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A comparative mobile Raman study for the on field analysis of the *Mosaico de los Amores* of the Cástulo Archaeological Site (Linares, Spain)

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Abstract

An in situ archaeometrical campaign was organized in 2018 for the physico-chemical analysis of the exceptional *Mosaico de los Amores* of the Cástulo archaeological site (Linares, Spain). Several mobile instruments were brought on the field to investigate the colourful tesserae of the mosaic. The main aim of the current research paper is the comparison of different mobile instruments and their applicability on measuring in open air environments. In this study, the comparison of four mobile Raman instruments, using different excitation lasers and technologies, is discussed. Three portable, the EZRaman-I dual Raman analyser from TSI Inc. (USA), the i-Raman® EX from BWTEK (USA), and the BWS445-785S InnoRam™ Raman spectrometer from BWTEK (USA), and one handheld system, the Bravo Raman spectrometer from Bruker (Europe), are compared in terms of their characteristics, applicability, and performance when conducting non-invasive and non-destructive analysis.

KEYWORDS

Cástulo project, in situ analysis, mosaic, portable Raman spectroscopy, tesserae

1 | INTRODUCTION

Located 5 km south of the present Linares (Spain), the Ibero-Roman city of Cástulo constituted one of the most important centres in the Iberian Peninsula during the Antiquity, not only due to its extension (~50 ha) but also due to its strategic position in the Upper Guadalquivir Valley. The historical sequence of Cástulo spans more than 4,000 years ranging from the Chalcolithic (third millennium BC) to the end of the Modern Age (15th century AD). During its occupation, Cástulo was an important meeting point for the coexistence of indigenous cultures and different civilizations from the Mediterranean area, although the most important phases of occupation took place during the Iberian and Roman times (seventh century BC to the fourth century AD). In fact, in the course of the Iberian period (seventh to second centuries BC), Cástulo became the largest city on the Iberian Peninsula, configuring an *oppidum* surrounded by an impressive wall and up to seven necropolis arranged out and around the city walls.[1,2]

During the Roman period, especially by the end of the first century AD, the city reached an outstanding splendour and relevance. One of the most outstanding buildings of this period is the one dedicated to the cult of Emperor Domitian (Building D), recovered during the archaeological excavations carried out in the years 2011–2013. The so-called *Mosaico de los Amores* stands out from the set of mosaics distributed among the numerous rooms of this building that have been excavated so far. This mosaic is constructed mainly with colourful stone and glass-paste tesserae in order to render its highly technical iconography. Moreover, the mosaic was found in an outstanding state of preservation.[1,2] This study focuses on the direct investigation of the tesserae of the *Mosaico de los Amores* by the means of multiple mobile Raman instrumentation. More specifically, four different Raman instruments are compared, and their applicability on in situ archaeometrical campaigns is discussed.

Raman spectroscopy is among the most favourable techniques in archaeometrical research.[3–7] The technique can be applied non-destructively, on both treated and untreated samples, revealing the molecular characteristics of organic and/or inorganic compounds and their mixtures. Furthermore, Raman spectroscopy is one of the few techniques that when applied non-invasively or directly on the field, provides high-quality results.[8,9]

In general, mobile Raman instruments are using larger collecting spots in comparison with laboratory instruments, share a greater wave number instability, and fluctuate more due to environmental conditions and transportation vibrations. Moreover, positioning and focusing of the laser might be challenging as well as the limited measuring time and the absence of complete darkness when measuring on open air environments.[10–12] Although benchtop Raman instruments perform, in general, better than their mobile counterparts, the last technological advances brought new state-of-the-art mobile Raman instruments onto the market and as a consequence onto the field.[13]

Long fibre optics cables attached to light spectrometers allow the analysis remotely and directly on site. Moreover, compact and lighter handheld Raman spectrometers without fibre optics probes attached have been introduced as a more flexible alternative that can easily be transported and that typically allows short measuring times. From the Fourier transform (FT)-Raman to dispersive Raman microscopy and from Si multielement detectors to compact semiconductor detectors, Raman instrumentation proves to be versatile and following the scientific demands of the research. Nowadays, the compact mobile Raman instruments used for direct analysis are dispersive systems coupled with charge-coupled-device (CCD) or semiconductor detectors, depending on the laser excitation used.

