Application note

Terrain mapping for Raman imaging of copper patinas on irregular surfaces

Introduction

Terrain mapping is a Raman imaging technique where the vertical position of the microscope stage is adjusted to keep the sample in focus while collecting data across irregular or tilted sample surfaces. A tightly focused laser spot provides higher laser power density, which gives more Raman intensity from the analysis volume. Maintaining a tight laser focus while moving across a sample ensures good spatial resolution and Raman intensity.

An advantage of Raman imaging is the ability to visualize the spatial distribution of a component/components across a sample area. Variations in sample focus during imaging complicate the interpretation of Raman intensity, as it is difficult to differentiate the changes in intensities associated with the sample itself from those caused by fluctuations in sample focus. A significant loss of Raman intensity and spatial resolution can also affect the quality of the Raman spectra and the ability to use the spectral data as a spatial or spectral identification tool.

Typically, flat samples are the most ideal for Raman imaging because the focus is preserved when moving across the sample. However, it is not always possible or practical to produce flat samples. (i.e., the physical nature of some samples might prevent the generation of a microscopically flat surface.) Some samples, such as coatings, could be damaged or completely removed when trying to produce a flat surface. In other cases, the sample cannot be modifier because it needs to remain intact and unaltered. Even if there are no restrictions in terms of what can be done to a sample, the methods required for producing microscopically flat samples are, at times, too complicated and time consuming to be practical. It is therefore necessary to have a way of imaging rough, sloped, or uneven samples by using methods such as terrain mapping.

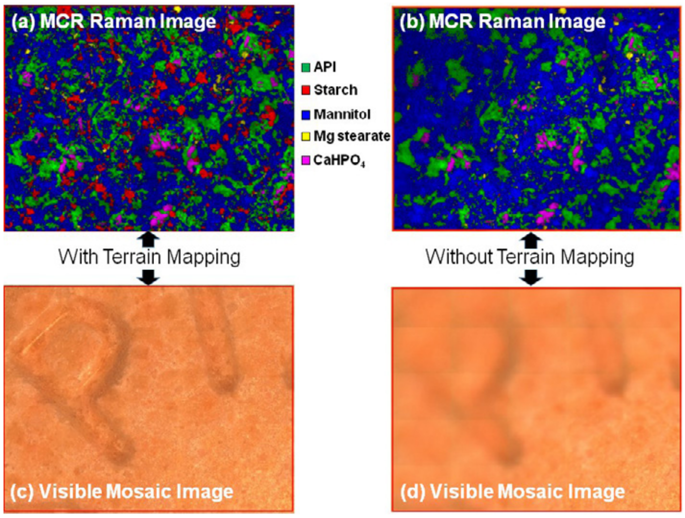

Figure 1. Raman imaging of a tablet surface with and without terrain mapping. A) Multivariate curve resolution (MCR) Raman image collected with terrain mapping. B) MCR Raman image collected without terrain mapping. C) Composite visual mosaic image using terrain mapping. D) Visual mosaic without terrain mapping.

The effect of terrain mapping can be seen in Figure 1, which shows a curved tablet with letters stamped into its surface. With terrain mapping, sample focus is maintained across the sample surface; this is clearly seen when comparing the visual mosaic images. Maintaining good sample focus also affects the Raman MCR (multivariate curve resolution) image; the image collected with terrain mapping shows much better definition of the sample components. The component particles in the image without terrain mapping are not as distinguished and some component particles are missing altogether.

thermo scientific

This application note will show how terrain mapping can be used to analyze thin films (patinas) formed on uneven copper surfaces. Patinas can form by natural exposure to environmental conditions (air, acid rain, salt water, etc.) but they can also be intentionally created to give objects the appearance of age or to create textures or colors. Copper patinas form as a result of oxidation of the exposed surface, but the exact nature of the compounds formed depends on how the patinas develop. The presence of different copper oxides (Cu_2O and CuO) as well as hydroxide, carbonate, chloride, nitrate, and sulfate can all give an indication of the formation mechanism, and thus, the source of the patinas.

Figure 2. United States one-cent coin (penny).

Experimental

The samples used in this application note are United States one-cent coins (pennies) (Figure 2). The minting process results in raised number and letters above the surface of the penny and provides an easily recognizable example of how terrain mapping can be used with uneven surfaces. The current version of the penny consists of a copper layer over a zinc interior. Four pennies were intentionally exposed to a range of conditions to generate different types of patinas. While these patinas were created intentionally, they do involve constituents found in naturally occurring patinas.

