. munsell.com)*

㊳ *Tolerance or accuracy requirements in their manufacture, i.e., allowed deviations from the primary standard and consequently different prices.*

Guiding principles:

The NCS System: section of the colour solid through the vertical axis.

colour print on inside back cover



- The NCS was developed as a *descriptive colour notation system* on the basis of extensive experimental documentation and the concept that "colour is what we see, i.e., a subjective visual sensation".
- The system orders colours according to their perceptual *elementary attributes*, based on the resemblance of colours to the 6 *elementary colours* Red, Yellow, Green, Blue, Black, White. From the elementary attributes, the NCS *chromaticness* (c) and *hue* (ø) are derived, and together with *blackness* (s) constitute the descriptive NCS notations, the Swedish Standard. The notations are derived from absolute estimations of the visual attributes ($s+w+c=100$). This means that a colour can be fully described by specifying how closely it resembles black s, white w and the full hue c. Only blackness s and chromaticness c are explicitly indicated, as whiteness w can be easily derived by the formula $w = 100 - s - c$.
- Visual equality of spacing is not a characteristic feature of the system.

Variables:

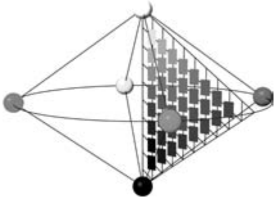
Hue (ø) is defined in terms of the resemblance of the test colour to the two nearest chromatic elementary colours. The resemblance is expressed in percentage: e.g., Y30R means a hue which resembles Yellow at 70% and Red at 30%, i.e. the resemblance is expressed in % of the second hue.

Chromaticness (c) is defined as the degree of resemblance of the test colour to the colour of the same hue having the maximum possible chromatic content.

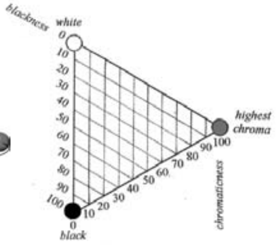
Blackness (s) is defined as the resemblance of the colour to the perfect black. (For achromatic colours, lightness $v = (100 - s)/100$.)

The relationship between whiteness, blackness and chromaticness ($w/s/c$) is called the *nuance* of a colour.

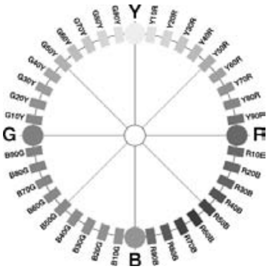
Saturation (m) is the relationship between the chromaticness (c) and whiteness (w) of a colour; it is defined as $m=c/(c+w)$ and expresses the relative amount of chroma as compared with white and chroma taken together. 🗀42



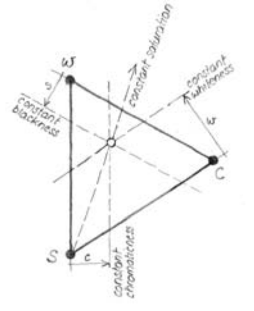
The NCS Colour solid



NCS Colour triangle



The NCS Colour circle



A nuance: the relationship (principles) between whiteness (w), blackness (s) and chromaticness (c)

Colour prints on inside back cover 🗀43

Colour Notation: (s c - ø) 7010 - G50Y (NCS 1979) S 7010 - G50Y (NCS Edition 2, 1995)

nuance hue

Tools, NCS Products:

The NCS edition 2 products offered by the Scandinavian Colour Institute (Stockholm) are of three quality levels: standard (the highest), level 1 and level 2. The tools most commonly used for colour assessment are:

- The **NCS Colour Atlas**, which illustrates the standard colour notation system, the NCS colour space. It is designed for general use under daylight conditions. Quality level 1.
- The **NCS index** edition 2 as a low-cost alternative, which provides an overview of the 1750 colours. Quality level 2.
- The **NCS selection** which gives 908 colours mainly used for building purposes. Quality level 2.

Costs vary with the quality levels.

A relatively new instrument is the **NCS Colour Meter** which gives readings in the NCS system.

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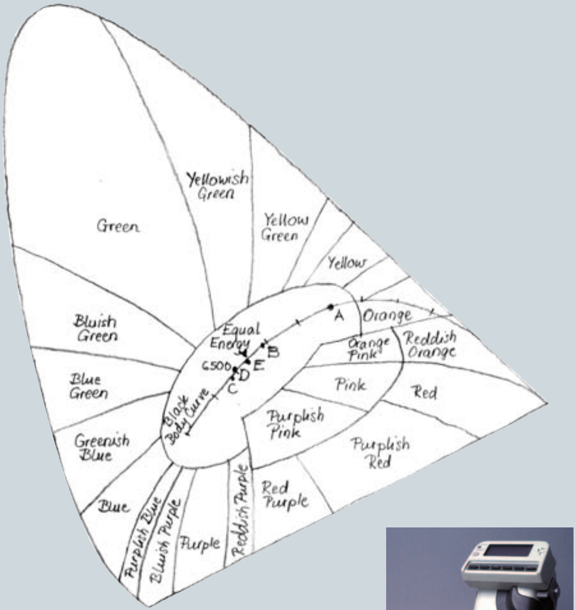
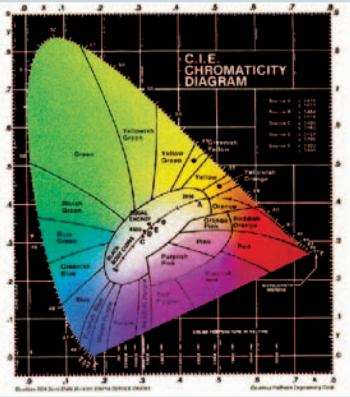
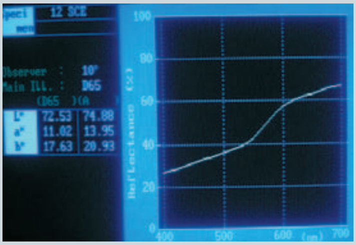
With regard to the selection, applicability or efficacy of the systems and tools mentioned, no endorsement or recommendation is implied on behalf of ICCROM, and no criticism is implicit in the non-mention of any system or product.





CIE chromaticity diagram.
(This printed version gives only an approximate idea of the colours.)

A portable colorimeter and test sample

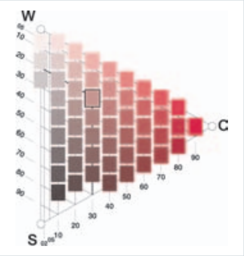

12 SCE
Observer : 10°
Main Ill. : D65
(D65)(A
L* 72.53 74.88
a* 11.02 13.95
b* 17.63 20.93

The spectral reflectance curve of the test sample colour and the L*,a*,b* readings

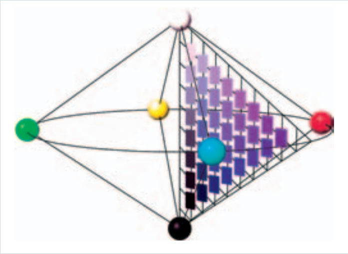
Photodocumentation of the façades

The NCS System

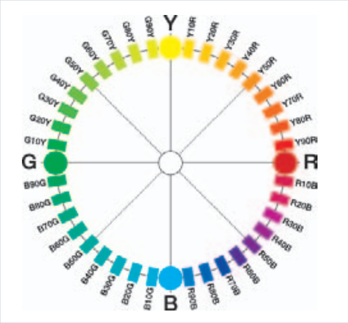
Section of the colour solid through the vertical axis



The NCS Colour solid



The NCS Colour circle



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