Mobile is a generic description of stable Raman systems that are designed, by the manufacturers, to be transported outside the laboratory and brought on the field to measure the precious artefacts non-invasively and non-destructively. Systems that can be carried with no more than one person, usually battery operated and attached to long fibre optics cables, are described as portable. The latter are ideal when measuring works of art inside a museum environment or in open space. Lighter and more compact Raman spectrometers using fixed optical heads, and usually operated by one person, are ascribed as handheld. Palm and ultra-mobile Raman instruments, found commercially available, are further miniaturize.[14,15]

In this study, four mobile Raman instruments, namely, the EZRaman-I dual Raman analyser from TSI Inc. (USA), the i-Raman® EX from BWTEK (USA), the BWS445-785S InnoRam™ Raman spectrometer from BWTEK (USA), and the Bravo Raman spectrometer from Bruker (Europe), which have different laser wavelengths and technologies, are compared and evaluated in the case of colourful tesserae from the *Mosaico de los Amores* (Linares, Spain). Also, their applicability on measuring in open air environments is examined. This research is part of a wider scientific project under the name "Cástulo: archaeometric research and social transfer," where a series of analytical techniques, such as direct X-ray fluorescence (XRF) analysis, are employed to illustrate the nature of raw materials and the work processes involved in the manufacture of the artefacts into study.

2 | EXPERIMENTAL

2.1 | Materials

Six Eroti or *Amores* in half circles located along the sides of a mosaic found in the Cástulo archaeological site (Linares, Spain) gave the name to *Mosaico de los Amores* (Figure 1a). The archaeological site is recognized as a part of global cultural heritage monument. The central main themes of the large-scale mosaic (11.75 m × 6 m or 70.5 m^2) are a northern circle depicting the myth of the judgement of Paris and a southern circle depicting the myth of Selene and Endymion. Moreover, the mosaic has four quarter-circles in each corner, representing the four seasons, and six half circles between the corner scenes, depicting hunting scenes with Eroti or *Amores*.

On a field campaign conducted in 2018 (Figure 1b), a large amount of (227) tesserae were examined by four mobile Raman instruments that resulted in a total of more than 1,000 measurements. The mosaic's tesserae were analysed directly on the field without any sample preparation or sample extraction. Only, prior to their analytical examination, the tesserae were dedusted with a brush and cleaned with a sponge drenched in ethanol.

2.2 | Instrumentation

2.2.1 | EZRaman-I dual analyser

The portable EZRaman-I dual analyser (TSI, Irvine, USA) is a battery-operated, fibre optics-based spectrometer coupled with two lasers: a red diode laser (785 nm) and a green Nd:YAG laser (532 nm). The spectral ranges, of the two grating spectrometer, are 100–2,200 cm^{-1} and 100–3,100 cm^{-1} with a spectral resolution of ~7 cm^{-1} for the red and green laser, respectively. The system is equipped with a thermo-electrically (TE)-cooled (−50°C) CCD detector and uses three interchangeable lenses for each wavelength: a standard lens (STD), a long working distance lens, and a high numerical aperture lens. The selected standard lens has a working distance of ~7 mm. The laser power was kept sufficiently low to avoid damaging or altering the tesserae. To secure the absence of ambient light and environmental interference, a plastic cup equipped with a protective foam layer was slid over the standard objective lens (fixed working distance), and the positioning was accomplished by hand. The measurement time and number of accumulations were selected to obtain spectra with good signal-to-noise (S/N) ratios. Wavelength calibration was accomplished with sulphur, epsilon-caprolactone (Acros Organics), cyclohexane (Kaiser), polystyrene pellets (Aldrich), and acetonitrile (Panreac)/toluene (UCB; mixed in 50/50 volume%).[16,17] Postprocessing of the data performed by using Thermo Grams/AI 8.0® suite software (Thermo Fischer Scientific).

2.2.2 | i-Raman® EX

The dispersive i-Raman® EX portable system (BWTek, Newark, USA) is a fibre optics spectrometer that works on net power. The spectrometer is coupled with a 1,064-nm excitation laser, using a spectral range from 100 to 2,500 cm^{-1} and with a resolution of less than 10 cm^{-1} at 1,296 nm. The instrument is equipped with a high-sensitivity TE-cooled InGaAs detector and an adjustable laser power controller. The laser power was kept low in order to avoid any transformation of the components of the mosaic, and the measurement time and accumulations were adjusted in order to obtain good signal-to-noise (S/N) ratios. The lens selected for measuring on field has a working distance of 5.9 mm. An adjustable light blocker can be fixed on the fibre optics probe. No

FIGURE 1 (a) The *Mosaico de los Amores* depicts six Eroti or *Amores* in half circles located along its sides. The central themes of the mosaic depict the myth of the judgement of Paris (a contest between the three most beautiful goddesses: Minerva, the goddess of wisdom; Juno, the goddess of marriage; and Venus, the goddess of love) and the myth of Selene and Endymion. The mosaic has four quarter-circles in each corner, representing the four seasons and six half circles between the corner scenes, depicting hunting scenes with Eroti or *Amores*. (b) Different mobile Raman and XRF instrumentation were applied on the colourful scenes of the *Mosaico de los Amores* from the Cástulo archaeological site (Linares, Spain)

special calibration was applied, but the system was checked on site using cyclohexane (Kaiser). During the measuring time of *Mosaico de los Amores*, the instrument was powered by using a portable generator. Posttreatment of the acquired spectra was performed by using Thermo Grams/AI 8.0® suite software (Thermo Fischer Scientific).