Portions of the pennies were imaged using a Thermo Scientific™ DXR3xi Raman Imaging Microscope employing the terrain mapping feature of Thermo Scientific OMNICxi Software. A 455 nm laser was used because it produced spectra with the best combination of low fluorescence artifacts and high Raman intensity.

The first step in terrain mapping is to collect visible mosaic images of the sample at different focal points, spanning the lowest to highest points in the area of interest. This data is then used to create a terrain mosaic where pixels from the various in-focus points are combined to produce a composite visual image containing all the points in focus. The vertical stage positions of the in-focus points are then used during Raman data collection to ensure that the Raman spectra are collected with the sample surface in focus.

The focal position information is retained so that a 3D representation of the sample surface can be displayed, and the Raman imaging data can be superimposed on top of it.

Penny	Conditions	Focal range (µm)	Interval (µm)	Objective	Figure
1	Gentle heating (150°C, 30 min)	150	3	20x	3
2	Heating to 250°C	95	0.7	50x	6
3	Ammonia vapor (room temperature)	74	0.7	50x	8
4	Exposure to carbon dioxide in air	31	3	20x	10

Table 1. Sample treatment conditions and terrain mapping details

Results

Table 1 shows the conditions used to generate the patinas as well as the parameters for collecting the terrain mosaics. The focal range is the total vertical distance the stage was moved from the highest to the lowest focal point, and was based on the highest and lowest points of the sample in the area of interest. The interval indicates the increments the stage position was moved through the focal range and is based on the objective's depth of field. The figures show both a 2D and 3D representation of the terrain mosaics.

Table 2 provides details on the parameters used for Raman data collection as well as identified components. The step size is the horizontal spacing between points across the sample surface and was selected based on the objective used and the size of the area analyzed. The Raman images generated from the spectral data are superimposed on top of the 3D representations of the terrain mosaics in the figures.

Penny	Area imaged (µm)	Step size (µm)	Number of spectra	Components	Figure
1	3475 × 1535	10	53592	Cu_2O	4
2	940 × 630	5	24003	Cu_2O, CuO	7
3	930 × 1040	5	39083	Cu_2O, $Cu(OH)_2$	9
4	1515 × 1580	10	24168	Cu_2O, $CuCO_3(OH)_2$	11

Table 2. Raman imaging parameters and components identified

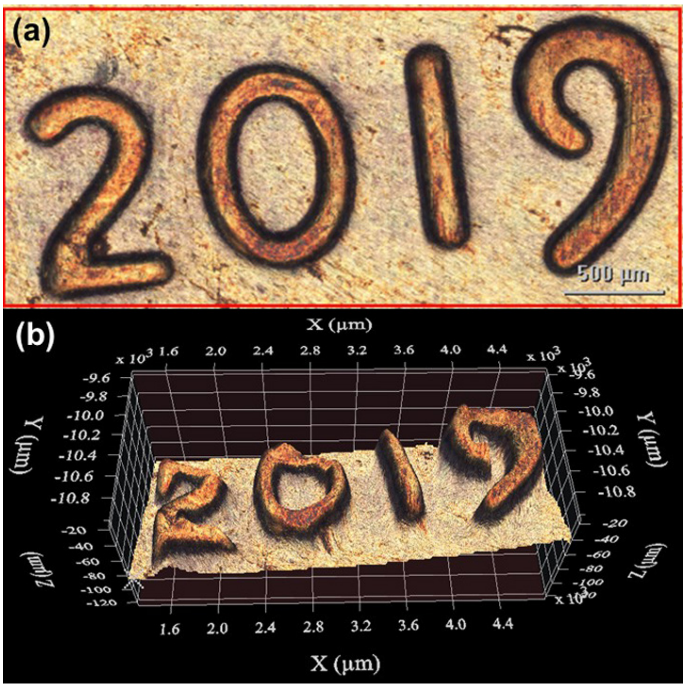

Figure 3. Visible terrain mosaic from Penny 1. A) 2D image. B) 3D image with the z-axis expanded to demonstrate surface topography.

Penny 1 was heated gently until a slight change in surface coloration was observed. Figure 3 shows an area of this penny with raised numbers (the year the penny was minted) as well as a slightly tilted surface. The z-axis in the figure has been expanded to better show the topographical features of the sample.

