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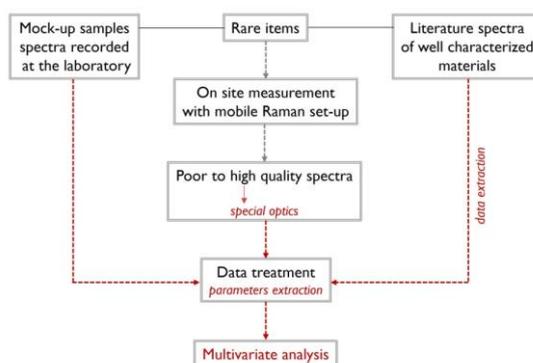
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In this introduction special issue dedicated to “Advanced Raman procedures applied to natural / cultural heritage and forensic questions: mobile set-up, data treatment and associated techniques” the aim is to assess the state of the art in the field and to highlight potential new perspectives regarding data treatments, spectrum collection and mobile set-up



Advanced Procedures in Raman Forensic, Natural and Cultural Heritage Studies: mobile set-up, optics and data treatment. State-of-the-art and perspectives.

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Advanced Procedures in Raman Forensic, Natural and Cultural Heritage Studies: mobile set-up, optics and data treatment. State-of-the-art and perspectives.

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Abstract

In this introduction to the Journal of Raman Spectroscopy special issue “Advanced Raman procedures applied to natural / cultural heritage and forensic questions: mobile set-up, data treatment and associated techniques” the aim is to assess the state of the art in the field and to highlight potential new perspectives. The novel approaches employed in the published papers are described and can be grouped as such: application of multivariate statistical analysis to Raman spectra, use of mobile instrumentations directly in situ for both cultural and forensic contexts, tackling with optics and spectral range issues, and coupling with mobile instrumentations based on different analytical techniques.

Keywords: mobile instrumentation, multivariate statistical analysis, optics illumination, cultural heritage, forensic

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1. The context

The expertise concerning objects of Cultural Heritage and the natural or synthetic materials constituting them, has been carried out for a very long time, and since the rise of societal interest in nature, by recognized individuals with a strong authority.^[1,2] Analyses have gradually become essential to support or replace expert opinions, providing vital information on the raw materials used and the manufacturing process of objects remaining recorded in their final aspect and material structure.^[3,4,5,6] The lowering of costs and the miniaturization of numerous instruments including Raman spectrometers have broadened the possibility of application of these analyses,^[7-10] including by people whose mastery of spectroscopic techniques and theoretical interpretation tools is not their main skill. In addition, the latest generations of compact instruments (often the least expensive)^[8] has significantly modified the spectrum collected, to maximize the reading of the components ("peaks") considered by the software as intelligible, generally to the detriment of renderings of broad bands of amorphous phases. These compact devices are designed for other applications such as the receipt and delivery of pure or formulated chemicals, customs or police control and forensics.

On the other hand, in many countries, regulatory inflation and the societal context make it increasingly difficult and expensive to move valuable objects to a laboratory; furthermore the conservation requirements and the cultural heritage-connected ethic minimizes the possibility of sampling. Therefore, the (non-invasive) analyses must be often carried out on site, with mobile devices.^[6-12] In this way, only the surface - we can call it the "skin" - of the objects, accessible to the optical systems involving laser illumination and collection of scattered light, can be analyzed (Figure 1). Very often Raman measurement are coupled with portable X-ray fluorescence spectroscopy (pXRF)^[12-14]. The constraints then become quite similar to those experienced by forensic analyses which have adapted to the study of traces in a non-invasive manner to satisfy the regulatory requirements. It follows that the working procedures – that is to say the collection of the Raman signal, processing and interpretation of the signals – are evolving, in a positive direction (possibilities of studying new populations of objects and phenomena) but also with a negative implication (the quality of the spectroscopic signal collected by a compact mobile instrument is often low: intense and complex continuous background, low resolution, limited spectral window, etc.)^[14,15,16] and the Raman technique users are not expert in the understanding and modeling of the variety of light-matter interaction in the solid state. Data processing must compensate for the mediocre or even low quality of the spectra. This problem is not new and has been encountered in other disciplines: defects in telescope optics have led to the development of correction tools through calculation^[17-19]; the great variability of biological compounds (medicine, agronomy, environment)^[20-40] as well as the use of spectral zones where harmonic components and combinations overlap, in a way that it is difficult to identify by visual observation (reflection and NIR absorption), have led to the use in spectroscopy of multivariate analysis techniques (in particular supervised ones) - this scientific discipline is also called chemometrics - applied to all kind of vibrational studies, FTIR, NIR and Raman (including SERS). Although thousands of papers with this application have been published in agriculture, environment, biology/medicine and forensic fields from three decades, the number of papers published in the field of heritage^[41,42] is limited (a few tens, see Figure 2 and paragraph 3). Representative works using Raman spectroscopy are listed.^[41-56]



