

Material Analysis Methods Applied to the Study of Ancient Monuments, Works of Art and Artefacts *¹

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Cultural heritage resources are often subject to the singular or combined action of different weathering phenomena. To study these deleterious processes conservation scientists can rely on a whole variety of analysis techniques, which provide both bulk and localised (micrometer scale) chemical information. In this presentation an overview is given of the analytical approaches that are at present most commonly applied to solve cultural heritage related problems. The use of some of these techniques is illustrated with a case study on the weathering of two historically important Belgian building stone types. Future cultural heritage related research at the IMR (Tohoku University) is briefly discussed.

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1. Introduction

Material analysis techniques are used to solve a wide variety of cultural heritage (CH) related (analytical) problems. The nature of these problems generally falls into one of four groups:

- The study of *weathering* (or degradation) *phenomena* (e.g., pressures exerted by salts when crystallizing inside a porous substrates, chemical reactions at the surface of a CH object).
- Study of the behaviour of *protective treatments* (e.g., long-term effectiveness of consolidants or hydrophobic treatments on the weathering rate of building stones).
- Characterization of the (micro-) *environment* that affects CH objects (e.g., analysis of atmospheric particulate matter that is deposited on the objects).
- *Archaeometry* (e.g., authentication of CH objects or studying correlations between archaeological finds).

The CH researcher generally addresses these problems by making use of bulk and/or local analysis techniques.

2. Bulk Analysis

The most frequently encountered bulk analysis techniques in CH related studies are Ion Chromatography (IC), Atomic Spectroscopy (AS) and X-ray Fluorescence Spectrometry (XRF). Each one of these techniques has its own advantages and areas of application:

2.1 IC

Offers the unique advantage of selective and rapid determination of low concentrations (down to the ppb level) of anions and cations in wet atmospheric deposition and stone run-off and leachate samples. It is a reliable and accurate method for the simultaneous determination of many inorganic and or-

ganic ions. Minimal sample preparation is required and the precision is generally within 10%. IC offers a wide dynamic range (ppb-%).

2.2 AS

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) is at present probably the most frequently applied AS technique in the field of cultural heritage. It allows the determination of almost all the elements in the periodic table. Detection limits are in the ppm to ppb range, with a precision that is generally in the order of 1–2% and an accuracy of around 10% and a wide dynamic range. Samples may be solid or liquid. Solid samples may require extensive sample preparation and dissolution procedures. Compared to other atomic spectroscopy techniques such as AAS or conventional FE-AES, ICP-AES offers superior detection limits with minimal matrix effects. ICP-AES is employed to analyse aqueous solutions such as wet atmospheric deposition and run-off and leachate samples.

2.3 XRF

Compared to classical Wavelength Dispersive X-ray Fluorescence Spectrometry (WDXRF), Energy Dispersive (ED) XRF is cheaper and more suitable for rapid screening of heavier elements, while the accuracy is generally somewhat inferior. Detection limits of bulk EDXRF are typically in the order of magnitude of 1 ppm with low-Z elements (e.g., Si and Al) having detection limits of about 1000 ppm and heavy elements (e.g., Pb) of about 20 ppm. XRF is a bulk analysis technique with the depth of sample analysed varying from less than 1 mm to 1 cm depending on energy of the emitted X-ray and the sample composition. The precision depends on the analysis parameters, but is on an average less than 1% for most elements (Al–U). Most samples can be analysed “as is” for most qualitative analysis and quantitative analysis.

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Table 1 Most commonly used micro-analytical techniques in CH related studies.

	SEM/EPMA	μ -XRF	μ -PIXE	SIMS	FTIR	LMMS	XPS/ESCA
Excitation	electrons	photons	protons	ions	photons	photons	photons
Detection	photons	photons	photons	ions	photons	ions	Electrons
Lateral resolution	< 0.1 μ m	0.7–10 μ m	0.3–5 μ m	0.5–10 μ m	10 μ m	1–2 μ m	100 μ m
Beam penetration	1–10 μ m	100–1000 μ m	1–100 μ m	< 0.1 μ m	1 nm	10 μ m	5–10 nm
Morphology information	excellent	no	no	poor	poor	poor	no
Element detection	Na \rightarrow U	Na \rightarrow U	Na \rightarrow U	all elements	no	all elements	Some
Molecular information	no	no	no	yes (org., inorg.)	yes (org., inorg.)	yes (org., inorg.)	yes
Isotope information	no	no	no	yes	no	yes	no
Quantification	yes	yes	yes	poor	poor	poor	yes
Detection limit	1000 ppm	0.1–100 ppm	1–100 ppm	10 ppb–100 ppm	1 ppm	1 ppm	0.1–1%

