

## Combined SEM and Raman spectroscopy A new analytical tool for corrosion and oxidation studies - analysis of an ancient artefact

### Introduction

The Renishaw structural and chemical analyser (SCA) shown in Figure 1 allows corrosion and oxidation scientists to benefit from the imaging and analytical capabilities of scanning electron microscopes (SEMs) combined with the chemical and structural characterisation available from Raman spectroscopy. The SEM-Raman system is unique, allowing both rapid observation and elemental analysis at macro and micro scale. An overview and detailed classification of the sample is now available in a single instrument.

Oxidation and corrosion are related processes, and refer to the conversion of metals into various compounds. The conversion process can be gradual, self-limiting, or rapid, and an understanding of the mechanisms and kinetics involved is fundamental to determining the performance of metal components throughout their lifetime.



Figure 1  
The SEM-SCA at Bologna University

Traditional methods of analysing oxides and corrosion products - such as x-ray analysis, x-ray diffraction, and surface analysis - are either limited to "bulk" samples, or are poor at determining their precise chemical composition. Raman spectroscopy, although unable to collect spectra from native metals, can provide specific chemical identification of most metal oxides and corrosion

products. Raman spectroscopy has traditionally been carried out in parallel with optical microscopy, but the limited depth of field, spatial resolution, and contrast mechanisms of the latter means that identification of regions of interest can be quite difficult. Combining Raman microscopy with an analytical SEM, however, capitalises on the imaging and elemental analysis capabilities of the SEM, and the chemical specificity of Raman.

### SEM-Raman investigation into corrosion of ancient artefacts

The ancient city of Zeugma in Turkey now lies underwater - flooded as a result of damming the river Euphrates. Prior to the flooding an urgent archaeological investigation - funded principally by the Packard Humanities Institute - discovered, recorded, recovered, and preserved many spectacular artefacts.

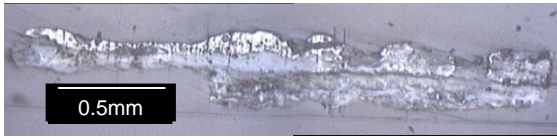


Figure 2  
The 155 cm tall bronze statue of the god Ares (Mars) now at Gaziantep museum.

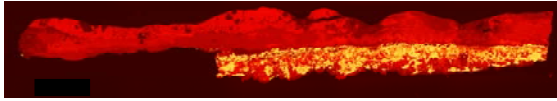
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A bronze depicting the Roman god Ares (Mars) was recovered (Figure 2), and during preservation unusual patination was noted. A flake of the oxide was collected and provided for analysis - it is the subject for this study.

The spalled oxide flake was potted in epoxy resin, and polished so that a cross-section could be observed. Optical microscopy (Figure 3) of the cross-section reveals three indistinct layers, but fine structure is not apparent even at higher magnifications, although some variations in colour are apparent.

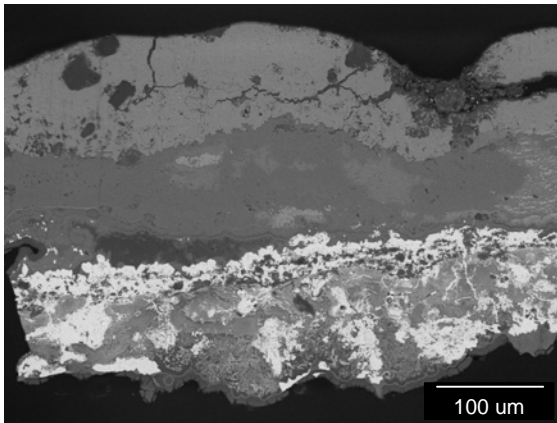


**Figure 3**  
Optical micrograph of the spalled oxide flake (5x objective)



**Figure 4**  
Backscattered electron image of the oxide flake – pseudo-coloured for clarity

Since the sample was non-conductive and uncoated it was examined using low vacuum SEM - in this mode the SEM image contrast is the result of variation in mean atomic number. Figure 4 shows the SEM image of the oxide flake (pseudo-coloured for clarity), and Figure 5 shows the area that was selected for examination using x-ray analysis and Raman spectroscopy.