Figure 1. On-site Raman analysis: top, HE532 Horiba Jobin Yvon coupled with 532 nm Ventus laser and SuperHead® equipped with a ULWD 200X Mitutoyo microscope objective (bottom, zoom).

2. Constraints of the Raman analyses in the Heritage field

2.1 Intrinsic constraints of the studied objects

Unlike most materials produced since the middle of the 19th century, formed of well-controlled, almost pure phases, prepared from increasingly purified ingredients, the heritage materials of the previous eras – i.e. the majority - are synthesized starting from heterogeneous/not well purified natural products. Even the crystals constituting a rock can present a strong non-stoichiometry, with a variation in composition in the crystal itself (for geologically rare chemical elements and phases, this variability can be a signature of provenance and its conservation in the untransformed relic phases a source of information). Furthermore, the action of temperature, when dealing with products subjected to firing, induces the formation of new phases depending also on the composition of the raw materials^[56], the detailed characterization of which is rarely available.

2.2. Experimental constraints

Two main possible experimental constraints consist in the impossibility of sampling, which implies a study at or through the surface of the objects, and a limited access time to them (the most relevant objects relating to the history of art or techniques are on display and not in storage). Thus, it is required that the operator knows or can make hypotheses about the material structure and stratigraphy. Appropriate techniques such as Optical Coherence Tomography (OCT)^[57,58] could provide this information, but are rarely used, the common approach being to presume that the characteristics of the objects are comparable to those of similar ones (incomplete, broken and revealing their stratigraphy). Suitable optics and a good knowledge of the volume of material generating the Raman signal are also necessary. Furthermore, the low purity of the raw materials as well as the final products porosity or roughness (it is not always possible to clean them before the analysis, especially when cracks and pores are present) can favor the different types of luminescence which raise the level of the continuous background and mask the Raman spectrum. The choice of the excitation laser or better the study with different excitation wavelengths makes it possible to maximize the number of phases that can be identified. Empirically, a blue laser is preferable for inorganic phases (maximization of the scattered intensity, laser cleaning of the surface of organic/biological residues source of fluorescence) while a nIR laser is better suited for polymer leases and organic phases.

3. PCA for Raman spectroscopy – brief overview

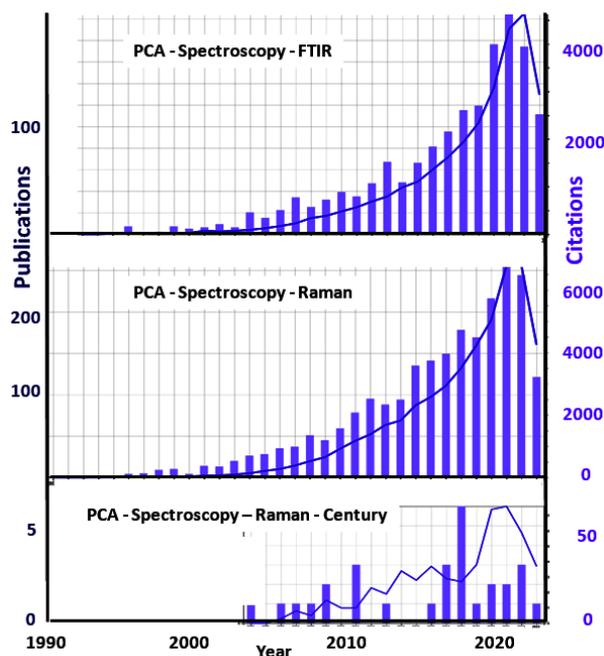


Figure 2. Number of publications (vertical bar, left axis) and of citations (curve, right axis) from 1990 to 2023 from Web-of-Science® database using « PCA-Spectroscopy-FTIR », « PCA-Spectroscopy-Raman » and « PCA-Spectroscopy-Raman-Century » keywords.

