

Mobile Spectroscopic Instrumentation in Archaeometry Research

Peter Vandenaabeele¹ and Mary Kate Donais²

Applied Spectroscopy
2016, Vol. 70(1) 27–41
© The Author(s) 2015
Reprints and permissions:
sagepub.co.uk/journalsPermissions.nav
DOI: 10.1177/0003702815611063
asp.sagepub.com



Abstract

Mobile instrumentation is of growing importance to archaeometry research. Equipment is utilized in the field or at museums, thus avoiding transportation or risk of damage to valuable artifacts. Many spectroscopic techniques are non-destructive and micro-destructive in nature, which preserves the cultural heritage objects themselves. This review includes over 160 references pertaining to the use of mobile spectroscopy for archaeometry. Following a discussion of terminology related to mobile instrumental methods, results of a literature survey on their applications for cultural heritage objects is presented. Sections devoted to specific techniques are then provided: Raman spectroscopy, X-ray fluorescence spectrometry, Fourier transform infrared spectroscopy, laser-induced breakdown spectroscopy, and less frequently used techniques. The review closes with a discussion of combined instrumental approaches.

Keywords

Mobile instrumentation, Portable instrumentation, Art analysis, Archaeometry, Archaeology, Cultural heritage, Field research, Spectroscopy, In situ

Date received: 20 April 2015; accepted: 22 May 2015

Introduction

Archaeometry is a growing research area that covers the use of techniques from natural sciences (e.g., chemistry, physics, spectroscopy, geology, biology, etc.) to contribute to research in humanities (archaeology, art history, anthropology, etc.). This research field includes among others the application of analytical techniques and the use of geophysical techniques, and can include statistical methods to solve questions on provenancing, dating, prospection, landscape reconstruction, etc. Also, research in conservation science can be considered as part of archaeometry. Analytical archaeometry,¹ the focus of this review, however, is the research area focused on the analysis of archaeological and art objects, rather than on landscapes or prospection.

When performing research in analytical archaeometry, it is often a requirement not to damage the object as each manipulation involves a certain risk. Therefore, researchers should aim to minimize any potential damage or risk of damage (D) to the artwork. On the other hand, there is also the goal to extract as much valuable information (I) as possible and when planning research, one should try to maximize the information-to-(risk-on-) damage ratio: I/D. This can be achieved by trying to obtain more information (e.g., by using complementary analytical techniques), by

reducing the risk on damage (e.g., by using nondestructive or micro-destructive techniques), or by a combination of these approaches.

In this context, it should be remarked that there is slight confusion in literature concerning the use of a number of related terms to describe analytical techniques such as non-destructive and non-invasive. Nondestructive analytical techniques are methods that do not consume the sample during the analysis; after the analysis, the sample is still available for further investigation. Many spectroscopic methods can be considered as nondestructive, whereas other approaches, such as chromatographic techniques, should be considered as destructive. Micro-destructive techniques cause small damage to the sample, as this often involves some subsampling on a micrometer scale, as in the case of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). So where the terms destructive, micro-destructive, and non-destructive apply on the level of the sample, the terms invasive

¹Department of Archaeology, Ghent University, Ghent, Belgium

²Department of Chemistry, Saint Anselm College, Manchester, NH, USA

Corresponding author:

Mary Kate Donais, Department of Chemistry, Saint Anselm College, 100 Saint Anselm Drive, Manchester, NH, USA.
Email: mdonais@anselm.edu

and non-invasive apply to the object as a whole. Non-invasive techniques require no sampling of the artifact, whereas invasive approaches do. The use of non-invasive techniques implies that direct analysis is performed: the object and the laboratory instrumentation are in such a way that the artifact can be analyzed, typically by causing no damage or only micro-damage. So, typically, non-invasive techniques are nondestructive or micro-destructive approaches. In situ studies are direct investigations where the instrumentation is brought outside the laboratory, to the cultural heritage object, and they typically involve mobile instrumentation. Examples include field campaigns on archaeological sites or geological outcrops, direct analysis of wall paintings or rock art, or measurements in the exhibition room of a museum.

Direct or even in situ analyses are good approaches to optimize the I/D ratio and therefore favor the use of mobile instrumentation. Different factors determine the degree of mobility of analytical instrumentation, including the weight and size of the instruments, their robustness, and their degree of independence of resources (e.g., electrical power, cooling water, liquid nitrogen, etc.). Smith discriminates between “portable” and “transportable” instrumentation based on whether the instrument is portable by a single man or by four men.² In previous work we distinguished different types of mobile Raman spectrometers,^{3,4} and these definitions as provided below and illustrated in Figure 1 are easily adaptable to other spectroscopic techniques:

- *Transportable instrumentation.* Most analytical instruments can be considered as transportable: they can

be moved from one lab to another in cars or vans and require some installation when brought in the lab.

- *Mobile equipment.* Instrumentation typically designed for mobility. Stability of the spectrometer was taken into account when designing it, and the operator does not need to adjust internal parts (e.g., outlining) when it is brought on site. Usually, no elaborate calibration procedure is required after moving the instrument.
- *Portable spectrometers.* Portable instruments are mobile spectrometers that can be carried by a single person. These instruments are often battery-operated and fit in a suitcase or backpack – typically the size of hand luggage allowance for airplanes. Usually these instruments have no moving parts, which enhances the robustness during transport.
- *Handheld instruments.* These spectrometers can be operated while being held in the hand by the operator. Normally measurement times are relatively short, as the operator should be able to hold the instrument in the appropriate position during the measurement. Sometimes tools can be used for a more stable positioning (e.g., tripod).
- *Palm instrumentation.* A palm instrument is a very small instrument that is very lightweight and has very small dimensions – it fits more or less in the palm of one’s hand. Due to the very small dimensions, usually spectral resolution is low and these instruments can be used for fast discrimination between products with clearly different spectral properties.