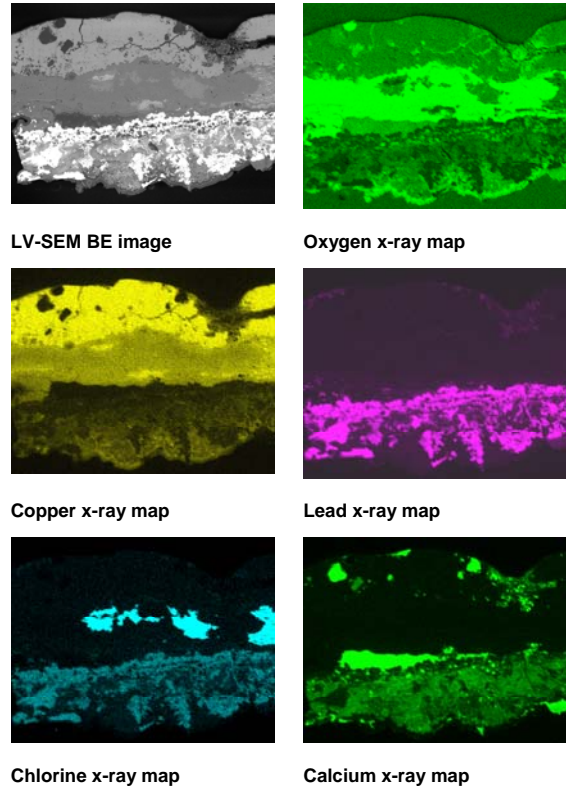


**Figure 5**  
Backscattered electron image of the area selected for analysis

X-ray mapping (Figure 6) reveals three principal layers within the flake all of which contain oxygen to varying degrees:

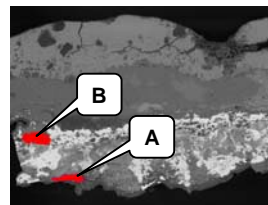
- A copper-rich [top] layer that was originally in contact with the metallic bronze, with areas rich in calcium
- An oxide rich [middle] layer that also contained significant levels of chlorine in places, and calcium at the interface with the lead layer
- A lead-rich [bottom] layer - the outermost layer in contact with soil

X-ray mapping is a fast and convenient way of determining the spatial distribution of the elements within a sample. Insensitivity to light elements and the difficulties of stoichiometry-based quantification, however, mean chemical identification of oxides and corrosion products must be regarded with caution.

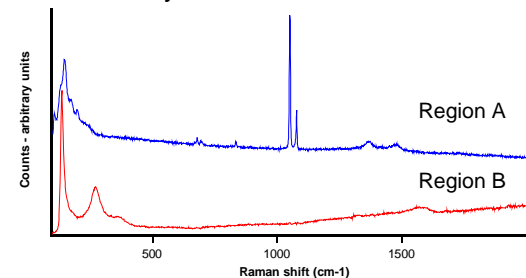


**Figure 6**  
X-ray maps collected from the area shown in Figure 5

In contrast, Raman spectroscopy is able to determine the chemical composition unambiguously and was used to probe regions of interest identified by the x-ray mapping.



**Figure 7**  
Regions of interest selected in the lead-rich layer

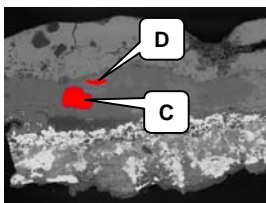


**Figure 8**  
Raman spectra from the areas shown in Figure 6

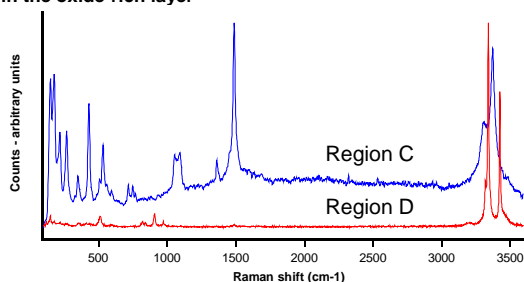
X-ray analysis of region A shown in Figure 7 showed it contained Pb, O, and C. A Raman spectrum (blue in

Figure 8) collected from the region is identified as **cerrusite** - lead carbonate  $Pb(CO)_3$ . There are also weak bands from carbon at  $1400\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$ .

The x-ray spectrum from the region B showed it contained mainly Pb, and O, with small amounts of C, Si, Ca, and Cu. The Raman spectrum (in red in Figure 8) from the region identified it as **lead dioxide** ( $PbO_2$ ).