Figure 2 compares the number of publications related to the use of multivariate data processing for FTIR and Raman spectroscopies independently from the field of application. The keywords “PCA” (Principal Components Analysis, as one of the most used unsupervised techniques within multivariate statistical analysis), “spectroscopy”, “FTIR” and “Raman” were inserted in the Web-of-Science® (Clarivate Analytics) search tool. The count is certainly imprecise but it anyway provides a view of the evolution of the scientific publications connected to these keywords in the last 30 years. The use of this type of processing of molecular vibrational spectral information began around 2000^[41,42,43] with an almost parabolic progression as the studies related with Cultural Heritage. Representative studies published since 2000s are given^[41,59-62]. The number of studies concerning NIR spectroscopy (mainly used in the field of agronomy and polymer control) is comparable to that represented for FTIR spectroscopy, which means that the use in infrared is certainly broader, since related to both techniques. The number of citations follows a similar law with a strong multiplier coefficient (average of 30 citations/publication) showing the attention paid to this type of works.

To visualize the use of multivariate techniques in the field of Heritage Raman studies we have incorporated the keyword "century" because in almost all of the studies dealing with real case studies the objects are dated and this word is used in the text^[41-62]. The much more limited number of works is evident, and they are reported within a dedicated review article in this issue by Coccato and Caggiani,^[63] to which be referred for a more detailed discussion. In this field, the development of the use of multivariate methods has not been constant in the last decades, as mentioned above being mainly used in the field of agronomy and industrial control,^[64-68] as well as in forensic issues^[69-74] (the contribution of Lei and Massonet presents an overview of car paints identification).^[75] The editors hope that this special issue (Table 1) will contribute to the development of multivariate treatments of Raman spectra in the Heritage sector.

4. Novelty of the approaches

This special issue includes different contributions organized according to three criteria, multivariate analysis of spectral data, special optics for illumination and signal collection and the use of mobile devices for on-site analysis (Figure 3), several contributions responding to more than one of these criteria (Table 1). Furthermore, coupling with information coming from several mobile instruments is documented (generally XRF, FORS or Hyperspectral camera), as well as the exploitation of the entire spectrum collected by a Raman spectrometer, that is to say both the Raman spectrum itself and its “continuous background” which contains the components of luminescence, information related to the natural materials used but also to the production process, in particular the pollution induced by grinding operations^[15].

Table 1: List of the papers published in the present special issue of Journal of Raman Spectroscopy “Advanced Raman procedures applied to natural / cultural heritage and forensic questions: mobile set-up, data treatment and associated techniques”.

Contribution	Criteria	Multivariate analysis	Optics & spectral range	Mobile Raman set-up	Coupling With other Mobile instrument	Field	Refs.
Lei & Massonet	X					Forensic	75
Coccatto & Caggiani	X					Review/Cultural	63
Burlot et al. I	X	X	X	X	X	Cultural	76
Burlot et al. II	X	X	X	X	X	Cultural	77
Caggiani et al.	X			X		Cultural	78
Privitera et al.					X	Cultural/Forensic	79
Almehmadi & Lednev	X	X	X	X		Forensic	80
Fornasini et al.				X		Cultural	81
Vermeersch et al.				X		Natural	82
Vieira et al.			X	X		Cultural	83
Pasetti et al.				X		Natural	84
Bouvier & Elliott			X			Cultural	85
Ruiz Moreno et al.			X			Cultural	86