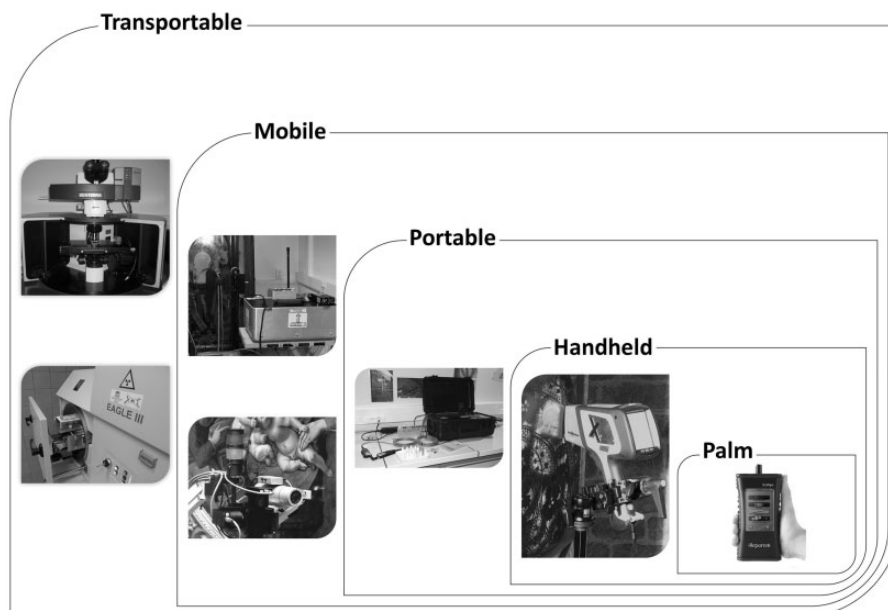


Figure 1. Examples of the different categories of spectroscopic instrumentation, according to the degree of mobility. Transportable: Bruker Senterra Raman instrument and EDAX Eagle III XRF spectrometer; Mobile: Mobile Raman instrument (MARTa) and Bruker ARTAX (Image from: www.bruker.com); Portable: Enwave EZ-Raman -I-Dual; Handheld: Olympus InnovX Delta XRF spectrometer; Palm: SciAps ReporteR Raman instrument (Image from: www.SciAps.com).

In this paper we want to provide an overview of recent research performed with mobile instrumentation on cultural heritage objects. The work focuses on spectroscopic techniques, so we will not discuss other approaches such as methods of visualization like infrared reflectography, ranking light photography, 3D scanning, or in situ microscopy. Figure 2 gives an overview of the evolution of the number

of research papers that were published in this field, along with the evolution of the citations. These data are based on a simple query in ISI Web of Science, and although this approach might miss some references (e.g., publications in archaeological survey reports, documentation in museums, or local publications), it clearly shows some trends. It is evident that the number of publications (and citations) in

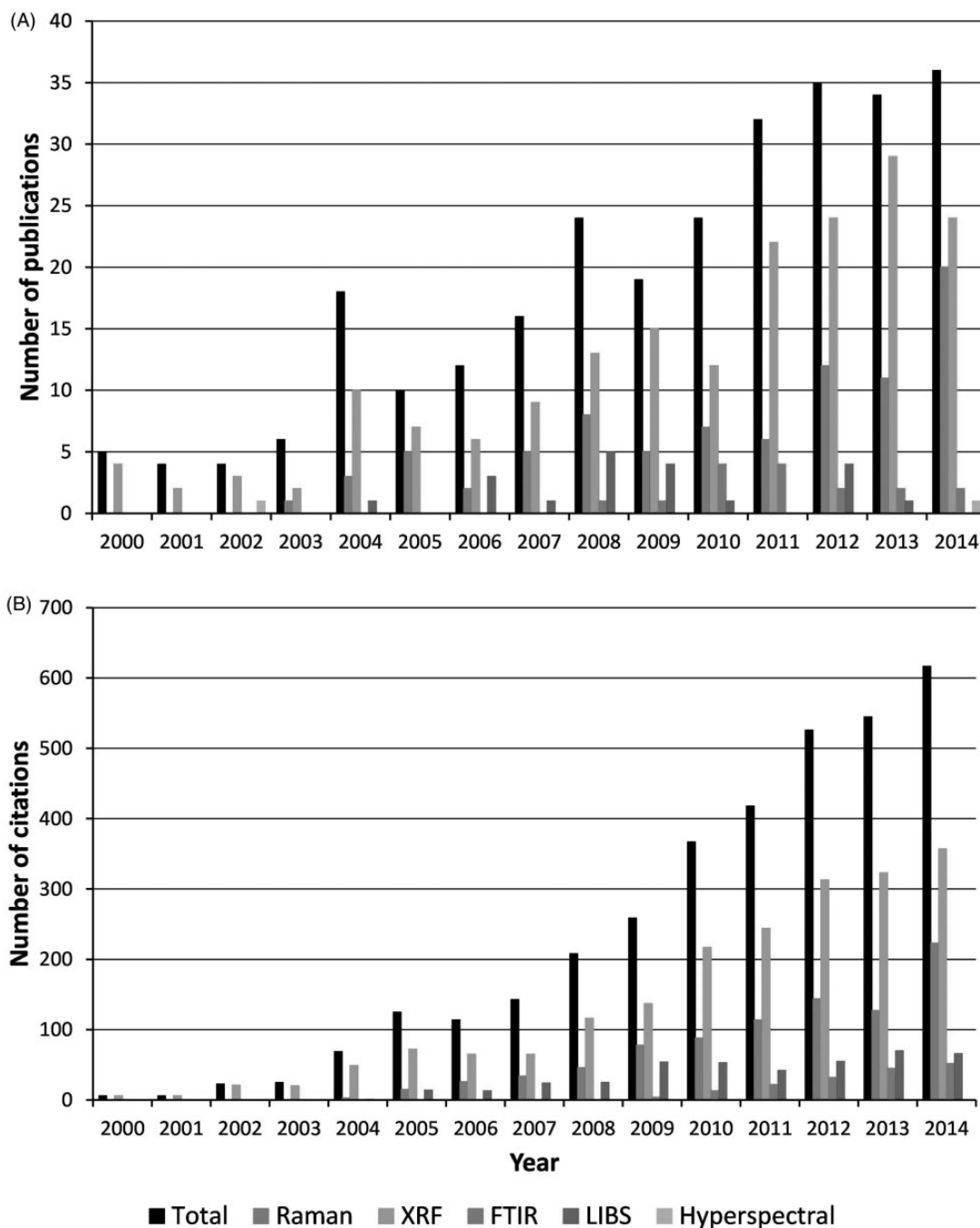


Figure 2. Overview for the number of publications (A) and citations (B) retrieved from ISI Web of Science (2000–2014) for the query: TOPIC: ((mobile OR portable OR handheld) AND (cultural heritage OR archaeo*) AND (spectr*)) and combined with, respectively, AND (Raman); AND (XRF OR X-ray OR X ray); AND (FT-IR OR infra-red or infra red); AND (LIBS OR laser-induced OR laser induced); AND (hyperspectral imaging).

this research field is steadily growing and that the most frequently used mobile analytical techniques are X-ray fluorescence (XRF) and Raman spectroscopy. This observation is supported by the significant number of references included in the XRF and Raman sections of this review. The other techniques, while reported to a lesser extent in the literature, demonstrate the expanding repertoire of portable instrumentation available to researchers and researchers' quests to better characterize the many sample types encompassed within cultural heritage analysis.

