

PORTABLE RAMAN SPECTROSCOPY IN ARCHAEOLOGY AND ART

APPLICATION NOTE RAMAN-004 (A4)

Author: A.J.R. Bauer, Ph.D.

Abstract

Raman spectroscopy is an important instrument in the arsenal of art conservators and archaeologists. This application note summarizes some recent literature on the selection of portable instruments in this field and also documents some successful work done utilizing background correction to elucidate the composition of some challenging green pigments.

Background and Motivation

The stewardship of cultural heritage, involves the conservation, protection and restoration of tangible artwork, archaeological artifacts and museum collections. The need to protect and preserve valuable works of art is clear, and has been a focus of museum activity for centuries. Within the last 150 years, the field of art conservation has increasingly included scientists, whose emphases are as varied as a better understanding of the action of environmental damage to methods to clean artworks without harming them. It could be said that the profession of art conservation was begun in 1888, when the Koniglichen Museen in Berlin hired chemist Friedrich Rathgen. It was there he published the first handbook of art conservation (Die Konservierung von Altertumsfunden) in 1898. His legacy today stands with the Rathgen Research Laboratory, the world's oldest scientific museum laboratory.

Today, art conservation is very tightly intertwined with science, and along with it technology. The modern art conservation lab is very similar to any other type of analytical chemistry lab, and includes the use of Raman spectrometers, gas chromatography mass spectrometers (GC-MS), high performance liquid chromatographs (HPLC), scanning electron microscopes with energy dispersive X-ray spectrometers (SEM-EDS), inductively coupled plasma mass spectrometers (ICP-MS), X-ray diffractometers (XRD) and X-ray fluorescence spectrometers (XRF). Spectroscopic and imaging techniques are now no longer used only in the museum environment, but also in the field. This addresses the many archaeological specimens that will never be removed to a museum, having been built into infrastructure or otherwise permanently affixed in a similar way. The primary goal of art analysis, wherever performed, is to extract as much information as possible from the object without causing damage. In keeping with this goal, nondestructive spectroscopic tools like XRF and Raman spectroscopy are of particular value. These two techniques have been successfully miniaturized and made rugged for field use and are frequently employed together, as they produce complementary data. The XRF is used to establish the elemental composition of an object or portion of an object, while Raman spectroscopy gives data descriptive of the molecular structures involved in the material.

The focus of the work presented here, Raman spectroscopy, can be used to identify both organic and inorganic materials, and can therefore readily distinguish newer synthetic pigments from traditional ones that are largely made from ground minerals. Raman spectroscopy has been applied to a vast array of matrices, and has been successfully utilized in the study of complex mixtures in paintings^{1,2}, ceramics^{3,4}, manuscripts^{5,6}, gemstones⁷, glass⁸, wall paintings^{9,10} and rock art¹¹. These studies provide data that can be used to date artwork and to identify counterfeits. Raman spectroscopy has also been used to identify the impacts caused by environmental factors and restorations. Raman mapping has even been utilized to assess the efficacy of innovative stabilization treatments. An example of this application can be found in Joseph and coworkers' study demonstrating that the fungus *Beauveria Bassiana* precipitates copper oxalates when applied to soluble copper patinas such as hydroxysulfates.¹²

Raman spectroscopy is so useful in art and archaeology that there have been recent reviews by well-known researchers in this field on available instruments applied to measurements outside the laboratory.² The majority of the instruments that have been reviewed are commercially available. These publications naturally focus on those features that are most useful to those working with Raman spectrometers in the conservation field. Colomban's recent review begins with a historical brief from the first commercially available Raman instrument, Molecular Optics Laser Examiner (MOLE) from Lirinord (now Horiba) to today's portable and hand-held units.¹³

He then discusses the pros and cons of using portable instruments to perform art conservation measurements outside the laboratory. Amongst the successes, he identifies the benefits of optical fiber delivery permitting study of large and immovable objects or those in awkward places, like stained glass windows, sculptures, wall paintings and rock art. Portable instruments, which he identifies as those that are sufficiently small and free of any moving parts, therefore readily relocated and deployed, also typically do not require much time to set up. Lastly, he states his interest in those optical heads that contain cameras, which allow control of the illuminated area but recognizes that the addition of the camera increases overall weight and size.