2.2.3 | BWS445-785S InnoRam™

The portable BWS445-785S InnoRam™ Raman spectrometer (BWTek, Newark, USA) is a nonbattery-operated system with a 785-nm excitation laser that covers a spectral range from 65 to 3,000 cm^{-1} with spectral resolution at ~4 cm^{-1}. The spectrometer is attached to TE-cooled, back thinned, 2D binning CCD detector. For measuring the tesserae from the *Mosaico de los Amores*, the fibre optics probe was focused by hand, and the lens used had a 5.9-mm working distance. The laser power was kept low, and the measurement time and accumulations were adapted in order to acquire acceptable signal-to-noise (S/N) ratios data. No special calibration was applied. The system was powered by the portable generator. Thermo Grams/AI 8.0® suite software (Thermo Fischer Scientific) was used for data processing.

2.2.4 | Bravo

The Bruker Bravo handheld Raman spectrometer (Bruker, Ettlingen, Germany) is a battery-operated, light-weighted system. The DuoLaser™ system uses two lasers from 700 to 1,100 nm, covering a wide spectra region, from 300 to 3,200 cm^{-1} and is coupled to a CCD detector. The spectral resolution is 10–12 cm^{-1}, and the power of both lasers is kept below 100 mW.

The Bravo Raman spectrometer has a fixed optical head. The instrument is using an integrated wavelength calibration and a docking station to recharge. The spectra are collected with automated settings and can be exported for processing in OPUS™ software. The data were further processed by using Thermo Grams/AI 8.0® suite software (Thermo Fischer Scientific).

3 | RESULTS AND DISCUSSION

3.1 | Characteristics and on field applicability

For the comparative study of *Mosaico de los Amores* (Linares, Spain), four mobile Raman instruments were brought on the field (among other instrumentation). The main characteristics of the equipment used are summarized in Table 1. During this campaign, the focus was on the investigation of the tesserae used in this beautiful mosaic. Tesserae are small, colourful, squared, pieces of rock or glass, which are used to compose the mosaic. The glass tesserae are composed of silica from sand, with some fluxing agents (e.g., sodium carbonate), and small concentrations of opacifiers, decolourants, or colourants are added intentionally.[18–20] In general, it is thought that the most important opacifier is hydroxyapatite, probably originating from deliberately adding bone powder to the glass.[21] During the production process also, β-rhenanite and wollastonite are formed. Galli et al.[22] gave an overview of common colourants and opacifiers that are encountered in Roman tesserae. Previous studies were performed on samples[23] or by direct methods, using Raman spectroscopy as single technique[24] or in combination with other analytical methods.[25]

The measuring campaign of the Cástulo archaeological site was conducted during the day, whereas measuring the fibre optics probes or the optical head of the mobile Raman instruments were in complete contact with the tesserae of the mosaic (with or without light blockers) on fixed working distances.

Three of the spectrometers (EZRaman-I dual, i-Raman® EX, and BWS445-785S InnoRam™) were portable,[14,15] operated with or without battery, coupled with long fibre optics cables that allowed the measurements to be conducted remotely. In general, this kind of Raman spectrometers, which are medium weighted (expected from the EZRaman-I dual system that includes two spectrometers in its packaging) and can be transported by one person on site, are preferred in archaeometrical studies.[14,15] The coupling of the fibre optics cables is an advantageous property, as the probe can be positioned and focus by several ways (e.g., microscope, translation stage, tripod, articulated arm, or manual). The longer the fibre optics, the easier the positioning of the probe on large-scale objects (wall paintings, sculptures, etc.) compared with the handheld instruments that have fixed optical heads. In terms of spectra quality, the length of the fibre is almost independent of possible intensity loss, which is more prominent at the connections (entrance and exit) of the fibres to the spectrometer and the probe head. In the case of the mosaic found in the Cástulo archaeological site, the positioning of all the portable instruments was made by hand, and the spectra acquisition was possible in time-limited measurements in order to avoid possible focusing loss.

The same tesserae measured with the three portable instruments were examined with the Bravo handheld Raman spectrometer. This light-weighted, compact system is completely automated. Although for the portable

TABLE 1 Overview of the main characteristics of the mobile Raman instruments used in this study (data as reported from the manufacturers)