The main focus of this review is on direct analysis, inside and outside the laboratory (the latter approach being called "in situ"), using mobile instrumentation. We will highlight the topics according to the analytical techniques that are involved, namely Raman spectroscopy, X-ray fluorescence (XRF) analysis, Fourier transform infrared (FT-IR) spectroscopy, laser-induced breakdown spectroscopy (LIBS), and less commonly reported mobile techniques such as hyperspectral imaging and others. This review will conclude with a discussion on combined method approaches.

Spectroscopic Analysis

A number of instrumental techniques originally developed and utilized for laboratory-based research have been adapted, miniaturized, and/or reconfigured for use in the field. While those discussed here are all based in spectroscopy, the chemical information gleaned from each technique ranges from elemental to molecular and exploits various phenomena including absorption, emission, and scatter. A separate section devoted to each technique is below.

Raman Spectroscopy. The first applications of Raman spectroscopy in art analysis date to the late 1970s, when Dhamelincourt et al.⁵ coupled a Raman spectrometer with microscope optics and applied it to the investigation of artworks, followed by the groups of Delhay⁶ and of Guineau and Coupry in the 1980s.⁷⁻⁹ This limited use of Raman spectroscopy for art analysis lasted until the end of the 1990s when the technique became increasingly popular following the publication by Bell et al.¹⁰ of a database of pre ca. 1850 pigments, a work that was later reproduced and expanded by the same research group.¹¹ Since then, the number of papers in this research field grew expansively.¹²

Raman spectroscopy is very well-suited for investigations of cultural heritage objects. Indeed, the method's non-destructive character combined with its ability to obtain molecular spectra of particles down to 1 μm are very favorable characteristics when studying brittle artworks or archaeological objects. Moreover, micro-samples can be examined, but direct analysis is often also possible provided the laser power is kept sufficiently low.

Small objects can easily be positioned on the microscope stage of a micro-Raman spectrometer (cfr., transportable instrumentation). This approach has been applied to the study of the pigments in medieval manuscripts and loose

leaves.¹³⁻¹⁶ A similar approach was used for the analysis of 19th century porcelain cards that were positioned under the Raman microscope.^{17,18} The difference between the two strategies is that in the first case the instrument was transported to the museum, while in the latter case the artifacts were brought into the laboratory. Apart from the possible cumbersome transport of sensitive scientific equipment, proper room darkening in the location where the analysis takes place is essential: ambient light can overwhelm the Raman signal.

In 2001, the first experiments were published where fiber optic probe heads were used to perform direct analysis on objects of art. By using a fiber optic probe head mounted to an FT-Raman instrument, Raman spectra of the paint layer were obtained through the varnish layer of paintings by Lucebert, Degas, de Chirico, and Magritte.¹⁹ Thus, feasibility of the fiber optic approach was proven and led to the development of portable fiber optic Raman instrumentation specifically designed for art analysis. The probe head was equipped with a color camera and the laser power could easily be adjusted. The dedicated software package allowed for easy calibration of the instrument and also made it possible to store all essential meta-information on the analysis at hand along with the spectrum. As soon as commercial mobile instrumentation became available on the market, comparative studies were organized, with mock-up samples, to test their usefulness for archaeometrical studies.²⁰ Today, several high-quality commercial instruments are available that easily can be applied for art analysis. However, it must be remarked that, to our experience, instrument engineers often underestimate the importance of good macro- and micro-positioning equipment. A comparative overview of commercially available mobile Raman instrumentation has been published.³ The use of mobile Raman instrumentation in archaeometry was recently reviewed.^{3,21}

For the in situ analysis of medieval manuscripts, mobile instruments were brought into a library²² or museum,²³ where the analyses took place. Often these investigations took place in a separate dark room where there was little interference from ambient light. If it is not possible to block out the light, tents have been used to avoid the interference.¹⁶ Several papers also reported on bringing mobile Raman instrumentation into museums.²⁴⁻²⁶ In these cases, investigations were performed in storage rooms, conservation studios, or in the exhibition room itself. Apart from the technical limitations that the latter option poses (darkening, spatial limitations for instrumental setup, etc.), special care must also be taken to inform the public about the investigations that take place, as well as to avoid possible injuries (e.g., people walking over cables or bumping into instrumentation, visitors staring into the laser beam, etc.).

If it is not possible or allowed to sample wall paintings, in situ investigations are the only possibilities. Direct Raman analysis was performed on medieval wall paintings on

several occasions.^{27,28} When working in churches or chapels, darkening the room is not always straightforward, and therefore it can be a good strategy to work at night. As the wall paintings are often situated at elevated heights (e.g., on the ceiling), the Raman spectrometer may need to be positioned on scaffolding. However, working on scaffoldings or elevated platforms often involves stability issues: if during the analysis (typically lasting for some minutes) somebody is moving on the platform, the probe head can move many millimeters, and consequently the area under study moves in and out of focus. Several solutions have been tested to eliminate this problem: the use of micro stepper motors to fine-focus the probe head remotely (and not moving during analysis) is one option;²⁹ the use of separate scaffoldings for instrument and operators is another option;²⁷ or while analyzing the wall painting on the famous church of Pianazzola⁴ a stair was positioned next to the wall painting and the probe head was manually positioned. In the last case, advantage was taken of the dual laser system (green 532 nm laser and red 785 nm laser) to obtain quality spectra of the pigments as well as of some degradation products (e.g., oxalates). When measuring in the Tomb of Menna in Luxor (Egypt),³⁰ the probe head was positioned using an articulating arm. Measurement conditions were rather difficult, including a dusty and sandy environment, uneven ground, elevated temperatures, the need to work with several teams in a small space, and the need to work with an electrical generator. Similarly challenging conditions were encountered during in situ Raman data collection at the Sant'Ansano site located in an agricultural field in Allerona, Italy, and included a dusty environment, uneven ground, elevated temperatures, full exposure to sun, and the required use of a ladder to gain access to the fresco of interest.³¹

