Proceedings of

The XVIIth International Conference on

Raman Spectroscopy

Peking University, Beijing, China
August 20–25, 2000

Edited by
Shu-Lin Zhang and **Bang-fen Zhu**

WILEY

NEW DATA FOR THE APPLICATION OF NON-DESTRUCTIVE RAMAN MICROSCOPY TO ARCHÆOLOGICAL CORRODED METALLIC OBJECTS.

M. Bouchard*, D. C. Smith

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

The efficiency of Raman Microscopy (RM) in the study of archæological or artistic objects has already been established [e.g. Smith *et al.*, 2000]. From the study of famous paintings [Guineau, 1987; Smith *et al.*, 1999a] to the study of archaeological human skin [Edwards, 1996] many research fields exist, such as gems [Pinet *et al.*, 1992], ivories [Brody *et al.*, 1998], stained-glass [Smith *et al.*, 1999b], etc..

Another new application has been developed for metallic materials. If the study of the metal itself is very difficult, if not impossible, by Raman Microscopy, the identification of the associated corrosion products is easy. In this way the first studies were made on the corrosion of copper water pipes, on the corrosion of nickel-chrome alloys in tooth fillings or on the corrosion of galvanised iron [e.g. Phillips, 1993; Abourazzouk, 1996], but these all concern modern and industrial materials. Specific applications to archæological metals appeared recently [Bouchard & Smith, 1999; McCann *et al.*, 1999] since the same chemical processes and analytical methodologies are applicable.

Thus RM presents itself as a vital polyvalent non-destructive transportable tool for:

- Identification : characterising the physico-chemical and mineralogical nature of different corrosion products for interpreting the corrosion process(es).
- Prevention : detecting the active and dangerous corrosion products on the supposed "saved" material.

The different objects involved in this study are physically, temporally and geographically heterogeneous. They are constituted of modern or antique coins, Mesoamerican objects from the "Département d'Amérique" of the French "Musée de l'Homme" (bronze masks, bronze ceremonial axes, mirror made of pyrite, silver vases, ...), medieval buckles, or diverse artefacts from the Roman or Middle Ages (arrows, spears, nails, etc.) (work in progress). The metal composition of this material is also variable: gold, silver, platinum, copper, tin, lead, zinc...

The two main aims of this work are: (a) the identification of the different corrosion products with the goal of tracing the corrosion process specific to each sort of corrosion species; and (b) the detection of dangerous corrosion products which could evolve and still endanger the object. Nine samples are presented here with their various associated corrosion products (see Table). The products (including some less common species like connellite) have been identified by comparison with existing literature or with our own mini-library of Raman spectra of corrosion products (in prep).

TABLE: Raman bands of some archæological corrosion products of metal.

Material & Period	**Chemical formula**	**Wavenumbers of the main peaks (/cm^{-1})**
Roman lead sheet	$Pb_3(CO_3)_2(OH)_2$	***hydrocerussite*** (~ 300, 400, 420, 1049, 1380, 3532 cm^{-1})
Roman or medieval lead sheet	PbO	mixture of ***litharge*** (145, 285, 336 cm^{-1}) & ***massicot*** (143, 289, 385 cm^{-1})
Roman or medieval mineralised copper alloy tool	Cu_2O	***cuprite*** (~90, 147, 186, ~200, 218, ~ 414 (weak), ~ 525 (weak) & ~ 625 (weak) cm^{-1})
	$Cu_3(CO_3)_2(OH)_2$	***azurite*** (136, 155, 175, 250, 267, 285, 335, 404, 543, 740, 765, 839, 940, 1098, 1295, 1424, 1458, 1579 cm^{-1})
	$Cu_2CO_3(OH)_2$	***malachite*** (155, 180, 220, 270, 355, 436, 512, 538, 722, 753, 1058, 1094, 1370, 1492, 3308, 3377 cm^{-1})
	$Cu_4SO_4(OH)_6.2H_2O$	***langite*** (171, 195, 230, 242, 320, 365, 389, 430, 449, 483, 506, 597, 610, 620, 730, 769, 785, ~845, 911, 974, 1077, 1099, 1125, ~3259, 3369, 3398, 3563, 3585 cm^{-1})
	$Cu_3SO_4(OH)_4$	***antlerite*** (145, 173, 216, 230, 250, 268, 297, 340, 417, 444, 470, 483, 502, 605, 630, 750, 785, 843, 989, 1077, 1134, 1171, 3487, 3579 cm^{-1})
Roman or medieval small copper alloy nail	$Cu_{19}Cl_4SO_4(OH)_{32}.3H_2O$	***connellite*** (~255, 404, 984 cm^{-1})
Precolombian feline copper mask	$Cu_2CO_3(OH)_2$	***malachite***
	$Cu_2Cl(OH)_3$	***atacamite*** (149, 357, 412, 449, 510, 582, 820, 842, 911, 974, 3328, ~3350, ~3440 cm^{-1})
	$Cu_2Cl(OH)_3$	***paratacamite*** (149, 365, 420, 449, 510, 582, 802, 894, 910, 930, 974, 3310, ~3350, ~3440 cm^{-1})
Roman Tetricus bronze coin		***cuprite***, ***malachite***
Precolombian bronze weapon		***paratacamite*** / ***atacamite***
17th century Louis XVI coin		***cuprite***, ***malachite***, ***paratacamite***
Roman or medieval iron arrow head	α-Fe_2O_3	***hematite*** (225, 247, 293, 299, 412, 498, 613 cm^{-1})
	γ-FeO(OH)	***lepidocrocite*** (245, 373, 493, 522, 650 cm^{-1})