Characteristics	EZRaman-I dual	i-Raman® EX	BWS445-785S InnoRam™	Bravo
Manufacturer	TSI	BWTek	BWTek	Bruker
Type	Portable	Portable	Portable	Handheld
Laser excitation (nm)	785 (R) 532 (G)	1,064	785	700–1,100 (two lasers in-between this range)
Laser power (max. mW)/ power control	300 (R)/adjustable 50 (G)/adjustable	499 (>430 at excitation port)/adjustable	>300 (at excitation port)/ adjustable	<100 (for both lasers)/ automated
Detector	TE-cooled CCD	TE-cooled InGaAs	TE-cooled CCD	CCD
Spectral range (cm^{-1})	100–2,200 (R) 100–3,100 (G)	100–2,500	65–3,000	300–3,200
Spectral resolution (cm^{-1})	6 (R) 6.5 (G)	<10 (at 1,296 nm)	~4 (at 912 nm)	10–12
Probe/length (m)	Fibre optics probe/5	Fibre optics probe/1.5	Fibre optics probe/1.5	Optical head
Weight (kg)	~17	3,4 (main unit)	~10	1.5
Size (cm)	55 × 35.5 × 24	17 × 34 × 28	41 × 22 × 30.3	27 × 15.6 × 6.2
Positioning equipment	Micro- and macro- and manual positioning	Micro- and macro- and manual positioning	Micro- and macro- and manual positioning	Manual positioning
Power	Battery or electrical power supply (230 V)	Electrical power supply (230 V)	Electrical power supply (230 V)	Battery (charged via a docking station)
Operation	Integrated laptop	Laptop	Laptop or intergraded touchscreen	Integrated touchscreen
Calibration	Five products			Integrated
Data acquisition	In-house software	Provided by the manufacturer	Provided by the manufacturer	Provided by the manufacturer

systems, the laser power, measuring time, and accumulations are adjustable by the user, the Bravo spectrometer has an integrated smart system that automatically preselects or reselects when measuring the aforementioned conditions. Although such preselection ensures quick analysis and set-up (valid, e.g., on quality control analysis), the user cannot interfere on the steps of the procedure. In cultural heritage, the materials under analysis may undergo matrix transformations or damage while exposed for prolonged time under high-energetic lasers and/or high laser power. The user of a Raman spectrometer is advised to have complete control of the conditions of the system when conducting research on works of art. Although the Bravo analyser preselected the measuring total conditions, no damage or alterations were observed on the mosaic's tesserae. Moreover, Bravo has a fixed optical head that hampers the, by hand, positioning on artefacts and thus hinders the analysis more.

When measuring on field and directly on the artefact with mobile instrumentation, the calibration procedure should be very meticulous in order to ensure wave number stability. The noncalibrated Raman systems ensure that environmental conditions, vibrations, and so forth will not introduce fluctuations, with that in practice to be unavoidable when measuring in open air environments or when transportation causes vibrations to the instrument. The higher the amount of products, meant for calibration, measured and the wider the spectral region that their Raman bands can be found, the better the calibration curves are fitted.[17] The EZRaman-I dual analyser is using an in-house calibration and acquisition software that uses five calibration products,[16] whereas Bravo handheld spectrometer has an integrated calibration. The i-Raman® EX and BWS445-785S InnoRam™ systems are not calibrated, but they can be frequently checked for their wave number stability by measuring the most intense band of a pure product (e.g., sulphur or cyclohexane).

On the *Mosaico de los Amores* (Linares, Spain), different excitation lasers (and different Raman systems) were used in order to retrieve the maximum information of the materials that constitute the tesserae. The laser wavelengths used were a 532 nm; two 785 nm (two different manufacturers); a 1,064 nm; and a 700–1,100 nm. When selecting the appropriate laser for the investigation of the unknown, someone should consider that the Raman intensity is proportional to the fourth power of the laser excitation frequency.[13] In other words, the higher the laser wavelength, the lower the scattering capability. In order to compensate for the intensity loss, high laser power and measuring time should be adapted resulting in damaging risks on the artefact.[6,13,26,27] On the other hand, the higher the laser wavelength, the less fluorescence emission is induced resulting in better spectral quality. Although a diode 785-nm laser can be the first choice when analysing massive collections with versatile materials, other options are now commercially available. Near infrared (IR) lasers for Raman applications were often associated with FT technology and benchtop instrumentation.[28] Although FT technology gains in sensitivity, one problem with the FT-Raman instruments is that their miniaturization is not straightforward regarding the optics used and the interferometers.[26,28] Moreover, in order to maintain the sensitivity of the FT-Raman systems, solid state detectors are used compared with the less sensitive in the near IR region, silicon-based CCD detectors.[13,28] Until now, in art analysis, few dispersive portable systems have been used for in situ analysis, except for the analysis of minerals.[29] Dispersive portable systems coupled with 1,064-nm excitation laser are available in the market. In order to compensate for the loss of sensitivity of the dispersive technology, the portable near IR Raman systems are using greater laser powers risking the overheating of the material under study.[28] Indeed, the maximum laser power of the i-Raman® EX system is 499 mW, as reported by the manufacturer, so extra caution should be taken when adjusting the laser power, in order to avoid damaging the artefact.