In terms of the drawbacks of the portable instruments, Colomban points out that compact optical instruments cannot be expected to compete with larger, laboratory-sized versions. In particular, he focuses on the greater control over system noise in the case of liquid nitrogen cooled detectors over those chilled with a Peltier cooler. The resolution of laboratory instruments is often better because longer spectrographs can be utilized, but this is not done in portable units due to the added size and weight. At the time that Colomban wrote his review in 2012, excitation wavelength removal was chiefly performed with edge-filtering, limiting the collected Raman spectrum on the low side to 250-200 cm^{-1} . Since his description, better edge filters have been developed and released, enabling Raman Stokes spectra to be acquired using portable instrumentation between 50 and 100 cm^{-1} from the excitation line.¹⁴

A more structured review of available portable Raman instrumentation (all but one commercially available) for use in art conservation applications was done by a group of three European universities in 2007 and documented by Vandenabeele, et al.¹⁵ Five different instruments were tested on a suite of samples at Ghent University, University of Bradford and the University of the Basque Country at Bilbao. These instruments ranged from larger portable units (28 kg) to hand-held units (2 kg), but they all had excitation lasers operating at 785 nm.

The study tested the instruments for spectral resolution (neon lamp), Raman shift calibration (polystyrene beads) and made measurements of TiO_2 which has Raman features very close to the excitation line (white paint on cardboard). Additionally, samples of yellow azo-pigment on cardboard were used to demonstrate measurements of organic pigments and pigments through varnish. Lastly, they covered the bottom of a ceramic container with beeswax to demonstrate Raman measurements requiring a probe head.

The researchers found that while the low weight of hand-held units made them very useful in places otherwise inaccessible to spectroscopic instrumentation, they lacked sufficient resolution to differentiate between many important minerals. In general, they preferred the flexibility of the larger portable instrumentation, stating that miniaturization is important, but that the performance cannot be unduly compromised in its pursuit. Lastly, the authors state that it was

desirable to have an instrument with two laser sources (514.5/532 and 785 nm) for the best outcomes in artwork analysis, in order to accommodate commonly encountered blue and green pigments for which the green lasers are often necessary.

Last year, a subset of the researchers that performed the above comparison also reviewed the EZRaman I-Dual (Enwave, now TSI Incorporated) during the course of their description of characteristics necessary for a portable Raman instrument to be applicable to archaeometric analysis.¹⁶ Indeed, during the course of this work, the group submitted the EZRaman-I to many of the same tests described in the 2007 publication. The evaluated model has two excitation lasers, one doubled Nd:YAG at 532 nm and one frequency-stabilized diode laser (785 nm). The spectral range of the spectrometer is, of course, contingent on the wavelength of the excitation laser, and is 100-2350 cm^{-1} for the 785 nm laser and 100-3200 cm^{-1} for excitation in the green. The instrument was delivered with a variety of accessories to enable different working distances to be used.

The instrument was submitted to testing that included spectral resolution and range (neon lamp and a sample of anatase), and a test of calibration of reported Raman shift (five standards having ASTM-reported reference values).¹⁷ The results show that spectral resolution was accurately stated upon delivery, and that the $\text{CO}_3 \nu_1$ symmetrical stretch in calcite, aragonite, dolomite and magnesite can be differentiated, even though they vary by less than 10 cm^{-1} . This is accomplished through the use of careful calibration in the 700 cm^{-1} region where the $\text{CO}_3 \nu_4$ bend appears. Figure 1 shows where the calibration comparison curve deviates slightly from linear at about 500 cm^{-1} . Vandenberg and coworkers also monitored stability of wavelength readings and laser output, and found them to be highly reproducible.