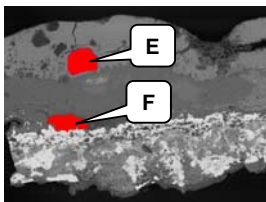
**Figure 9**  
Regions of interest selected in the oxide-rich layer



**Figure 10**  
Raman spectra from the areas shown in Figure 9

X-ray analysis from region C in Figure 9 detected Cu, C and O. A Raman spectrum (blue in Figure 10) from the region identified it as **malachite** -  $CuCO_3 \cdot Cu(OH)_2$ .

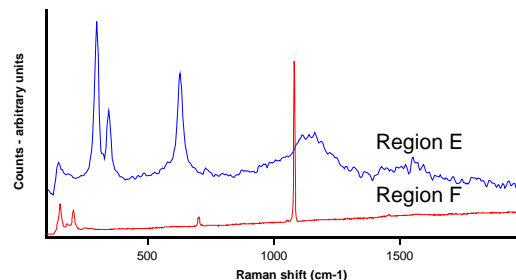
X-ray analysis from region D in Figure 9 detected only Cu, Cl, and O. The Raman spectrum (red in Figure 10) from the region identified it as **atacamite** -  $CuCl_2 \cdot 3Cu(OH)_2$ .



**Figure 11**  
Regions of interest in the oxide and copper-rich layers

X-ray analysis from the region E in Figure 11 detected Cu and O. The Raman spectrum (blue in Figure 12) from a point within the region identified it as **cupric oxide** -  $CuO$ .

The x-ray spectrum from the region F in Figure 11 indicated it contained mainly Ca, C and O but with some Si, Pb, and Cu. The Raman spectrum (red in Figure 12) from the region identified it as **aragonite** -  $CaCO_3$ .



**Figure 12**  
Raman spectra from the areas shown in Figure 11

During preservation, the conservator noted the unusual colouration of this sample. Normally bronzes form a *patina* comprising copper oxide and malachite (the latter gives the characteristic green colour).

The sample exhibits layers consistent with normal patination - copper oxide (closest to the native metal), capped with a malachite and atacamite layer (hydrated copper carbonate and chloride respectively).

There is also a lead-rich outer layer, which contains aragonite ( $CaCO_3$ ) and carbon inclusions – this is unusual.

Bronze is an alloy comprising copper and tin, but in ancient times it would also typically contain up to 20% lead. The lead does not enter into solid solution with the copper and tin and this accounts for the outer lead-rich layer. The  $CaCO_3$  inclusions and the presence of silicon are likely due to interaction with the soil in which the artefact was buried. The presence of the carbon inclusions lends credence to the theory that the city was once devastated by fire.

In this example, Raman spectroscopy carried out using NIR and VIS excitation combined with SEM observation and x-ray analysis has enabled the sample to be characterised much more quickly and thoroughly than the analytical techniques used in isolation.

X-ray analysis provides only elemental data, and although this can be quantified, the stoichiometry has to be known in advance to get the “right” answer. Whilst this approach can be effective for simple oxides, it is unreliable for hydrated compounds (atacamite -  $CuCl_2 \cdot 3Cu(OH)_2$  for example).

Backscattered electron imaging and x-ray mapping allow regions of interest to be located quickly – many of these are simply not visible to an optical microscope. The regions can then be chemically characterised using *in situ* Raman spectroscopy, and the identification can be cross-referenced and verified by comparison with the elemental data from EDS.

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## Advantages of SEM-SCA for oxidation and corrosion studies

- Raman can identify unambiguously the oxidation state and chemical composition of regions that EDS only identifies as “oxide”
- SEM visualisation can often reveal subtle variations in composition that are invisible to optical microscopy
- Raman analysis can be carried out *in situ* so that the spatial context is maintained
- EDS analysis complements Raman spectroscopy by revealing either subtle variations or consistency in concentration and the presence of trace elements
- LV-SEM observation means samples can be examined “as prepared” - subsequent analyses are not affected
- Full characterisation of sample components can be carried out quickly and easily



## Why choose Renishaw?

Renishaw is an established world leader in metrology, and has been providing high performance solutions for measurement and control since 1973. In 1992, Renishaw combined several new technologies, including its metrology expertise, into its Raman microscopes and rapidly became a world leader in the design and manufacture of Raman spectroscopy systems. Renishaw has a global network of subsidiary companies, distributors, and agents, providing a level of service second to none. Its teams of highly qualified engineers and scientists can provide you with rapid and comprehensive product, technical, and application support.

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