The Bravo handheld Raman spectrometer that was used for the analysis of this exceptional mosaic became commercially available on the market in 2015. This type of instrument was used for the analysis of painted artworks,[28] and also, some field applications were published for the identification of minerals under extreme conditions.[30–32] Bravo uses the sequentially shifted excitation patented technology—SSE™, patent number US8570507B1, for fluorescence mitigation by using temperature-tuned diode lasers with wavelengths from 700 to 1,100 nm (DuoLaser™-two excitation lasers).[26,33] As reported by Cooper et al., in 2013,[26] the sequentially shifted excitation method deploys a single temperature-controlled distributed Bragg reflector diode laser that emits single-mode 785-nm radiation at 25°C. Different distributed Bragg reflector laser temperatures provide shifted excitation wavelengths. The actual Raman features change with different excitation wavelength, whereas other intensities such as fluorescence background, stray light, noise, environmental signals, and absorbance effects remain consistent in spectral space. In the Bravo instrument, the shifted spectra from different temperatures are collected in two steps with two lasers (DuoLaser™), ranging from 300 to 2,200 cm^{-1} and from 1,200 to 3,200 cm^{-1}, respectively. Shifted excitation data processing results in an extracted ultimate Raman spectrum in the range of 300 to 3,200 cm^{-1} that covers both the fingerprint (<1,800 cm^{-1}) and some part of the CH stretching region (>2,700 cm^{-1}).[34]

In practice, Bravo collects three different spectra for each laser that are slightly shifted resulting in a seventh reconstructed final spectrum. The manipulated data or the final extracted spectrum is not always completely straightforward. Moreover, though Bravo has an extended spectral region, its spectral cut-off is at 300 cm^{-1}. The latter poses certain difficulties on the identification of several pigments (e.g., oxides and sulfides), corrosion products, etc., commonly found in works of art that vibrate in low Raman wave number modes. The spectral cut-off of the portable Raman instruments, used in this study, is ~100 cm^{-1}.

3.2 | Comparative analysis of tesserae from the *Mosaico de los Amores* (Linares, Spain)

The colourful tesserae from the *Mosaico de los Amores* (Linares, Spain) were examined by means of mobile instrumentation. Mobile Raman systems, among other techniques, were brought on the field in order to non-destructively and non-invasively examine the tiles of the mosaic. The Raman systems were selected to cover a wide range of state-of-the art mobile equipment using different technology and coupled with different lasers. The results presented here are not reflecting the vast majority of rock and glass materials (for the same and/or the different colours found within the same and/or different scenes of the mosaic) used for composing the tesserae, as here, we are focusing on the application of different mobile Raman instruments on site, in open air environments.

The mobile Raman instruments were selected to have different excitation wavelengths in order to understand and examine their influence on the investigation of the unknown. The problem of the influence of fluorescence when using the 785-nm laser, particularly for the EZRaman-I dual analyser, is described before.[10] Certain luminophores may cause excess fluorescence that can mask Raman bands, making the identification of the materials very challenging. In Figure 2b,c (785-nm laser of the EZRaman-I dual analyser and the BWS445-785S InnoRam™, respectively), fluorescence patterns can be observed, from ~1,000 to 1,700 cm^{-1}. There are still visible broad bands at wave numbers that correspond to noncrystalline carbonaceous matter[34]: In this carbonaceous matter, the arrangement of the structural units is far from graphite structure. In Figure 2d,e (when measuring with the 1,064-nm laser of the i-Raman® EX and the Bravo system, respectively), the fluorescence is supressed, and the bands of carbon-based material are revealed (~1,600 and 1,300 cm^{-1}).[35] Other materials identified on the black tessera located at the bottom of the dress of Minerva at the judgement of Paris scene are anatase (TiO_2; EZRaman-I dual: 632, 392, 197, and 144 cm^{-1}, BWS445-785S InnoRam™: 142 cm^{-1}, i-Raman® EX: 643, 515, and 144 cm^{-1}, Bravo: 641, 514, and 393 cm^{-1})[36] and α-quartz (EZRaman-I dual: 460 cm^{-1}, Bravo: 465 cm^{-1}).[36]

The 532-nm laser of the EZRaman-I dual analyser did not contribute much to the overall analysis of the mosaic's tesserae as can be observed from Figures 2a, 3a, and 4a. It is expected that the 532-nm excitation laser yields higher Raman intensities (higher scattering capabilities induced from more energetic lasers and thus more energetic photons). On the other hand, the shorter the laser wavelength, the more fluorescence is introduced, resulting in bad quality spectra. However, in some cases, the materials' identification was possible. In general, the green excitation lasers are successful candidates for Raman signal enhancement (resonance Raman effect) of some materials found on works of art.[13,37] Sometimes, a band at 100 cm^{-1} was identified with the 532-nm laser, possibly characterized as a laser side band or a lattice vibration of the solid.