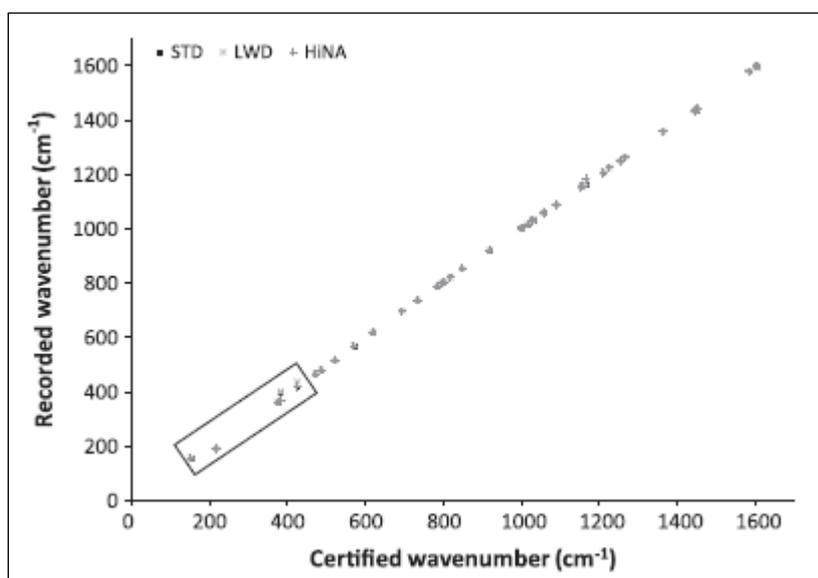


Figure 1. Acquired Raman shift (cm^{-1}) from standards vs certified Raman band positions, excited with the 785 nm laser.

The authors also developed a test which can be used to compare the sensitivities of Raman systems. This is an important metric, as a more sensitive spectrometer permits shorter measurement times at lower laser powers. This in turn permits data to be collected without undue exposure of a valuable, and likely fragile, object to laser excitation. Additionally, sensitive measurements can also expose materials present in lower concentrations, such as degradation products, during the identification of the dominant components.

This test is based upon the creation of mixtures of well-known concentrations of lead tin yellow pigment type I (Pb_2SnO_4) and vermilion (HgS) in NaCl matrices. Curves of growth are created and measured under conserved conditions.¹⁶ Through the use of this clean and fluorescence-free matrix, limits of detection (LOD) were easily calculated using the definition given in equation 1 below.

$$LOD = 3 \times \sqrt{I_{Raman} + I_{Signal}} \quad \text{Eqn. 1}$$

The LODs were calculated using the most intense Raman band (120 cm^{-1} and 252 cm^{-1} for lead tin yellow type I and vermilion, respectively). These limits of detection were reported as 9.8 mg/g for lead tin yellow type I and 43.8 mg/g for vermilion. The conditions used in this paper could easily be used to compare instruments under evaluation before a purchase.

This work also encompassed a field test where the TSI EZRaman-I was used to examine pigments in a medieval wall painting on the outside walls of a church in Pianazzola, Prov. Di Sondrio, LO, Italy. The device was used in bright sunlight while positioning the probe by hand, and it successfully identified ultramarine and calcite and also discovered some features of gypsum, perhaps caused by reaction of calcite with acidic atmospheric components.

An EZRaman-I instrument has also been utilized in the field for pigment identification by Donais and coworkers.¹⁸ They have paired Raman spectra from fresco pigments with XRF signals and fused the data to identify and classify pigments found at the Coriglia

archaeological excavations, near Orvieto, Italy.⁷ The fresco pigments identified thus far at Coriglia – vermilion, various ochres, gypsum, and hematite – are typical to Roman frescos and wall paintings. These materials are indicative of the ancient origin of these sites; the first pigments to be used in artistic endeavors were ground and processed minerals.