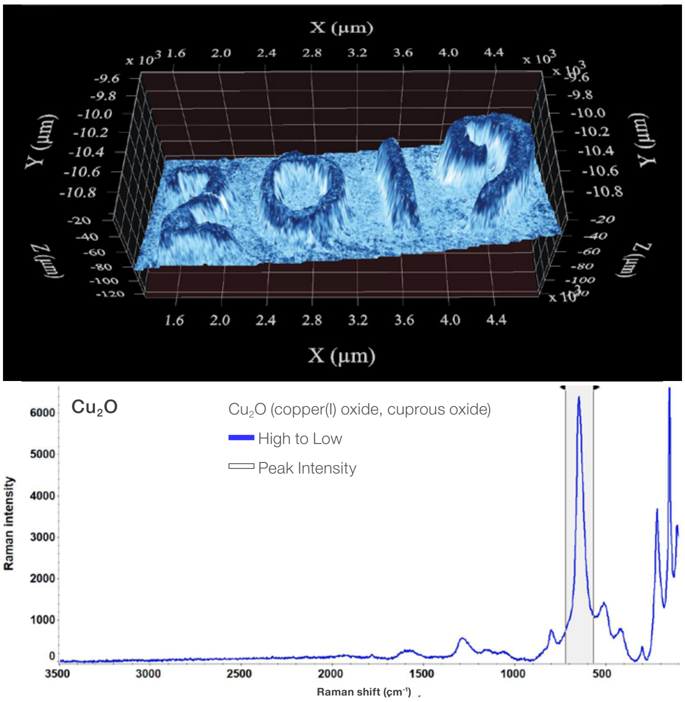

Figure 4. Raman peak area intensity image from Penny 1 based on the Cu_2O peak at 645 cm^{-1}.

The Raman image shown in Figure 4 was generated from the peak area intensity of the 645 cm^{-1} peak associated with Cu_2O, which was detected across the whole surface but with varying intensity. The darker blue areas in the figure indicate a higher concentration on the tops of the numbers compared to the lighter blue and white areas. Note that copper metal itself is not Raman active so the thin coating of oxide is what allows for Raman visualization of the surface.

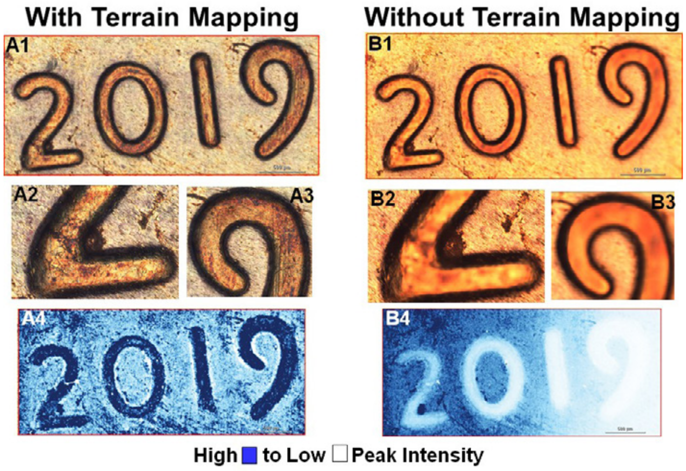

Figure 5. Comparing results collected with terrain mapping (A1-A4) and those collected at a single focal point without terrain mapping (B1-B4). A1-A3 and B1-B3 are visual mosaic images. A4 and B4 are Raman images based on the peak area of Cu_2O at 645 cm^{-1}, where the darker blue color indicates higher peak intensity and white represents lower peak intensity.

Figure 5 illustrates the advantages of terrain mapping. It is clear that using a single focal point for collecting both the visual (Figure 5B 1-3) and Raman (Figure 5B 4) images results in significantly poorer results than terrain mapping (Figure 5A 1-4). There is a loss of visual detail as well as significant loss of Raman peak intensity. The raised numbers and tilt of the sample observed in Figure 3 and 4 clearly affect both the visual and Raman data. Images in Figure 5 were collected using a 20x objective; at higher magnifications the effect of sample topography should be even more pronounced.

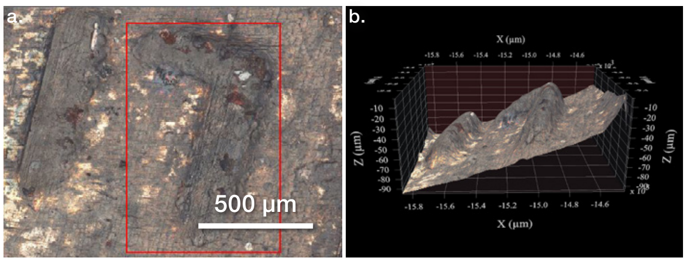

Figure 6. Visible terrain mosaic from Penny 2. A) 2D image. B) 3D image with the z-axis expanded to demonstrate surface topography.