Another aspect of changing between different laser excitations, but inherently also between different Raman instruments, is shifting of the bands. An example is arising from the haematitic composition found on the dark red tesserae in one of the four quarter-circles (Spring scene). Haematite (α-Fe_2O_3)[38] was identified as the main component with the 785-nm laser of the EZRaman-I dual (606, 493, 407, 289, 242, and 223 cm^{-1}; Figure 3b), the BWS445-785S InnoRam™ (613, 500, 412, 294, and 226 cm^{-1}; Figure 3c), the i-Raman® EX (616, 412, 295, and 228 cm^{-1}; Figure 3d), and the Bravo system (612, 499, and 412 cm^{-1}; Figure 3e). These differences between different lasers may be due to different excitation sources that may shift the Raman bands and/or also excite different modes. Alternatively, this can be related to calibration procedures, as some instruments were meticulously calibrated compared with others. Also, a difference in background noise may shift not only the wavelengths but also the different absorption effects. Another component identified in the mixture with only the EZRaman-I dual and Bravo Raman systems is calcite ($CaCO_3$).

The importance of using Raman instruments with high spectral resolution is crucial especially for mixtures of components that have Raman bands close to each other. According to the producer, the EZRaman-I dual and the BWS445-785S InnoRam™ have the highest spectral

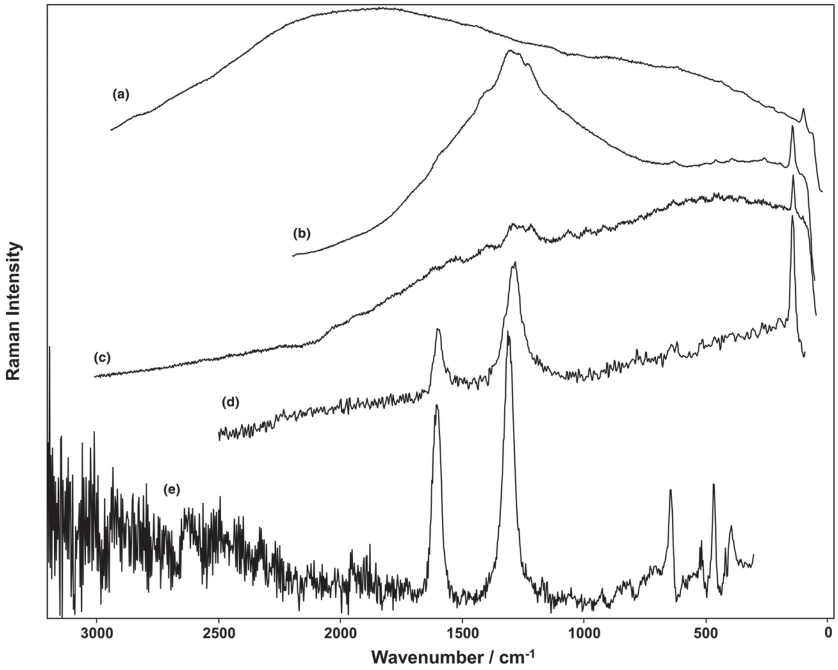

FIGURE 2 Spectra from a black tessera located at the bottom of the dress of Minerva at the judgement of Paris main scene collected with (a) the 532-nm laser of the EZRaman-I dual; (b) the 785-nm laser of the EZRaman-I dual; (c) the BWS445-785S InnoRam™; (d) the i-Raman® EX; and (e) the Bravo system