Transport of archaeological artifacts away from an excavation site can be extremely difficult, due to a myriad of practical and political constraints. The use of portable instrumentation, therefore, is needed to study many such sample types. Donais' work shows how portable Raman and XRF tools can be used in tandem to generate spectral data fused to create more robust data sets. These combined data sets (both low and high voltage XRF and high voltage merged with Raman data) helped to correct for the tendency of the high voltage XRF to penetrate too deeply into (and through) the pigments, picking up fresco substrate material and signals from adhered soil.

With the data collected, the chemical makeup of most of the pigments was discovered successfully through comparison with known standards. The exception to this success was green pigments, which were fluorescent and not amenable to Raman spectroscopy. Representative spectra are shown in Figure 2. The bright pink pigment was shown by both instruments to be vermilion (HgS), the purple was α - hematite (hydrated Fe_2O_3). The brick red pigment and light pink pigments had similar components; the red compound was red ochre and was probably lightened with the

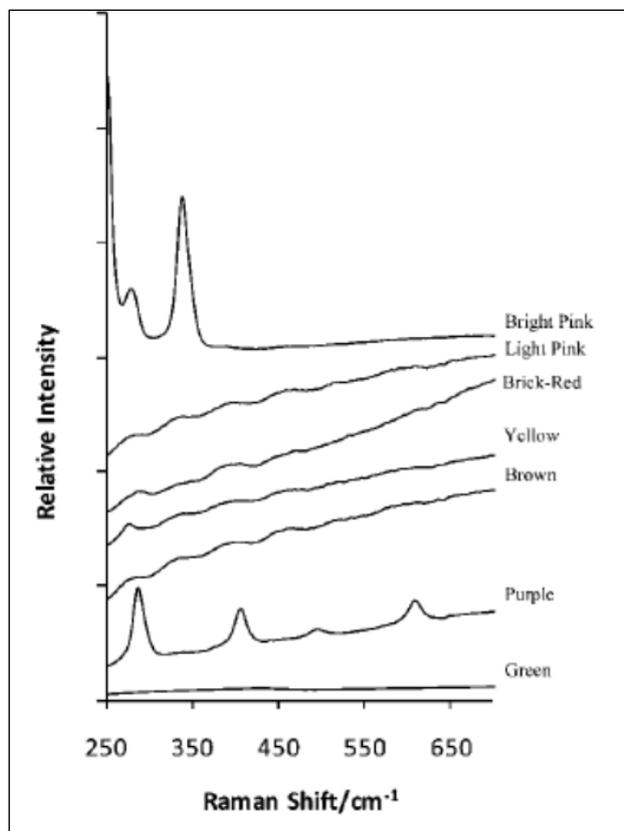


Figure 2. Raman spectra of fresco pigments from Donais et al.¹⁸

addition of gypsum or chalk. The brown and yellow pigments were ochre also, with the possible addition of some orange mineral pigment in the yellow samples (Pb_3O_4 and As_2S_3) to enhance the color.

Given the basic data, Donais and coworkers used combined data sets to improve the identification of the pigments. Initial steps involved correcting for XRF live time and comparisons of full spectra and integrated peak area were performed. Principal component analysis (PCA) was used to extract and compress the data variance and spatially look for data clustering. In some cases, the addition of the Raman spectra improved the differentiation between two types of pigments, as shown in Figures 3 and 4. In other cases, when the Raman signal levels were low, namely in the ochres and the terre verte, the fused data was not better than the XRF alone.