Along with Cu_2O, cupric oxide (CuO) is another product of copper oxidation. Heating Penny 2 at a higher temperature produced a darker color consistent with the formation of CuO. Figure 6 shows the terrain mosaic of the letter "L" in the word "liberty" on Penny 2. The Raman analysis of this sample also indicated that both Cu_2O and CuO were present.

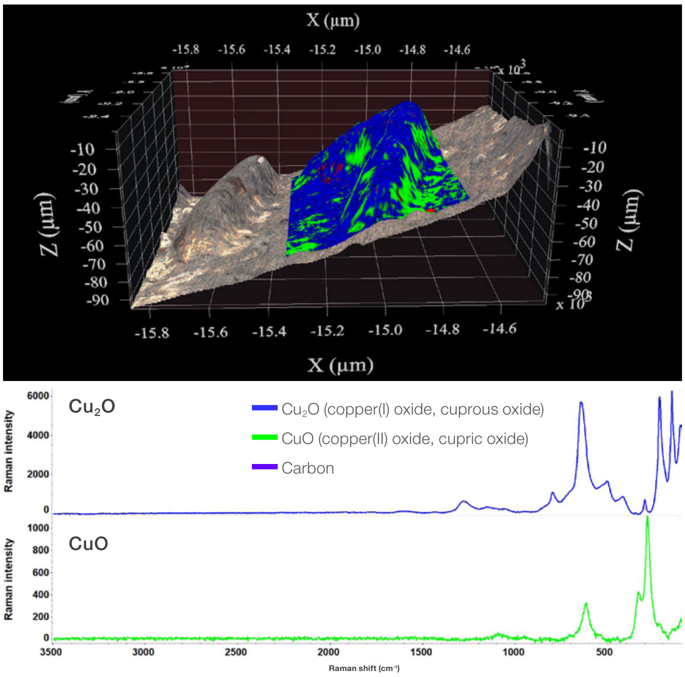

Figure 7. Raman MCR image from Penny 2 with Cu_2O shown in blue and CuO shown in green.

The Raman image shown in Figure 7 was generated from a multivariate curve resolution (MCR) analysis of the Raman spectra, which can be used to identify different components without prior knowledge of their spectral features. A few spots of carbon were also observed and could have come from organic material on the penny decomposing during heat treatment.

When copper or bronze surfaces are exposed to basic solutions, blue copper (II) hydroxide ($Cu(OH)_2$) can form. Copper hydroxide is amphoteric and will dissolve in some aqueous solutions. Penny 3 was exposed to aqueous ammonia vapors to produce a $Cu(OH)_2$ containing patina.

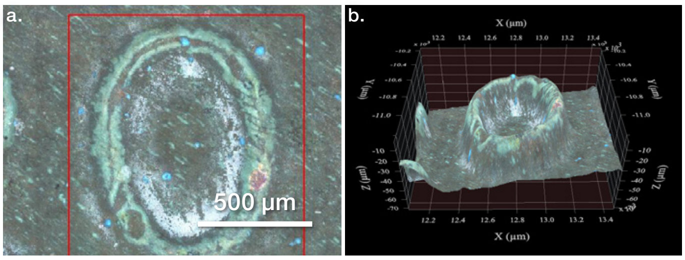

Figure 8. Visible terrain mosaic from Penny 3. A) 2D image. B) 3D image with the z-axis expanded to demonstrate surface topography.

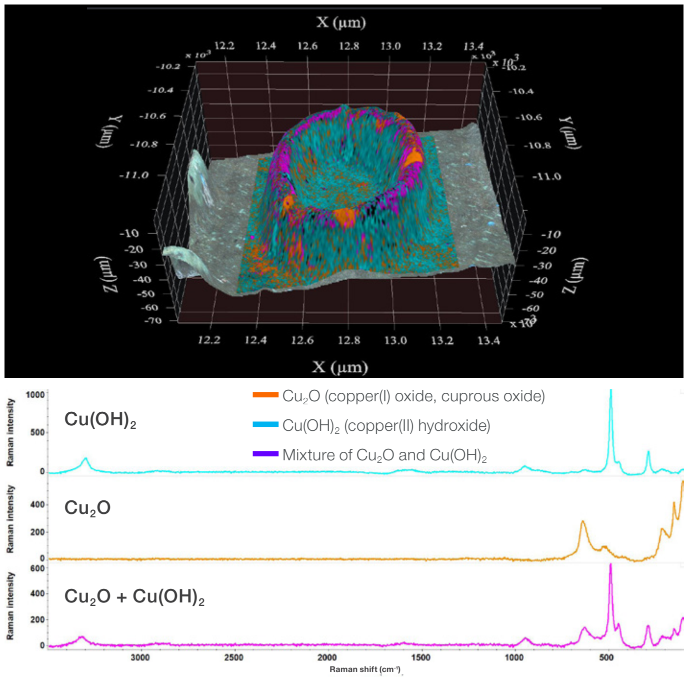

Figure 9. Raman MCR image from Penny 3 with Cu_2O shown in orange and $Cu(OH)_2$ shown in cyan. Mixtures of both are indicated in purple.