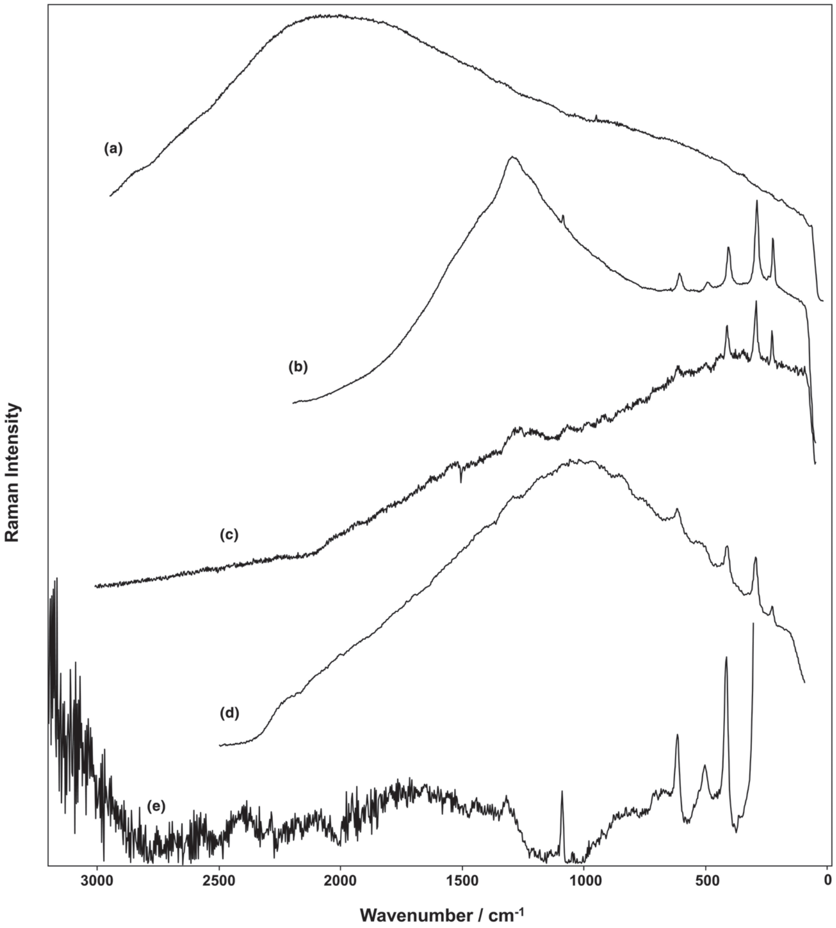

FIGURE 3 Spectra from a dark red tessera in one of the four quarter-circles embodied as spring collected with (a) the 532-nm laser of the EZRaman-I dual; (b) the 785-nm laser of the EZRaman-I dual; (c) the BWS445-785S InnoRam™; (d) the i-Raman® EX; and (e) the Bravo system

resolution from the Raman systems tested. A mixture of calcite and dolomite (CaMg $(CO_3)_2$) was positively characterized by their Raman bands[39] with the 785-nm laser of the EZRaman-I dual (Figure 4b; (calcite: 1,436; 1,086; 709; and 280 cm^{-1}, dolomite: 1,097; 727; 296; and 177 cm^{-1}, calcite/dolomite: 154 cm^{-1}) and the BWS445-785S InnoRam™ (Figure 4c; calcite: 1,086; 712; and 282 cm^{-1}, dolomite: 1,098; 300; and 178 cm^{-1}, calcite/dolomite: 156 cm^{-1}) on a red tessera from the left side of the dress of Minerva at the judgement of Paris scene. The results from the i-Raman® EX system identified as the main component calcite, but indications of dolomite could be found in an unresolved doublet of 726/714 cm^{-1} and at 177 and 157 cm^{-1} (Figure 4e). With the Bravo instrument, the presence of calcite was evident, but the same unresolved doublet of 727/712 cm^{-1} was again observed (Figure 4d). Moreover, a band at ~400 cm^{-1} found at the spectra acquired with the 785-nm laser of the EZRaman-I dual, the i-Raman® EX, and the Bravo system may point out the presence of a metal oxide.

The most challenging application of the campaign organized on the Cástulo archaeological site was the use of the Bravo system, both not only in terms of the manipulation and focusing of the optical head (no fibre optic cables) on the horizontal ground mosaic but also in terms of the interpretation of the data. In Figure 5, the shifted spectra (vertically sifted for clarity; Figure 5, a_{1-3} and a_{4-6}) and the ultimate reconstructed spectrum (Figure 5, a_7) of a baby blue tessera from an Eros scene is presented. On the part of C—H stretching region (around 3,000 cm^{-1}), the reconstructed spectrum is not analogous or representative of the shifted spectra generated by the two lasers. Such irregularities were observed in other examples of the tesserae when thoroughly examining the data. Nevertheless, the identification of the main component was successful by a band at 671 cm^{-1}, attributed to hexagonal calcium antimonate ($CaSb_2O_6$), the main opacifying agent of the glass.[24,40,41] This was verified by all the Raman instrumentation applied (except from the 532-nm laser of the EZRaman-I dual). Moreover, a band at ~995 cm^{-1} observed with the 785-nm laser of the EZRaman-I dual and the Bravo instrument may be attributed to a ν_1 vibrational mode of a sulphate, probably an alkali sulphate.[24] Also, given the colour of the tesserae, this Raman band can be assigned to a Ca or Al-silicate incorporating Co.[24,41]