Prehistoric rock art from different areas has been the subject of several Raman spectroscopic examinations. Often, the analyses were performed on removed samples and focused on the different phases of iron oxides/hydroxides present.³² Goethite, limonite, and hematite with different degrees of crystallinity are often encountered. In some cases it was possible to determine the presence of oxalates, which are often associated with microbiological activities. Recently, some groups also performed in situ investigations. The work performed by the groups of Prinsloo, Tournié, and colleagues in South Africa is remarkable.^{32–35} They clearly describe the difficulties associated with transporting the instrumentation on site (to be carried by men) and then, due to the rocky environment at the base of the shelter, the difficulties to position the tripod with the probe head. Other examples of direct in situ analysis of rock art by Raman spectroscopy were also performed in Spain³⁶ and France.³⁷

The Raman spectroscopy research group in Bilbao has gained extensive experience in studying stone construction materials under environmental stress: the influence of

airborne aerosols and salts and the formation of efflorescence on building materials, such as stones and mortars, was studied.³⁸ Thermodynamic equilibria were calculated, and based on the detected reaction products degradation pathways were proposed. They applied mobile Raman spectroscopy and similar mathematical models to monitor cleaning and consolidation processes of art objects.^{39,40} The same group also used Raman spectroscopy to investigate wall paintings and mortars in Marcus Lucretius' house in Pompei.⁴¹

A select number of papers were published demonstrating the possibilities of mobile Raman spectroscopy for gemstone analysis. A fiber optic probe was used in combination with a System-100 spectrometer (Renishaw), to study the gems in the Heinrich's Cross reliquary in the Basel Cathedral.⁴² In general, gemstone analysis might seem straightforward by Raman spectroscopy. However, when using mobile instrumentation, as the gemstones are mounted in a reliquary, they cannot be touched or oriented as a function of the polarization of the laser beam, which makes the analysis more difficult compared to laboratory studies. Another remarkable in situ investigation is the analysis of the gemstones and minerals from the Grotto Hall of the New Palace in Potsdam,⁴³ where it was even possible to identify mineral inclusions. Petrova et al.⁴⁴ studied the scepter of the Faculty of Science of Charles University in Prague using a handheld Raman spectrometer equipped with a 785 nm laser.

Raman spectroscopy can be applied for the analysis of glass and glazes. Typically these objects are investigated using a blue or green laser. The Colombar group demonstrated that the technique is well suited for the study of the structure of the amorphous silicate matrix.^{45,46} Several papers were published by this group on the analysis of different types of porcelain and enamels in museums.^{47–50} A review was published on the use of mobile Raman spectroscopy for the analysis of glass and glazes, including a detailed description of the mathematical approaches that can be used to extract information on the types of materials, as well as on their degradation.⁵¹ This research group also analyzed the stained glass windows in the Sainte-Chapelle (Paris) using fiber optic Raman spectroscopy.⁵² As sunlight was passing through the stained glass windows, the measurements could only be performed at times of the day when the sun did not reach the windows, thus avoiding this interference. Through application of appropriate data processing techniques, parts of the glass pieces were identified as medieval, while others are 19th century replacements. By using mobile Raman spectroscopy in a museum context, Ricciardi et al.⁵³ were also able to identify the types of glass from a series of glass objects dating from the 15th to 19th centuries.

X-ray Fluorescence Analysis. X-ray fluorescence (XRF) spectrometry is a nondestructive atomic spectroscopic technique that can provide both qualitative and quantitative

information regarding the elemental composition of a sample. The first portable XRF instruments, developed mostly for military and mining purposes, were reported in the literature about 50 years ago.^{54–58} These instruments utilized radioisotope sources and were largely laboratory-developed although a limited number of commercial instruments were available.⁵⁹ With the availability of air-cooled X-ray tube sources and thermoelectrically cooled X-ray detectors,⁶⁰ the development and applications of portable XRF instruments has increased exponentially in recent years. This is especially evident in the number of commercial portable XRF instruments now available to researchers.⁶¹ These energy-dispersive XRF (EDXRF) instruments, which have no moving parts, are compact and rugged – essential requirements for use outside a controlled laboratory environment. Portable EDXRF instruments are also lower cost relative to their wavelength-dispersive benchtop counterparts and are much simpler to operate compared to other atomic spectroscopic techniques such as inductively coupled plasma atomic emission spectroscopy. The increased use of portable XRF in archaeometry is not without controversy, however, as users with little training and knowledge in the proper application of the technique gain access to these simple point-and-shoot instruments.^{62–64}

Resources with detailed descriptions of instrument components and design, the theoretic basis of the technique, and its applications are available.^{65–67} With respect to equipment design, most instruments provide sufficient signals to detect elements $Z \geq 20$ (calcium) with some instruments capable of lower Z elements such as aluminum, silicon, and sulphur.^{68–70} The sample area exposed to the X-ray beam, referred to as the instrument spot size, also can vary considerably depending on instrument design. Some mobile XRF instruments are designed more for bulk analysis with larger spot sizes in the range of 9–170 mm².^{69,71,72} Instruments with smaller spot sizes, some of which are labelled as μ -XRF with diameters in the range of 40 μ m to 1 mm,^{68,73–77} have been reported for samples requiring finer spatial resolution.

While qualitative information is easily determined by matching XRF spectral peak energies to known elemental values, quantitation can be considerably more challenging for a variety of reasons including sample homogeneity, coatings, or contamination on the sample surface, sample shape, and the various interactions X-rays can have with a sample's matrix including attenuation, refraction, and absorption. Quantitative methods fall into two general categories: fundamental parameters methods^{78,79} and methods utilizing regression models, which often include Compton scatter normalization.⁷⁹ Both methods include standards of at least similar composition and ideally matched composition to the samples. Fundamental parameters methods are most often applied to metallic samples whereas regression methods are used for soils and other similar geological samples.