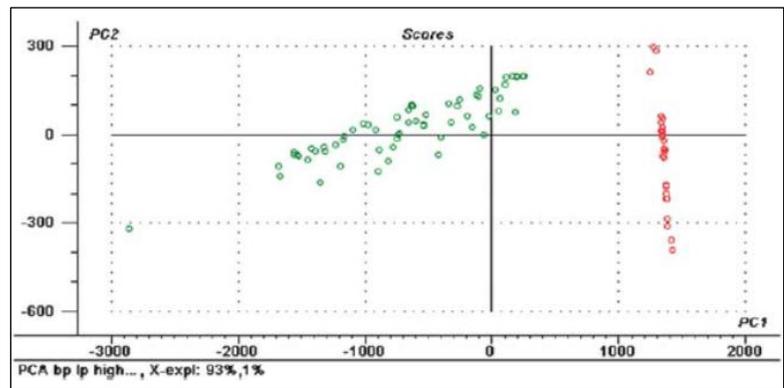


Figure 3. PCA scores plot for XRF data only on bright pink and red pigments.¹⁸

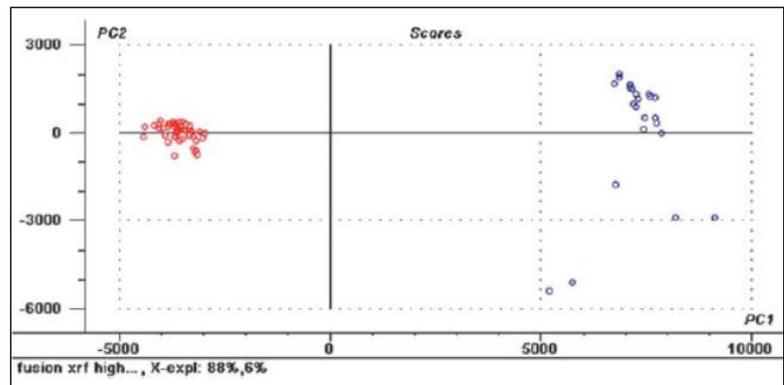


Figure 4. PCA scores plot for fused XRF and Raman data for bright pink and red pigments, showing better separation than XRF data alone.¹⁸

Given the benefits of Raman data to the field of art conservation, TSI personnel was interested in the improvement of some existing Raman spectra with the correction of fluorescence background. In a collaborative effort using Dr. Donais' data, TSI application engineers used their currently available background correction algorithms to improve the clarity of the available data. Using data presented in Figure 2, we applied the background correction algorithm, without in addition,

correcting for the system response curve. This algorithm performs a smoothing function on the data as the first step; it then finds the spectral minima, and conducts several iterations to identify the best curve to subtract. These results are shown in Figures 5 and 6. The removal of the background makes the identity of the primary compound clearer, and also clarifies the presence of a carbonate feature at about 1085 cm^{-1} . The spectrum of the vermilion (red, HgS) and calcite (CaCO_3) in the light pink spectrum were similarly treated. The spectra of the green pigments were more difficult, due to the dominance of the fluorescence.

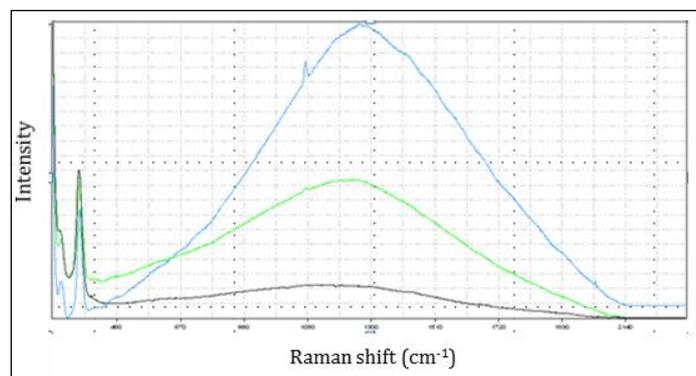


Figure 5. Raw Raman spectra acquired from purple pigment in the text (blue line), plotted with a standard α -hematite standard (black line). A carbonate feature is seen at 1085 cm^{-1} .

Because of this difficulty, several pigments known to be used during ancient, medieval and Renaissance periods were purchased and tested at TSI. The purpose of this work was to determine the effectiveness of the TSI background removal algorithm in the face of the difficulty presented by these fluorescent materials.