Figure 8 shows a terrain mosaic of a “0” embossed on that penny; Raman analysis showed the presence of $Cu(OH)_2$ on the copper surface. In the MCR Raman image in Figure 9, $Cu(OH)_2$ is concentrated in the blue areas, Cu_2O is present in the orange areas, and the purple areas show a mixture of both components.

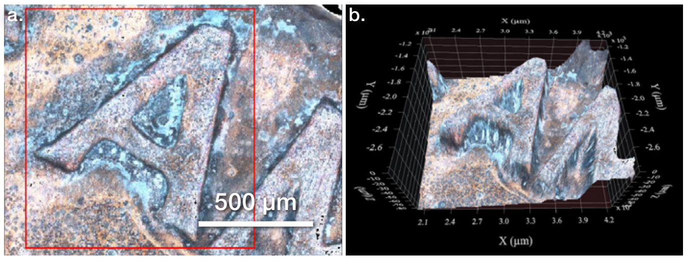

Figure 10. Visible terrain mosaic from Penny 4. A) 2D image. B) 3D image with the z-axis expanded to demonstrate surface topography.

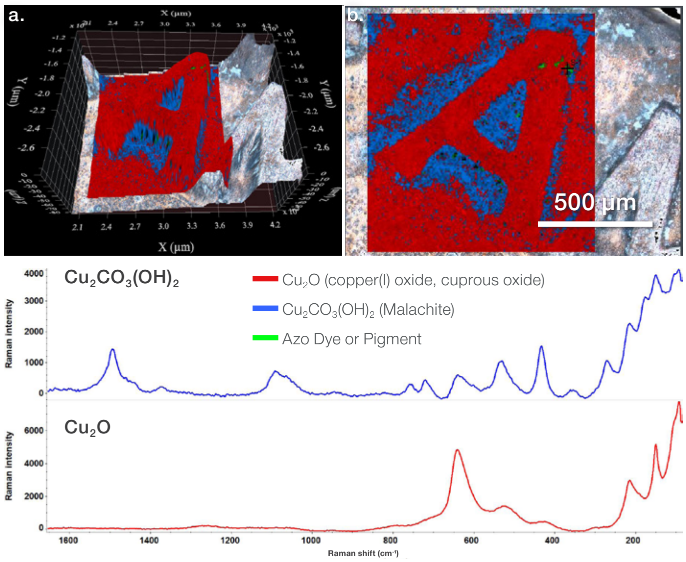

Figure 11. Raman MCR image from Penny 4. Cu_2O is shown in red and $Cu_2CO_3(OH)_2$ is shown in blue. A) Raman data superimposed on the 3D terrain mosaic. B) Raman data superimposed on the 2D terrain mosaic.

While copper hydroxide can be found as a component in copper patinas, it is more likely to appear if the patina forms slowly over time. Carbon dioxide from the air will form copper hydroxides that contain carbonate. Examples of these reactions include the formation of minerals like malachite ($Cu_2CO_3(OH)_2$) and azurite ($Cu_3(CO_3)_2(OH)_2$). Figure 10 shows a terrain mosaic of the letter "A" embossed on Penny 4; the MCR Raman image can be seen in Figure 11. $Cu_2CO_3(OH)_2$ was detected around the base of the letter "A" while primarily Cu2O was found on top of the letter. There were also a few small spots (the green areas in the image) that appear to be some type of azo dye or pigment. While not expected, it is interesting that this dye/pigment was present on the surface of the penny.

Conclusions

For various reasons it is not always desirable, feasible, or practical to flatten samples for Raman analysis, so it is important to have a method to preserve sample focus during Raman imaging of irregular surfaces. This way, the Raman intensity is retained as well as the spatial resolution. The use of terrain mapping was demonstrated through the analysis of patinas on copper pennies, as coins have surface structures formed during the minting process. Copper patinas were produced through surface oxidation under a range of different conditions. The ideas presented in this application note can be extrapolated to the study of a wide variety of thin films on numerous materials. Terrain mapping applications can include, but are not limited to, the study of art and cultural heritage objects, metal corrosion, and thin films on irregular surfaces.

Learn more at **thermofisher.com/raman**