3. Local (micro-) Analysis

During the last decades, a broad range of micro-analytical and surface characterization techniques have additionally become widely available, which can be applied advantageously to study the deterioration mechanisms of different cultural heritage artefacts. Various industries and *e.g.*, material research institutions already use most of these techniques intensively. Obviously they offer promising prospects too for the research on causes and mechanisms of damage to cultural heritage artefacts. Early stages of deterioration can be detected. When weathering processes, which have to continue for many years before causing apparent damage, are to be monitored over relatively short time intervals or when such processes are simulated in the laboratory it is essential to use techniques permitting measurement of chemical alteration in the uppermost layer of the surface or even the microscopic spots on it. The often non-destructive character of some of these techniques and the need of only very small samples is also advantageous in the analysis of precious historical objects. Of course, these techniques will never replace the valuable, generally accepted and widely applied bulk analysis procedures. Rather, micro- and surface analysis techniques should be considered as potentially valuable supplements.¹⁾ The most commonly used micro-analytical techniques are shown in Table 1.

3.1 SEM

Scanning Electron Microscopy (SEM) and related techniques are widely used in the study of material decay. SEM is by far the most applied micro-analysis technique in the study of stone deterioration. SEM uses a high vacuum and therefore its application is limited to the analysis of samples that are stable under low pressures. Most SEM's are equipped with a system to detect characteristic X-rays (SEM-EDX or EPXMA), locally induced in the sample by the electron beam, thus allowing local chemical analysis.

Environmental (E-)SEM offers similar imaging and analysis capabilities at a higher pressure (~ 0.9 kPa). SEM(-EDX) has been used to study *e.g.*, the effectiveness of protective treatments applied to historic building stones, the composition of individual micrometer-size particles deposited onto works of art, the deterioration of ancient paints and stained glass.²⁾

3.2 μ -XRF

Does not necessarily use a high vacuum (depending on the element to be detected) and is essentially non-destructive. μ -XRF in addition offers the possibility to perform *in situ* analysis, when portable devices are used (equipped with air-cooled radioisotope sources and Peltier cooled detectors). Micro-Synchrotron Resonance (μ -SR) XRF offers lower detection limits but requires large physical installations (which are very limited in number). μ -(SR)XRF has been used to *e.g.*, perform trace element fingerprinting of historic glass, study glass and metal corrosion and the composition of metal artefacts and ink on handwritten documents.³⁾

3.3 μ -PIXE

Micro-Particle Induced X-ray Emission Spectrometry offers a slightly higher lateral resolution and a lower background compared to μ -XRF, but the risk of inducing beam damage is considerably higher. μ -PIXE has been used to *e.g.*, study the corrosion of glass and pottery and the composition of metal artefacts and paints.⁴⁾

4. Building Stone Weathering

By way of illustration on the application of some of the above-mentioned analysis techniques a short outline will be given of a study on the weathering of two limestone types, which was performed by the research group of Prof. Van Grieken at the University of Antwerp.⁵⁾

It is essential to be able to quantify the decay mechanisms that affect historical building stones, and to understand which factors are relevant for their degradation. Quantitative weathering rates can be monitored in laboratory experiments, directly on the monument surfaces or in field exposure trials, using techniques that monitor surface roughness changes, recession rates, and/or chemical changes. The effects of air pollution on stone deterioration can be assessed by analyses of the corrosion products carried by run-off water (*i.e.*, rain water that has run over the surface of the studied stone). Many research programmes calculate the material loss of limestone based solely on the calcium ion concentration in solution. However there are a lot of indications that non-dissolved particulate matter suspended in the run-off water accounts for a significant additional amount of calcium loss. To elucidate the importance and the composition of this Total Suspended Particulate (TSP) run-off water was collected from freshly

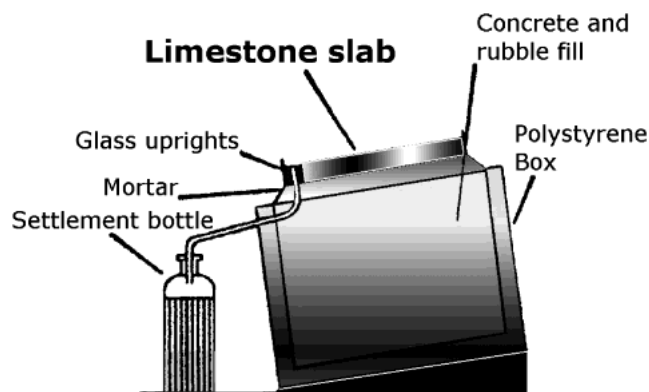


Fig. 1 Limestone slab exposed in a so-called 'Micro-Catchment Unit' (MCU).