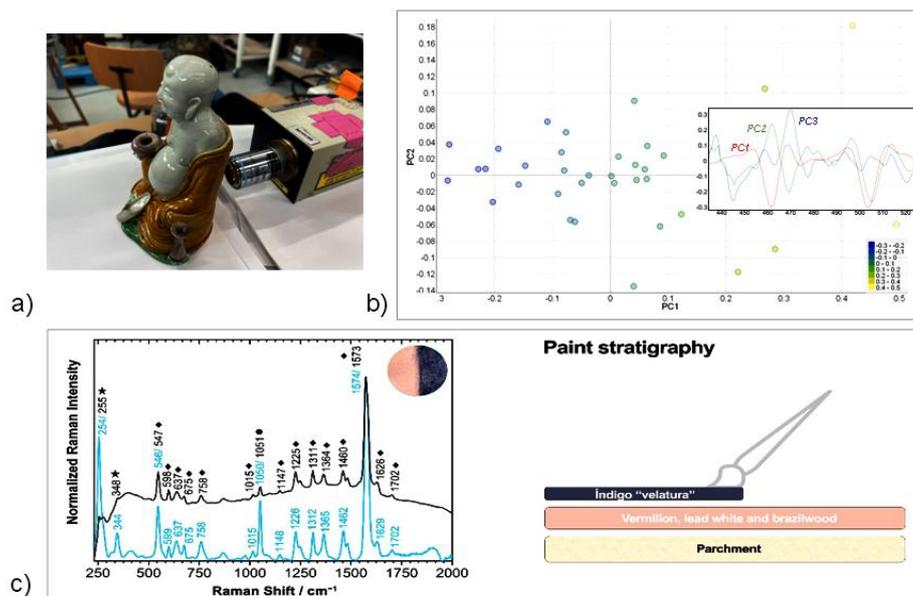


Figure 3: Representation of the three main approaches exemplified in the present special issue: a) mobile instrumentation with direct *in situ* analysis of a cultural heritage object, b) multivariate analysis of spectral data by means of PCA with scores graph of the first 2 PCs and loadings diagram of the first 3 PCs (modified from Caggiani et al.^[78]) and c) spatially offset Raman spectroscopy showing the possibility of detecting different compounds from the layers constituting a paint stratigraphy (from Vieira et al.^[83]).

4.1. Multivariate Statistical Analysis

The multivariate statistical analysis approach has been applied by (Lei & Massonet)^[75] to the forensic field, in particular using PCA for the discrimination of the Raman spectra of 54 white Volkswagen automotive paints. Correlations between paint characteristics and discriminating factors (such as model, topcoat color code, production year, assembly plant) were investigated.

In this issue, a review of the works applying PCA to Raman spectroscopy for cultural heritage-connected materials is included too (Coccatto & Caggiani)^[63]. In this, a delay of about a decade was observed with respect to PCA application to elemental quantitative data of archaeometric analyses, as well as a marked unbalance between the studies pertaining to the different sections with a strong preference of painting materials. Special attention was given to the pre-treatment of the spectra, which was observed to be essential to overcome the influence of several spectral issues. Within this field, a couple of parallel works considered Lead-tin/Naples Yellow (Burlot et al., I)^[76] and blue and yellow/green enamels (Burlot et al., II)^[77] of objects from French and Chinese productions of the 18th century, in both cases comparing different approaches. The purpose is to document the transfer of enameling technology from France to Chinese Court by the mean of Jesuit missionaries, using the information that remains embedded in the matter of enamels and glaze. A classical approach consisted in the observation and study of the parameters obtained from the spectral decomposition, the alternative one used multivariate analysis with Principal Component (PCA) or Hierarchical Clustering Analysis (HCA) of the spectra and of the band parameters originating from a spectral decomposition. The combination of a reasoned analysis of the Raman spectra with the PCA of spectroscopic parameters extracted from Raman spectral decomposition appeared effective in categorizing the different pigments.

A collection of Hellenistic–Roman glyptics was investigated *in situ* by Caggiani et al.^[78] also with the aim of testing the application of in-depth data treatment on spectra acquired with mobile

instrumentation. The results of the PCA carried out on a group of chalcedony items were successful in separating spectra with higher or lower contribution of the band due to the presence of moganite (a variety of silica hosting Si-O-H bonds).