The tested green pigments were celadonite and terre verte, along with red ochre (α -hematite) and vermilion (HgS), and were purchased from Natural Pigments²⁰ and Kremer's.²¹ Both watercolor pan and powdered forms were obtained. Using a TSI ProRaman-L at 785 nm (spectral range from 100-3300 cm^{-1}) at very low excitation laser powers due to the dark and absorptive nature of the samples, and long acquisition periods (as much as 5 minutes accounting for the averaging), we successfully collected spectra on these samples. In addition, we also measured the samples' elemental composition with an Olympus hand-held XRF.

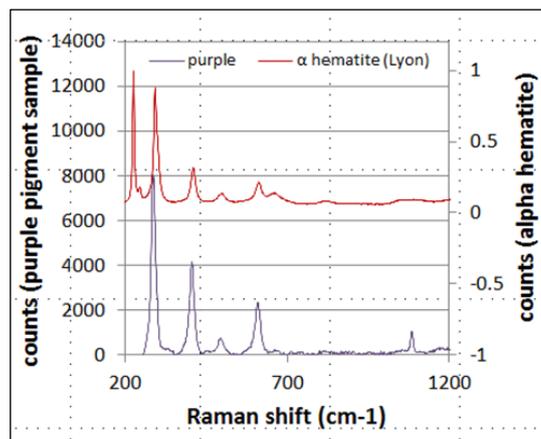


Figure 6. Background corrected spectrum for purple pigment, plotted with α -hematite spectrum from the Lyon Raman database.¹⁹ The carbonate feature is much more easily seen.

Early results are very promising. The tendency of the sample to burn and the fluorescence usually accompanying green mineral pigment Raman spectra were mitigated through the use of the low laser power, yielding data that is readily comparable to spectra obtained from mineral databases. Spectra of powdered terre verte and watercolor pan celadonite are shown in Figures 7 and 8. Interestingly, pure mineral celadonite does not contain iron, but the Natural Pigments watercolor material does, as discovered in the XRF analysis of the material. This result is confirmed because of the close match of the Raman spectra to those found in the database as ferroceldonite (Figure 7). The results of the Raman studies on terre verte material were also of interest. These data are shown in Figure 8, and seem to indicate that terre verte is also partially ferroceldonite, present with some other as-yet unknown minerals.

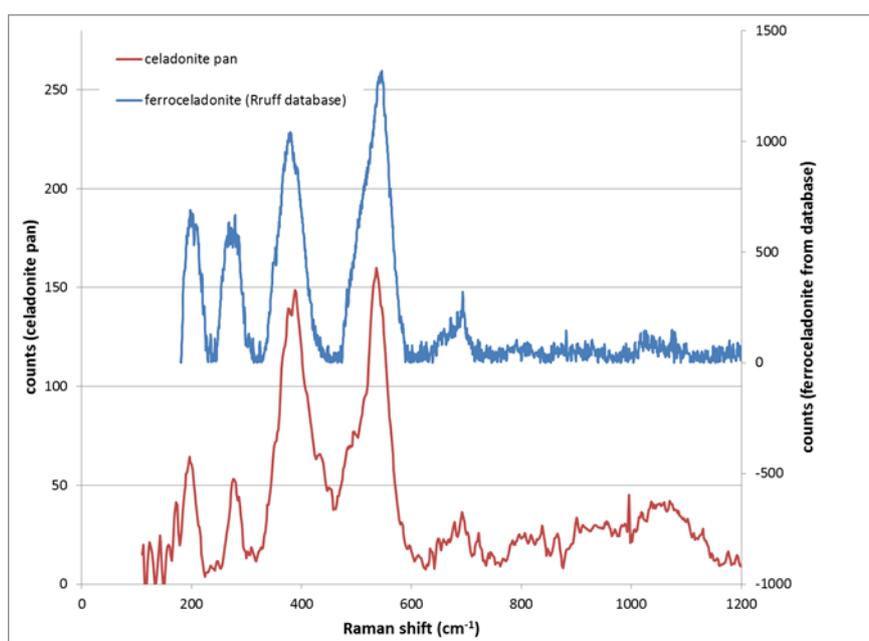


Figure 7. Raman spectrum of watercolor pan celadonite, overlaid with ferroceldonite (RRUFF database).²²