Pigments are the most common archaeometric sample type examined using mobile XRF. Typically, qualitative results for the major elements present are compared to the chemical formulae of known pigments of the time period of interest with the goal of identifying the specific pigment present. But while identification of an exact pigment present via only XRF analysis is difficult, pairing XRF data with data from structural techniques such as Raman or X-ray diffraction (XRD) can often lead to definitive results; a number of studies using both XRF and XRD or combination XRF–XRD instruments have been reported.^{80–83} Pigment identification is important for many archaeometric artifact categories including museum artworks,^{25,68,82,84–88} fresco and church artworks,^{27,71,75,82,89} cave art,^{81,90} illuminated manuscripts,⁹¹ ceramics,^{70,77,92–94} and sculptures.^{72,95,96} Beyond pigment identification, mobile XRF can aid in the detection and documentation of later conservation efforts,⁸⁴ to investigate possible forgeries,⁸⁵ and for sourcing minerals.⁹⁰ Duran et al.⁹¹ recently demonstrated that mobile XRF studies can be expanded to include not only pigments but also the paper, writing ink, and metal gilding on an illuminated parchment. Alfeld et al.⁹⁷ utilized two-dimensional scanning via mobile macro-XRF for in situ studies of paint layers in various museum works. And while qualitative pigment studies predominate the literature, a quantitative study of binary pigment mixtures also has been reported.⁹⁸

A limited number of obsidian studies utilizing mobile and in some cases handheld XRF have been reported.^{99–102} All discuss the feasibility of mobile instrumentation compared to traditional laboratory-based XRF and alternative techniques such as instrumental neutron activation analysis for achieving the high accuracy required for obsidian sourcing. Quantitation approaches included linear regression,¹⁰¹ quadratic regression,⁹⁹ fundamental parameters,¹⁰⁰ and corrections utilizing Compton scatter.¹⁰² And while the researchers all concluded that mobile XRF can be successfully used for obsidian sourcing, concerns were noted by some.

Examination of pottery and ceramics via mobile XRF can include any combination of pigments, slip, glaze, and body. Applications including quantitative determinations of elements present in the materials have been reported,^{73,77,103,104} while others only involve qualitative evaluation of spectra.^{70,92–94,105} Many studies focus on the examination of pottery fragments, commonly referred to as sherds.^{70,73,77,92,93,103,105} More unusual sample types include floor tiles⁹⁴ and clay figurines, tokens, and sling bullets.¹⁰⁴

The strengths of mobile XRF lend themselves well to the characterization of metallic objects. A diverse array of archaeometric artifacts including statues,^{68,106,107} a sword,⁹⁶ jewellery,⁷⁴ plates and dishes,^{74,108} and religious objects^{108,109} have been examined by researchers. And the metal compositions investigated included those consisting predominantly of copper,^{68,74,106,107,109,110} gold,^{74,96,108,110}

silver,^{74,108} and iron.⁹⁶ A set of calibration standards developed for heritage copper alloy analyses via XRF is available; while intended for all XRF instruments and not just with mobile XRF, use of these standards should improve the accuracy and quantitation range for copper alloy research.¹¹¹ One challenge noted by some researchers examining metallic objects is the common occurrence of a thin outer corrosion layer that differs from the object's bulk composition and may affect quantitative results.^{68,106,107} This unwanted outer layer is most typically caused by exposure to the environment and is often referred to as patina. Alternatively, the thickness of intentionally applied thin layers can be characterized as demonstrated in work reported by Hayakawa et al. on gold leaf⁹⁶ and Karydas and Ferretti et al. on gilding.^{74,108}

A lesser explored category within archaeometry is mobile XRF analyses of stone and construction materials. Weathering and environmental effects on stone surfaces have been reported by Angelini et al.,⁹⁵ Ogburn et al.,¹¹² and Potts et al.¹¹³ Sourcing–provenance of stone tools¹¹⁴ and bricks¹¹⁵ has also been reported. And mobile XRF data from floor tiles,⁶⁹ mortars, and hydraulic cements^{116,117} has been evaluated statistically to aid in site evaluation and phasing.

Soils, often examined from a geological or environmental point of view, have been demonstrated to be of importance for field archaeology. Some research has utilized quantitative XRF data collected via mobile instrumentation to better understand human activity patterns such as the location of house structures and areas for food preparation or consumption.^{118–120} Davis et al.¹²¹ were able to characterize the soil geochemistry at a site in Idaho so as to predict lithostratigraphic membership. And while not applied to actual cultural heritage samples to date, Hunt and Speakman propose detailed protocols for quantitative archaeological soil studies utilizing mobile EDXRF instrumentation.¹²²

Research on archaeological glasses and enamels also have been aided by the availability of mobile XRF instruments. Accurate quantitative studies on glasses are fairly easy to achieve utilizing the wide array of glass certified standards produced by a number of sources. Samples of interest include beads,^{123,124} amulets,¹²³ tesserae,^{125,126} flasks,¹²⁷ and enameled objects.^{128,129}

Fourier transform infrared spectroscopy. Despite the benefits of its ability to simultaneously characterize both inorganic and organic species, the need for micro-sampling with traditional salt plate-based FT-IR instrument designs makes this technique less than ideal for many archaeometry studies. Early mobile FT-IR instruments date to the 1980s^{130,131} with applications focused in environmental analysis. Weiner and Goldberg¹³² reported use of a portable FT-IR at an archaeology site in Israel in 1990. Small KBr pellets were made of sediment and bone samples, a preparation procedure noted by the authors as needing improvement as it effected sample throughput with a mere 15 samples analyzed per day and was obviously destructive to samples.

With the development of alternate sampling devices such as attenuated total reflectance (ATR) and fiber optic reflectance probes, the opportunities to apply FT-IR to cultural heritage analysis have broadened. Nel et al.¹³³ used mobile ATR FT-IR to characterize micro-samples of adhesives on repaired archaeological pottery in a Melbourne University collection. Although micro-destructive in nature, this approach did no damage to the pottery itself as only the adhesives were sampled. Research studies using fiber optic Fourier transform mid-IR reflectance spectroscopy (FORS) are more common with applications reported for synthetic conservation treatments on plaster,¹³⁴ plastic components on museum objects,¹³⁵ pigments,^{136,137} and pigment mixtures.¹³⁷ A significant advantage to FORS compared to pellet-based FT-IR and ATR FT-IR is its nondestructive nature. Nondestructive portable total reflection FT-IR also has been applied to characterize binders and verify the use of an egg-based medium by the artist on a triptych.¹³⁶

Laser-induced breakdown spectroscopy. The first mobile LIBS instrument was a man-portable suitcase design reported by researchers at Los Alamos in 1996 for toxic metals measurements in soils.¹³⁸ By 2004, instruments had shrunk to briefcase size,¹³⁹ and finally arrived at a backpack design¹⁴⁰ in 2005 but still focused on mostly hazardous and toxic materials analysis. An excellent review was recently published on portable LIBS;¹⁴¹ including both prototype and commercial units, considerable detail is included on instrument components and design. The only application in the field of archaeometry during this early instrument development period was by Gobernado-Mitre et al. in 1997 for online LIBS monitoring of limestone laser cleaning for an historic building.¹⁴² In 2007 Fortes et al.¹⁴³ expanded the utility of mobile LIBS for historic building research to include the elemental characterization of sandstone, limestone, marble, and mortar.