Finally, the work by Almealmadi & Lednev^[80] demonstrated that stand-off Raman spectra (the quality of spectrum is lower when recorded under such difficult condition) of bloodstains could be correctly identified using a previously built Support Vector Machine-Discriminant Analysis (SVM-DA) model for the identification of all main body fluids. This work illustrates the potential brought by sophisticated chemometric techniques and certainly the use of artificial intelligence processes. This study shows the importance of using sophisticated chemometric methods, an approach which is likely to develop with the increasing ease of access to Artificial Intelligence processes. Sophisticated data processing methods have already shown their effectiveness in extracting spectral information from very poor spectra according to the visual observation criterion.^[87-89]

4.2. Mobile instrumentation

Several fragments of “pietra ollare” (soapstone) artifacts, dating back to the Medieval period were analyzed by Fornasini et al.^[81] with both laboratory and mobile Raman instrumentations together with complementary techniques. Mobile Raman measurements assured a quick and effective evaluation of the samples’ composition thus constituting a preliminary identification that could be obtained directly in situ. The above-mentioned couple of papers concerning French and Chinese 18th century enameled objects (Burlot et al I, II)^[76,77] involved a large collection of spectra - previously acquired with a mobile Raman setup – that were effective for identification of yellow, blue and green pigments and for the study of the glassy matrices. Concerning pigments, another study (Vermeersch et al.)^[82] here published investigates five mineral samples of manganese oxides with different Raman instrumentations, including mobile systems, highlighting successes and challenges. The work by Vieira et al.^[83] showed the potential of a combined approach that complemented handheld Raman spectroscopy with micro-SORS for the characterization of Medieval paints.

In the field of cultural heritage, a different kind of material -semi-precious stones- has been studied by Caggiani et al.^[78] in the already mentioned work on a collection of Hellenistic-Roman glyptics. The Raman approach was totally noninvasive and carried out in situ with no sample preparation and minimal interference with the museum's activities. Pasetti et al.,^[84] instead, analyzed natural samples of gemstones, tourmalines (dravite-schorl series), to correlate the relative Mg-Fe content $[Mg/(Mg+Fe)]$ obtained from SEM-EDS with variations in Raman spectrum parameters and Raman measurements with a portable spectrometer were also performed in order to evaluate their results for in-situ application.

Finally, Almealmadi & Lednev^[80] collected bloodstain spectra using a handheld Raman spectrometer equipped with a standoff attachment and compared with spectra acquired with a benchtop Raman microscope. This technique starts also to be used for cultural Heritage studies.^[9,90,91,92] The two sets of spectra were visually similar, supporting the potential use of a handheld Raman spectrometer with stand-off attachment for blood detection at the scene of crime.

4.3. Optics and spectral range issues

To characterize pigments embedded in a glassy matrix (Burlot et al. I & II)^[76,77], the collection of a “pure” spectrum for each phase of the composite enamels (many crystalline and amorphous phases are present simultaneously) is required, which implies the use of a very high magnification microscope

objective (x200) for the collection of single pigment grains Raman signature. Micro-spatially offset Raman spectroscopy (micro-SORS) technique was tested on the multilayer systems mimicking the resulting stratigraphy of the Sfumato glaze technique and appeared to be able to distinguish between different stratigraphic samples, varying in concentration of the same carbon-based pigment, and the order of layers (Bouvier & Elliott)^[85]. Micro-SORS was also applied by Vieira et al.^[83] to the characterization of Medieval paints. This methodology was tested on a series of historically accurate reconstructions prepared as pure, mixture, and layered paints on parchment, based on historical information: micro-SORS proved decisive in differentiating between mixture and layered paints in most reconstructions examined, yielding detailed information about the stratigraphy of reference samples produced through the overlaying of different paints.

The optics problem of focusing and collecting scattered light from spots that cannot be reached by the operator, who, for various reasons, needs to stay far away from the analyzed material, can be overcome by the employment of stand-off Raman spectroscopy. Its usefulness is easily understood for forensic applications (e.g., when the crime scene cannot be contaminated)^[80], but also for cultural heritage cases (e.g. for wall paintings and architectural interiors)^[90-92].