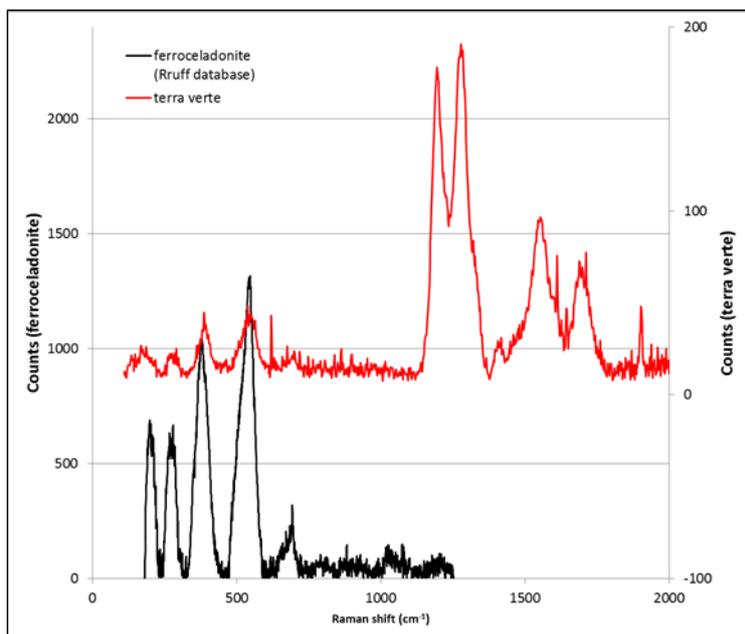


Figure 8. Powdered terre verte pigment plotted with RRUFF database's spectrum for ferroceldonite.

This simple laboratory study demonstrates the ability of low excitation power Raman spectroscopy, coupled with fluorescence removal with careful background subtraction, to elucidate the composition of difficult green pigments. It emphasizes the application of the EZRaman-I documented by Vandenbeebe and others to difficult and important field measurements, and shows that cautious method development can be used to obtain data on some difficult samples encountered in field archaeological work.

Summary

This application note documents the active use and acceptance of the TSI EZRaman-I instrument in the art conservation and archaeology communities. In addition, it provides some new data indicative of the vigorous interest of TSI applications specialists in this arena. Some promising new data is presented using the TSI Raman background correction methods on difficult green colors, with the intention of providing improvement of field data of these challenging pigments.

References

1. Gutiérrez-Neira, P.C., F. Agulló-Rueda, A. Climent-Font and C. Garrido, "Raman spectroscopy analysis of pigments on Diego Velázquez paintings," *Vibrational Spectroscopy*, **69**, 13-20 (Nov. 2013).
2. Pieta, E. E. Proniewicz, B. Szmelter-Fausek, J. Olszewska-Świetlik and L.M. Proniewicz, "Micro-Raman spectroscopy analysis of the 17th century panel painting 'Servilius Appius' by Isaac van den Blocke," *J. Raman Spectros.* **45**, 11-12, 1019 (2014).
3. Striova, J., C. Lofrumento, A. Zoppi and E.M. Castellucci, "Prehistoric Anasazi ceramics studied by micro-Raman spectroscopy," *J. Raman Spectros.*, **37**, 10, 1139 (2006)
4. Colomban, P., "Raman spectrometry, a unique tool to analyze and classify ancient ceramics and glasses," *Appl. Phys. A.* **79**, 167 (2004)
5. Muralha, V.S.F., L. Burgio, R.J.H. Clark, "Raman spectroscopy analysis of pigments on 16-17th c. Persian manuscripts," *Spectrochim. Acta. A.* **92**, 21 (2012).