Many of the reported uses of mobile LIBS for archaeometry focus on metallic artifacts. A prototype instrument was used by Orsorio et al.¹⁴⁴ to characterize a Japanese metal jug. The major elements as well as the thickness of the outer Cu layer were determined; environmental contamination likely as dirt also was identified on the object's surface. Copper-based alloy analysis with mobile LIBS includes studies on brooches from an Italian archaeology excavation,¹⁴⁵ fragments of bronze statues,¹⁴⁶ and Minoan bronze objects.¹⁴⁷ Various approaches to quantitation are presented in these studies. Mobile LIBS studies of gold jewelry¹⁴⁷ and Roman silver denarii (coins)¹⁴⁸ have also been reported. And it is worth noting that comparisons of quantitative LIBS results to results from other elemental techniques like XRF^{146,148} and LA-ICP-MS¹⁴⁵ are found in a number of studies.

A multi-technique approach including mobile LIBS with mobile Raman spectroscopy and XRD was used by Westlake et al.¹⁴⁹ to characterize wall painting fragments from the Bronze Age, Roman period, and Byzantine period

to explore variations in the painting materials and techniques across time. Portable LIBS was noted to be easier to use in the field compared to portable Raman but was micro-destructive to the samples and provided less spatial resolution.

A particularly interesting application of mobile LIBS for field archaeology was for submarine measurements in the Mediterranean Sea.¹⁵⁰ Solid objects examined included metallic alloys, ceramics, rocks, wood, and bones to fully evaluate the utility of the instrument. A fiber optic cable was used to deliver the laser pulse with an air flux to remove seawater from the sample surface during analysis. The main instrument housing was located on a ship's deck with the fiber optic cable deployed over the ship's side in the control of a researcher in dive gear. The researchers concluded that mobile LIBS shows considerable promise for the characterization of objects at underwater archaeological sites, although immersion depth does affect the signal for some elements.

Less commonly reported spectroscopic techniques. A handful of other mobile techniques have been applied to archaeology and art. Verri et al.¹⁵¹ report on a multi-instrument study using a portable fluorimeter, portable time-resolved fluorimeter, and a portable spectrophotometer capable of both fluorescence and reflectance measurements to characterize wall paint replicas. The reference samples examined in the study were previously characterized using a number of chromatographic and spectroscopic techniques through a project coordinated by The Getty Conservation Institute. A study using both in situ steady-state luminescence measurements and luminescence lifetime measurements was used by Romani et al.¹⁵² to study organic pigments on pages of The Book of Kells. Gil et al.¹⁵³ conducted in situ measurements with portable visible spectroscopy together with micro-sampling to document wall painting blue pigments in deteriorating churches in southern Portugal. Changes in the painters' material choices across four centuries were noted together with changes in the appearance of some paints from their original colors. The application of a novel portable micro-fading spectrometer for lightfastness measurements was reported by Lerwill et al.¹⁵⁴ paint samples from the studio materials of JMW Turner were studied. And lastly, a mobile hyperspectral imaging spectrometer was used to study an Alberto Burri painting at the Ex-Seccatori del Tabacco museum in Perugia, Italy.¹⁵⁵ A number of pigments were identified via the two-dimensional instrument output and corresponding false color images; results were confirmed through single-point measurements with a portable FT-IR spectrometer.

Combined Approaches

As discussed previously, an important goal in this research field is maximizing the useful information that is gathered while minimizing the (risk of) damage. Combining several

analytical techniques during in situ research seems a straightforward approach. When considering this, we should be clear on what we mean by "useful information". The results from two analytical techniques can be confirmatory: if they both point out the same result, the rationale behind using a second analytical technique might be that one technique confirms the results of the other, which strengthens the accuracy of the obtained results. On the other hand, often two techniques may also provide complementary information: when one technique does not yield useful information, another method may be of use. Third, if two techniques seem, at first sight, to provide contradictory information, it is the analyst's task to try to identify possible reasons.

When using multiple techniques on the same artifact, typically thorough site preparation is needed. In addition to the practical details such as safe positioning of and access to the artifact itself, electricity for equipment, etc., also clear plans have to be established on a prioritized timeline for the investigation. Typically, the access time to the artifact is limited, e.g., during closing hours of the museum, and one can choose to perform the different studies simultaneously or one after the other. Also, health issues have to be taken into account, for instance when working with X-rays. Moreover, if several analysts have to work in a small space, safety of the artwork has to be ensured. A good practice is to limit the number of people who are involved on site. Moreover, each analytical technique might require specific experimental conditions which can hamper the practical organization when working simultaneously (e.g., working in darkness for Raman spectroscopy, keeping a safety perimeter when using X-rays, vibration issues when working on a scaffolding).

For the ease of data interpretation, it is of the utmost importance to document the exact spot where the analysis took place, and it is a good practice to try to investigate the same spot with the different analytical techniques. Although this might seem straightforward, during interpretation it has to be taken into account that the techniques have different lateral resolution and penetration depth. All team members should fully understand the research questions on hand, so that they know exactly what needs to be studied.

Some research teams have a whole series of mobile analytical techniques available, and they can bring an array of instruments on site for direct analysis of artwork.^{156,157} This approach has proven to be very helpful for the analysis of important artwork.^{158,159} Despite this approach being very effective, bringing specialists on site to coordinate the work is often limited to the topmost important artwork, and time on site is always limited. On a smaller scale, a combined method approach using a smaller number of in situ techniques has been used for the analysis of Egyptian wall paintings,³⁰ panel paintings,²⁵ a majolica tile floor,⁹⁴ Roman fresco fragments,¹⁶⁰ and gemstones.⁴⁴ Typically, this research is started with macrophotography

and digital microscopy, and then combinations are made of a molecular spectroscopic technique (Raman spectroscopy) with an elemental spectroscopic approach (XRF). There has been a single instrument that combined both XRF and Raman analysis,¹⁶¹ but there is no convincing advantage to house both techniques in a single instrument compared to using two separate spectrometers. As noted early in this review, a number of studies utilizing combined XRF-XRD instruments for archaeometric studies have been reported and take advantage of a common radiation source.^{80,82} In the case of combining Raman spectroscopy with LIBS, the advantage is comparatively straightforward,¹⁶² as ideally both techniques can partially use the same optics. This approach was successfully applied in several cases for the direct analysis of cultural heritage materials,^{163–166} and the approach can even be combined with laser cleaning of stone artifacts, such as historical buildings. However, compared to a mobile Raman instrument, the combined LIBS-Raman setup is significantly larger and heavier.