The paper by Ruiz-Moreno et al.^[86], instead, investigated the potentiality of using different spectral ranges to exploit the information deriving from photoluminescence (PL). Actually, various research groups have recently made an important effort to try and make the best possible use of the spectral information often considered as “simple background”^[15,93]. In the paper published in this issue, six cobalt-based trademark pigments and two chemically pure compounds, cobalt aluminate and calcined alumina, were analysed with a Raman spectrometer and a red He-Ne laser as excitation source: an excess of calcined alumina was observed and detected in a few seconds thanks to the surprising and high intensity of PL that this residual product emits when it is illuminated with the He-Ne laser.

4.4. Coupling with other mobile instruments

Combination of Raman spectroscopy with other techniques that employ mobile instruments, such as portable EDXRF is exemplified in the paper by Privitera et al.^[79] involving cultural heritage and forensic fields, since it addresses the authenticity issue of fake potteries circulating in the illicit art market. The work aimed at studying ointment vases mimicking the “Etruscan-Corinthian” style identifying errors that the forger committed with respect to the original manufactures. It was possible to clarify the aspects characterizing the *modus operandi* of the forger, through the identification of anachronisms. The necessary information provided by pXRF is also underlined in Burlot et al. papers.^[76,77]

5. Perspectives

One of the perspectives that emerge from this special issue is the combination of different novel approaches at the same time (Figure 4). For example, when analyzing cultural heritage or forensic contexts directly in situ, the need of applying multivariate statistical analysis on a high number of spots/items can appear as useful to balance the drawbacks of mobile instrumentations. At the same time, the combined use of various and complementary mobile instrumentations, which is by now well-known and widely applied, can be added to the statistical data analysis – leading also to data fusion treatments – or to special optics devices/procedures employment.

As a consequence, it seems that, by now, the approach much employed in the last decades, mainly using mock-up or reference samples to simulate the analysis of heritage or forensic-connected

materials, can be partially overcome, especially for the much-studied classes of materials (e.g. pigments), with more attempts to the direct investigation of real items, exploiting the above-mentioned procedures and treatments.

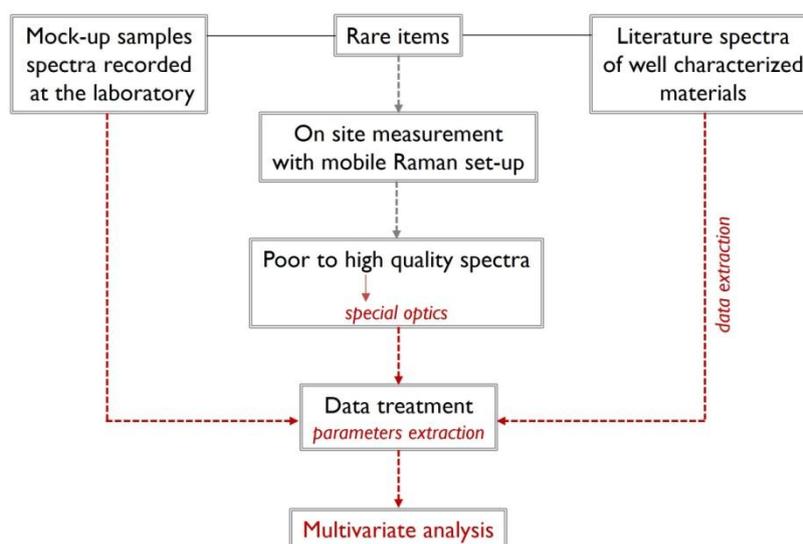


Figure 4: Scheme of the advanced procedures described, involving real items, mock up samples and literature spectra, with the consequent measurements and/or treatments to be applied.

Another new perspective is that of collecting data from the literature concerning one specific subject and put them together with a statistical treatment in order to better contextualize newly acquired data. For a long time, it has been necessary to request communication of primary data from the authors. Open access software makes it easy to convert published image spectra into usable digital data. The generalization of accessibility of primary data provided by numerous journals in Supplementary Information facilitates the creation of databases allowing multivariate analyses. This has been done for long time with quantitative elemental composition data in the archaeometric field, for example.

In conclusion, with this special issue, the editors want to encourage the Raman spectroscopy scientific community to apply the described advanced procedures in the fields of Cultural and Natural heritage and of forensic science, as well as to strive for the proposition of new ones.

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