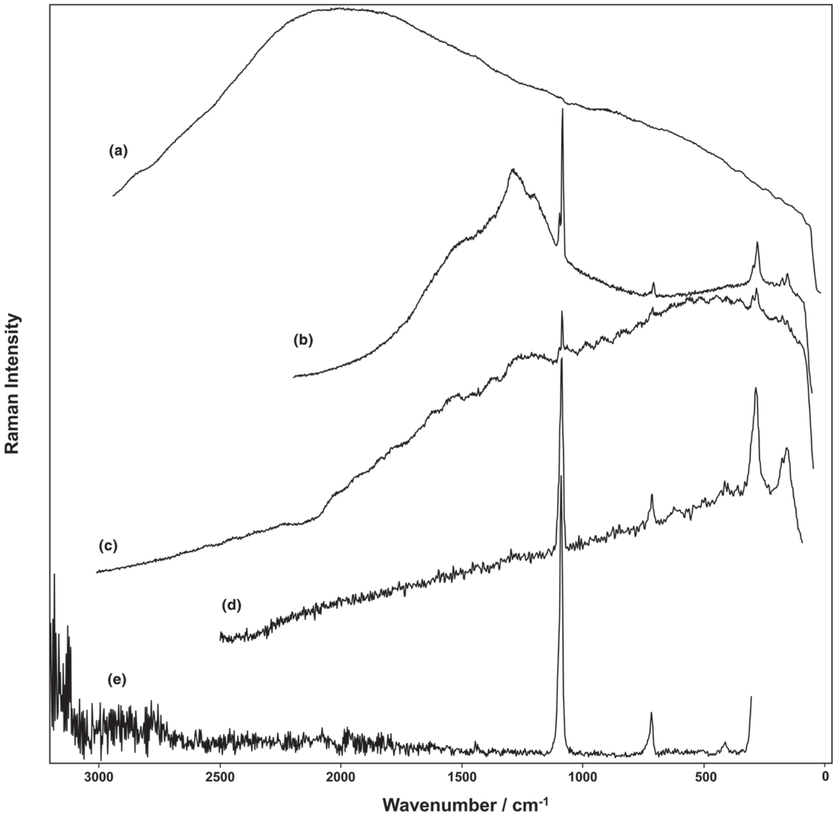

FIGURE 4 Spectra from a red tessera from the left side of the dress of Minerva at the judgement of Paris main scene collected with (a) the 532-nm laser of the EZRaman-I dual; (b) the 785-nm laser of the EZRaman-I dual; (c) the BWS445-785S InnoRam™; (d) the i-Raman® EX; and (e) the Bravo system

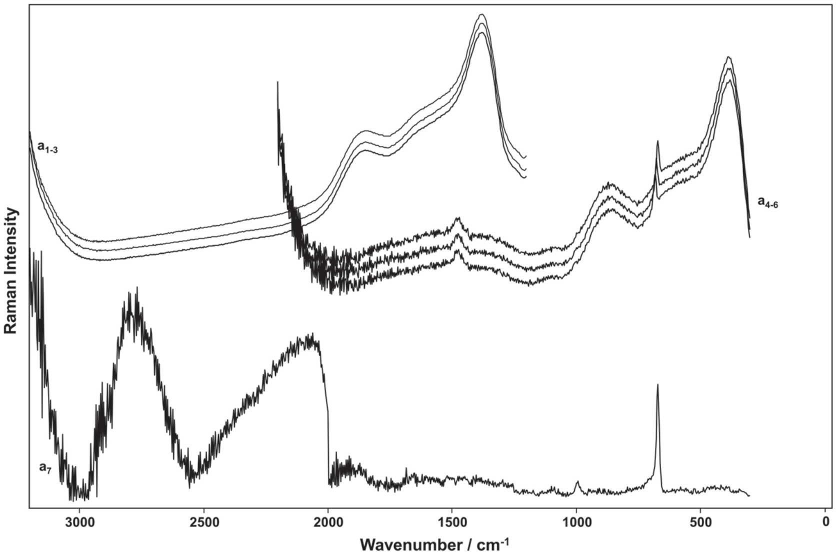

FIGURE 5 Shifted spectra (a_{1-3} and a_{4-6}; vertically shifted for clarity) and the ultimate reconstructed spectrum (a_7) from a baby blue tessera from an Eros scene generated with the Bravo handheld Raman system

TABLE 2 Overview of the applicability and performance of the mobile Raman instruments used, for this study (min. x, max. xxx)

Raman spectrometer	EZRaman-I dual	i-Raman® EX	BWS445-785S InnoRam™	Bravo
Applicability	+++	+++	+++	+
Performance	532 nm: — 785 nm: xx	++	++	++

4 | CONCLUSIONS

In 2018, a field campaign was organized for the analysis of the *Mosaico de los Amores* of the Cástulo archaeological site (Linares, Spain). Several mobile instruments were brought on site to measure directly, non-invasively, and non-destructively the colourful tesserae of the outstanding mosaic. The aim of the research was to compare and test several state-of-the-art mobile Raman systems on measuring on open air environments. This study is dedicated on the applicability of four Raman mobile instruments and the comparison of their performance in situ.

In Table 2, an overview of the applicability and the performance of the four Raman systems is presented. In general, the 532-nm laser of the EZRaman-I dual produces the least effective data from all the instruments applied. It is advised in mobile Raman campaigns, dedicated to cultural heritage studies, with limited time slots, to use this type of lasers when resonance Raman effects are anticipated or when it is proposed by literature. The best performing instruments were the ones coupled with the 785- and 1,064-nm excitation lasers. Their implementation combines the characteristics of good spectral resolution and fluorescence suppression for the identification of complex mixtures, respectively. Bravo system seems to be a good candidate that can be implemented successfully on demanding field analytical studies, considering the size/weight of the packaging and the new technology implemented. The main problem of the handheld instruments is the absence of a positioning probe that is sufficiently flexible for measuring artefacts that are oriented differently in space. Moreover, the data that Bravo generates need a more comparative insight when investigating works of art.

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