Conclusions

In this review, an overview is given of recent studies of cultural heritage materials using mobile instrumentation. The terminology is defined and then the major issues are discussed, depending on the techniques that are deployed. X-ray fluorescence and Raman spectroscopy are by far the most used mobile techniques in the field of art analysis. Their applications, advantages, and disadvantages are discussed. We also describe some applications of Fourier transform infrared spectroscopy, laser-induced breakdown spectroscopy, and other lesser used mobile spectroscopy techniques. Finally, some ideas on using combined method approaches are provided.

As demonstrated by the increasing number of publications and citations in this field, mobile instruments are playing a vital role in art and archaeology analysis. Instrument manufacturers are supporting this trend through improvements to current devices – smaller size, lower cost, improved capabilities – and adaptation of other devices to new mobile platforms. The archaeologists, art conservationists, chemists, and others using these practical and powerful instruments have much to look forward to as forge ahead to learn more about the chemistry behind cultural heritage objects.

Funding

This work was financially supported for PV by the Concerted Research Actions Programme (GOA) of the Special Research Fund of Ghent University.

Conflict of Interest

The authors report there are no conflicts of interest.

References

1. H.G.M. Edwards, P. Vandenabeele. *Analytical Archaeometry - Selected Topics*. Cambridge, UK: RSC Publishing, 2012.
2. D.C. Smith. "In Situ Mobile Subaquatic Archaeometry Evaluated by Non-Destructive Raman Microscopy of Gemstones Lying Under Impure Waters". *Spectrochim. Acta, Part A*. 2003. 59(10): 2353–2369.
3. P. Vandenabeele, H.G.M. Edwards, J. Jehlicka. "The Role of Mobile Instrumentation in Novel Applications of Raman Spectroscopy: Archaeometry, Geosciences, and Forensics". *Chem. Soc. Rev.* 2014. 43(8): 2628–2649.
4. D. Lauwers, A.G. Hutado, V. Tanevska, L. Moens, D. Bersani, P. Vandenabeele. "Characterisation of a Portable Raman Spectrometer for In Situ Analysis of Art Objects". *Spectrochim. Acta, Part A*. 2014. 118: 294–301.
5. P. Dhamelincourt, F. Wallart, M. Leclercq, A.T. Nguyen, D.O. Landon. "Laser Raman Molecular Microprobe (MOLE)". *Anal. Chem.* 1979. 51(3): 414A–420A.
6. M. Delhay, B. Guineau, J. Vezin. "Application de la Microsonde Raman a l'Etude des Pigments". *Le Courrier du C.N.R.S.* 1984. 58: 20–31.
7. B. Guineau. "Non-Destructive Analysis of Organic Pigments and Dyes using Raman Microprobe, Microfluorometer or Absorption Microspectrophotometer". *Stud. Conserv.* 1989. 34: 38–44.
8. B. Guineau. "Analyse Non Destructive des Pigments par Microsonde Raman Laser: Exemples de l'Azurite et de la Malachite". *Stud. Conserv.* 1984. 29: 35–41.
9. B. Guineau, C. Coupry, M.-T. Gousset, J.-P. Forgerit, J. Vezin. "Identification de Bleu de Lapis-Lazuli dans Six Manuscrits a Peintures du XII Siecle de l'Abbaye de Corbie". *Scriptorium*. 1986. XL(2): 157–171.
10. I.M. Bell, R.J.H. Clark. "Raman Spectroscopic Library of Natural and Synthetic Pigments (Pre- ~ 1850 AD)". *Spectrochim. Acta, Part A*. 1997. 53(12): 2159–2179.
11. L. Burgio, R.J.H. Clark. "Library of FT-Raman Spectra of Pigments, Minerals, Pigment Media and Varnishes, and Supplement to Existing Library of Raman Spectra of Pigments with Visible Excitation". *Spectrochim. Acta, Part A*. 2001. 57: 1491–1521.
12. P. Vandenabeele, H.G.M. Edwards, L. Moens. "A Decade of Raman Spectroscopy in Art and Archaeology". *Chem. Rev.* 2007. 107(3): 675–686.
13. R.J.H. Clark. "Raman Microscopy: Application to the Identification of Pigments on Medieval Manuscripts". *Chem. Soc. Rev.* 1995. 24(3): 187–196.
14. R.J.H. Clark. "Pigment Identification on Medieval Manuscripts by Raman Microscopy". *J. Mol. Struct.* 1995. 347: 417–427.
15. L. Bussotti, L. Giuntini, M.P. Carboncini, P.A. Mando, E.M. Castellucci. "Identification of Pigments in a Fourteenth-Century Miniature by Combined Micro-Raman and Pixe Spectroscopic Techniques". *Stud. Conserv.* 1997. 42(2): 83–92.
16. A. Deneckere, M. De Reu, M.P.J. Martens, K. De Coene, B. Vekemans, L. Vincze, P. De Maeyer, P. Vandenabeele, L. Moens. "The Use of a Multi-Method Approach to Identify the Pigments in the 12th Century Manuscript Liber Floridus". *Spectrochim. Acta, Part A*. 2011. 80(1): 125–132.