6. Deneckere, A., M. Leeftang, M. Bloem, C.A. Chavanne-Mazel, B. Vekemans, L. Vincze, P. Vandenabeele and L. Moens, "The use of mobile Raman spectroscopy to compare three full-page miniatures from the breviary of Arnold of Egmond," *Spectrochim. Acta A.*, **83**, 194 (2011).
7. Reiche, I., S. Pages-Camagna and L. Lambacher, "In situ spectroscopy investigations of the adorning gemstones on the reliquary *Heinrich's Cross* from the treasury of Basel Cathedral," *J. Raman Spectros.*, **35**, 8-9, 719 (2004).
8. Caggiani, M.C., P. Colomban, C. Valotteau, A. Mangone and P. Cambon, "Mobile Raman spectroscopy analysis of ancient enameled glass masterpieces," *Anal. Methods*, **5**, 4345 (2013).
9. Zucchuatti, A., P. Prati, A. Bouquillon, L. Giutini, M. Massi, A. Migliori, A. Cagnana and S. Roascio, "Characterization of early medieval frescoes by μ -PIXE, SEM and Raman spectroscopy," *Nucl. Instr. Methods in Phys. Res. B* **219-220**, 20-25 (2004).
10. Edwards, H.G.M., D.W. Farwell and S. Rozenberg, "Raman spectroscopy study of red pigment and fresco fragments from King Herod's Palace at Jericho," *J. Raman Spectros.*, **30**, 5, 361 (1999).
11. Tournié, A., L.C. Prinsloo, C. Paris, P. Colomban and B. Smith, "The first *in-situ* Raman spectroscopic study of San rock art in South Africa: procedures and preliminary results," *J. Raman Spectros.* **42**, 3, 399 (2011).
12. Joseph, E., A. Simon, R. Mazzeo, D. Job, M. Wörle, "Spectroscopic characterization of an innovative biological treatment for corroded metal artefacts," *J. Raman Spectrosc.*, **43**, 1612 (2012).
13. Colomban, P., "The on-site/remote Raman analysis with mobile instruments: a review of drawbacks and success in cultural heritage studies and other associated fields," *J. Raman Spectrosc.*, **43**, 1529 (2012).
14. <http://www.pressebox.com/pressebox/laser-2000-gmbh/Semrock-Introduces-a-New-Grade-of-Ultrasteep-Raman-Edge-Filters/boxid/147479>.
15. Vandenabeele, P., K. Castro, M. Hargreaves, L. Moens, J.M. Madariaga and H.G.M. Edwards, "Comparative study of mobile Raman instrumentation for art analysis," *Anal. Chem. Acta*, **588**, 108-116 (2007).
16. Vandenabeele, P., H.G.M. Edwards and J. Jehlička, "The role of mobile instrumentation in novel applications of Raman spectroscopy: archaeometry, geosciences, and forensics," *Chem. Soc. Rev.*, **43**, 2628 (2014).
17. ASTM E1840 – 96 (2014) "Standard Guide for Raman Shift Standards for Spectrometer Calibration."
18. Donais, M.K., D. George, B. Duncan, A. Daigle and S. Wojitas, "Scatterplots to Data Fusion – A Toolbox of Approaches for Processing and Evaluating Portable XRF and Raman Data for Fresco Pigments," presentation at FACSS 2011.
19. <http://www.ens-lyon.fr/LST/Raman/>
20. www.naturalpigments.com
21. www.kremerpigments.com
22. Downs R T (2006) The RRUFF Project: an integrated study of the chemistry, crystallography, Raman and infrared spectroscopy of minerals. Program and Abstracts of the 19th General Meeting of the International Mineralogical Association in Kobe, Japan. 003-13



TSI Incorporated – Visit our website www.tsi.com for more information.

USA	Tel: +1 800 874 2811	India	Tel: +91 80 67877200
UK	Tel: +44 149 4 459200	China	Tel: +86 10 8219 7688
France	Tel: +33 1 41 19 21 99	Singapore	Tel: +65 6595 6388
Germany	Tel: +49 241 523030		