Table 2 Relative abundance (%) of different particle types suspended in rain and run-off collected from Balegem limestone.

Sample	Si-Al	Si	Ti	S	Fe	Ca
Rain	64	14	1.2	1.2	17	2.0
Blank	61	18	2.0	1.4	17	1.7
Balegem	23	33	0.4	1.1	11	4.1

quarried limestone slabs exposed in the field (Figure 1 shows a schematic representation of the exposure setup).

Attention was focused on limestones of Balegem (CaCO_3 -content ~ 40 – 60%) and Massangis (CaCO_3 -content $>90\%$) for their historic importance and use in present restorations respectively. The exposed stones measured $25 \times 25 \times 5 \text{ cm}^3$ and were inclined 15° towards the south-west, the prevailing wind direction at the sampling location (Antwerp, Belgium). Run-off samples from the stones and from roughened inert glass (reference) surfaces were collected on a weekly basis, over a period of three years. The run-off water was filtered; the dissolved material was analysed with IC and AAS and the TSP was analysed with EDXRF and EPXMA.

EPXMA was used to analyse the (elemental) composition of individual suspended particles. The analysed particles were then grouped by computerised hierarchical cluster analysis, which resulted (for Balegem limestone) in the average particle abundances given in Table 2. These results indicate a distinctive difference in the composition of the suspended particles between blank and rain samples on the one hand and limestone run-off samples on the other hand. The main difference in the composition of the suspended matter between stone run-off samples on the one hand and blank and rain samples on the other hand is the higher contribution of calcium-rich particles for the former ones. This indicates that an important portion of the limestone loss is present in the suspended phase. This result was confirmed by bulk EDXRF analysis on the TSP, comparing the Ca/Ti and Ca/Fe ratios for blank and limestone run-off. Since Ti and Fe are believed to originate mainly from atmospheric deposition the enhanced Ca/Ti and Ca/Fe ratios found for limestone run-off indicate the significant contribution of Ca-loss in the suspended phase.

The recession rates based on the dissolved Ca^{2+} content in the run-off water averaged 1350 and 1050 mg/year for Massangis and Balegem limestone respectively. However,

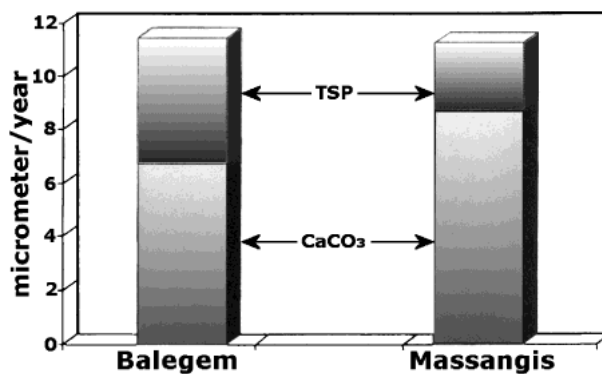


Fig. 2 Material loss ($\mu\text{m}/\text{year}$) of Balegem and Massangis limestone.

when taking into account the TSP, the average recession rates equalled 1740 and 2050 mg/year for Massangis and Balegem limestone respectively. Hence the total suspended particulate accounts for approximately 22% to the total material loss of Massangis limestone and for about 40% of the total material loss of Balegem limestone. These results are illustrated in Fig. 2, where the surface recession rates are expressed in micrometer per year. In order to account for other damage processes than the dissolution damage, it is evident that the total stone loss should be computed from both the net calcium concentration in solution and the net suspension load in the run-off water. Not considering the stone material that is eroded in the suspended phase results in a significant underestimation of the weathering rates of limestone.

5. Future Research

At the Institute for Materials Research (IMR, Tohoku University) the authors are currently developing an experimental setup that will allow 3-dimensional XRF analysis. By scanning the sample in front of a μm -sized X-ray beam a 2-dimensional element distribution (mapping) of the sample surface is obtained. When at the same time the fluorescence signal is resolved as a function of the take-off angle, depth profiles are obtained for every point of the surface mapping, thus potentially leading to 3-dimensional XRF analysis. This non-destructive technique is especially useful for the investigation of depth related characteristics of precious works of art, such as *e.g.*, the composition of layered structures or corrosion processes. To show the feasibility of this technique, it will be applied to study the Japanese 'Tamamushi-Nuri'.

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