METALLORAMAN: CORRODED ANTIQUE AND MODERN COINS STUDIED BY RAMAN MICROSCOPY

Michel BOUCHARD* and David C. SMITH

Laboratoire de Minéralogie, Muséum National d'Histoire Naturelle,
CNRS-UPRESA7058, 61 Rue Buffon, 75005 PARIS, France (mbouchar@mnhn.fr)

METALLORAMAN © [1] has been defined as the study by Raman Microscopy of metals, but in the context of identifying the chemical constituents of the original pure or impure metal or alloy by means of characterising the various corrosion products thereof, since metals themselves generally give a poor spectrum or no spectrum at all. Raman Microscopy is potentially a powerful technique for the non-destructive analysis of precious materials, such as coins and many kinds of metallic archaeological artefacts (cutlery, tools, weapons, sculptures, statues...), since non-precious metallic objects can simply be analysed quantitatively by one of many destructive analytical techniques. The products of corrosion are varied as their nature depends upon all the physical, chemical, geological and biological factors in the different environments (in the atmosphere; under water; under soil...) to which they have been exposed since their manufacture (or since their latest cleaning event), as well as upon the important time factor. Many metallic objects are not smooth such that corrosion products may be trapped, and fortunately thus conserved for Raman Microscopy, inside surface irregularities or re-entrant angles.

Coins are the most appropriate archaeological object for this study, firstly because they constitute the most common metallic material of which we dispose, secondly because of the several advantages that they offer (small size, large diversity of metals, a wide time range from antique to modern times), and thirdly because they are easily datable. The following coins of different metallic composition have been studied; the name in brackets giving the major constituent:

- {Silver}: a Parthes drachmae of Drodes II, *57-38 BC*, ref. Sear 7441 [2]
- {Silver}: a Roman antoninianus of Elagabale, *218-222 AD*, ref. Sear 2097
- {Silver}: a 20 Francs French coin, *1933*
- {Bronze}: a small coin of Tetricus, *270-273 AD*, ref. Sear 3171
- {Bronze}: a « Barbarian » coin
- {Bronze}: a very altered Roman coin (? of Augustus' reign), *27 BC-14 AD*
- {Bronze}: a "2 Sols" French coin of Louis XVI, *1793*
- {Zinc}: a 10 Centimes French coin, *1941*

A complementary study is in progress on other archaeological materials including an iron arrowhead (probably Roman) and two iron nails (Roman & Middle Age periods, by courtesy of Mme. C. Bouclet); these all display a mineralogical zonation in their corrosion products.

Several mineral species susceptible to be found in corroded metallic archaeological objects have been analysed by Raman Microscopy to provide standard Raman spectra and to complement those available in mini-catalogues [3,4,5]. These include:

anglesite {$PbSO_4$}, antlerite {$Cu_3SO_4(OH)_4$}, atacamite {$Cu_2Cl(OH)_3$}, aurichalcite {$(Zn,Cu)_5(CO_3)_2(OH)_6$}, azurite {$Cu_3(CO_3)_2(OH)_2$}, brochantite {$Cu_4SO_4(OH)_6$}, cassiterite {SnO_2}, chlorargyrite {$AgCl$}, covellite {CuS}, cuprite {Cu_2O}, langite {$Cu_4SO_4(OH)_6.2H_2O$}, linarite {$CuPbSO_4(OH)_2$}, malachite {$Cu_2CO_3(OH)_2$}, nantokite {CuCl}, phosgenite {$Pb_2CO_3Cl_2$} & rosasite {$(Cu,Zn)_2CO_3(OH)_2$}.

Concerning silver, a reproducible band at ~243 cm^{-1} has been observed in the Raman spectra of the surface of different silver coins as well as in the spectra of chlorargyrite. The intensity per second increases with the cumulated duration under the laser beam as if a new product is being formed by heating. It is deduced that it corresponds to an effect of the laser on the silver surface (possibly a silver oxide {Ag_2O} being formed). Other bands, less reproducible but grouping together in the same wavenumber zone (570-640 cm^{-1}) appear in some spectra.

Other common materials for metallic coins are the alloys of copper (often bronze with different proportions of components). Three products of corrosion have so far been identified on bronze coins:

- cuprite (reddish) characterised by the wavenumbers: ~90, 147, 186, ~200, 218, ~ 414 (weak), ~ 525 (weak) & ~ 625 (weak) cm^{-1} [6];
- malachite (green) with bands at 118, 155, 180, 220, 270, 355, 436, 538, 722, 753, 1058 & 1094 cm^{-1} [3], but with some additional bands at 170, 512, 1370, 1492 and the O-H bands at 3308, 3377 cm^{-1}; and
- atacamite (blue-green) with bands at 122, 149, 360, 513, 821, 846, 911 & 974 cm^{-1} [4], but with some additional bands at 142, 240, 420, 450, 590 (very weak), 802, 897, and the O-H bands at 3329, 3348, 3433 cm^{-1}.

A fourth corrosion product (clear blue) is observed on the Barbarian coin: its Raman spectra presents a very wide band between 400 and 800 cm^{-1} but this spectrum has not yet been correlated with any known standard.

The zinc coin presents a very thin layer of white-grey corrosion which gives three wide Raman bands attributed to the "zinc oxide" of ref. [7] : ~330 (weak), ~ 436 and ~556 cm^{-1} (this last band is in fact composed of three bands at 525, 543 & 571 cm^{-1}).

Several layers of corrosion products occur on both the iron arrowhead, and the iron nails. The first results reveal at least the following three mineral species by means of their characteristic bands [5]:

- hematite: 225, 244, 294, 299, 411, 496, 612, 660 (very weak) cm^{-1};
- lepidocrocite: 140 (weak), 328, 250, 297 (weak), 311, 348, 380, 530, 649 cm^{-1};
- goethite: 89, 244 (very weak), 300, 287, 481 (very weak), 554 (weak) cm^{-1}.

Raman Microscopy appears to be a promising tool for metal studies, especially in archaeometry, since Raman imaging and mapping on a micron scale can reveal the succession of chemical events during corrosion; also the SERS process may occur when dealing with very thin films on noble metals (Au, Ag, Cu). It is planned to artificially "age" metals in an environmental chamber and to examine them before and after treatments. Lastly, the identification of dangerous corrosion products (such as chlorides) of ancient or recent corrosion (e.g. climatic or pollution degradation of statues) may help to indicate urgent preservation and restoration schemes. Thus Raman Microscopy can contribute to *conserving* our cultural heritage, as well as *identifying* patrimony objects.

References:

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