17. A. Deneckere, L. de Vries, B. Vekemans, L. Van de Voorde, L. Ariese, L. Vincze, L. Moens, P. Vandennebeele. "Identification of Inorganic Pigments used in Porcelain Cards Based on Fusing Raman and X-Ray Fluorescence (XRF) Data". *Appl. Spectrosc.* 2011. 65(11): 1281–1290.
18. P. Vandennebeele, P. De Paepe, L. Moens. "Study of the 19th Century Porcelain Cards with Direct Raman Analysis". *J. Raman Spectrosc.* 2008. 39(8): 1099–1103.
19. P. Vandennebeele, F. Verpoort, L. Moens. "Non-Destructive Analysis of Paintings Using Fourier Transform Raman Spectroscopy with Fibre Optics". *J. Raman Spectrosc.* 2001. 32(4): 263–269.
20. P. Vandennebeele, K. Castro, M. Hargreaves, L. Moens, J.M. Madariaga, H.G.M. Edwards. "Comparative Study of Mobile Raman Instrumentation for Art Analysis". *Anal. Chim. Acta.* 2007. 588(1): 108–116.
21. P. Colomban. "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.* 2012. 43(11): 1529–1535.
22. D. Lauwers, V. Cattersel, L. Vandamme, A. Van Eester, K. De Langhe, L. Moens, P. Vandennebeele. "Pigment Identification of an Illuminated Mediaeval Manuscript De Civitate Dei by Means of a Portable Raman Equipment". *J. Raman Spectrosc.* 2014. 45(11-12): 1266–1271.
23. A. Deneckere, M. Leeflang, M. Bloem, C.A. Chavannes-Mazel, B. Vekemans, L. Vincze, P. Vandennebeele, L. Moens. "The Use of Mobile Raman Spectroscopy to Compare Three Full-Page Miniatures from the Breviary of Arnold of Egmond". *Spectrochim. Acta A.* 2011. 83(1): 194–199.
24. P. Vandennebeele, J. Tate, L. Moens. "Non-Destructive Analysis of Museum Objects by Fibre-Optic Raman Spectroscopy". *Anal. Bioanal. Chem.* 2007. 387: 813–819.
25. L. Van de Voorde, J. Van Pevenage, K. De Langhe, R. De Wolf, B. Vekemans, L. Vincze, P. Vandennebeele, M.P.J. Martens. "Non-Destructive In Situ Study of "Mad Meg" by Pieter Bruegel the Elder Using Mobile X-Ray Fluorescence, X-Ray Diffraction and Raman Spectrometers". *Spectrochim. Acta, Part B.* 2014. 97: 1–6.
26. D.C. Smith, A. Barbet. "A Preliminary Raman Microscopic Exploration of Pigments in Wall Paintings in the Roman Tomb Discovered at Kertch, Ukraine, in 1891". *J. Raman Spectrosc.* 1999. 30(4): 319–324.
27. A. Deneckere, W. Schudel, M. Van Bos, H. Wouters, A. Bergmans, P. Vandennebeele, L. Moens. "In Situ Investigations of Vault Paintings in the Antwerp Cathedral". *Spectrochim. Acta, Part A.* 2010. 75: 511–519.
28. P. Vandennebeele, K. Lambert, S. Mattys, W. Schudel, A. Bergmans, L. Moens. "In Situ Analysis of Mediaeval Wall Paintings: a Challenge for Mobile Raman Spectroscopy". *Anal. Bioanal. Chem.* 2005. 383(4): 707–712.
29. P. Vandennebeele, L. Moens. "Raman Spectroscopy: New Light on Ancient Artefacts". In: J. Nimmrichter, W. Kautek, M. Schreiner (eds) *Lasers in the Conservation of Artworks*. Berlin, Germany: Springer, 2007, pp. 341–347.
30. P. Vandennebeele, R. Garcia-Moreno, F. Mathis, K. Leterme, E. Van Elslande, F.-P. Hocquet, S. Rakkaa, D. Laboury, L. Moens, D. Strivay, M. Hartwig. "Multi-Disciplinary Investigation of the Tomb of Menna (TT69), Theban Necropolis, Egypt". *Spectrochim. Acta A.* 2009. 73: 546–552.
31. M.K. Donais, B. Duncan, P. Vandennebeele, D. George. "Characterization of Structure and Art at the Sant'Ansano Excavation Site". Paper presented at: SciX. Reno, NV; October 2 (2014).
32. A. Bonneau, D.G. Pearce, A.M. Pollard. "A Multi-Technique Characterization and Provenance Study of the Pigments Used in San Rock Art, South Africa". *J. Arch. Sci.* 2012. 39(2): 287–294.
33. A. Tournié, L.C. Prinsloo, C. Paris, P. Colomban, B. Smith. "The First In Situ Raman Spectroscopic Study of San Rock Art in South Africa: Procedures and Preliminary Results". *J. Raman Spectrosc.* 2011. 42(3): 399–406.
34. L.C. Prinsloo, W. Barnard, I. Meiklejohn, K. Hall. "The First Raman Spectroscopic Study of San Rock Art in the Ukhahlamba Drakensberg Park, South Africa". *J. Raman Spectrosc.* 2008. 39(5): 646–654.
35. L.C. Prinsloo, A. Tournié, P. Colomban, C. Paris, S.T. Bassett. "In Search of the Optimum Raman/IR Signatures of Potential Ingredients Used in San/Bushman Rock Art Paint". *J. Arch. Sci.* 2013. 40(7): 2981–2990.
36. M. Olivares, K. Castro, M.S. Corchón, D. Gárate, X. Murelaga, A. Sarmiento, N. Exebarria. "Non-Invasive Portable Instrumentation to Study Palaeolithic Rock Paintings: the Case of La Peña Cave in San Roman de Candamo (Asturias, Spain)". *J. Arch. Sci.* 2013. 40(2): 1354–1360.
37. S. Lahlil, M. Lebon, L. Beck, H. Rousselière, C. Vignaud, I. Reiche, M. Menu, P. Paillet, F. Plassard. "The First In Situ Micro-Raman Spectroscopic Analysis of Prehistoric Cave Art of Rouffignac St-Cernin, France". *J. Raman Spectrosc.* 2012. 43(11): 1637–1643.
38. H. Morillas, M. Maguregui, O. Gómez-Laserna, J. Trebolazabala, J.M. Madariaga. "Characterisation and Diagnosis of the Conservation State of Cementitious Materials Exposed to the Open Air in XIX Century Lighthouses Located on the Coast of the Basque Country: 'The Case of Igueldo Lighthouse, San Sebastian, North of Spain'". *J. Raman Spectrosc.* 2012. 43(11): 1630–1636.
39. I. Martínez-Arkarazo, A. Sarmiento, M. Maguregui, K. Castro, J.M. Madariaga. "Portable Raman Monitoring of Modern Cleaning and Consolidation Operations of Artworks on Mineral Supports". *Anal. Bioanal. Chem.* 2010. 397(7): 2717–2725.
40. J. Aramendia, L. Gomez-Nubla, K. Castro, I. Martinez-Arkarazo, D. Vega, A. Sanz López de Heredia, A. García Ibáñez de Opakua, J.M. Madariaga. "Portable Raman Study on the Conservation State of Four Cor-Ten Steel-Based Sculptures by Eduardo Chillida Impacted by Urban Atmospheres". *J. Raman Spectrosc.* 2012. 43(8): 1111–1117.
41. M. Maguregui, U. Knuutinen, I. Martínez-Arkarazo, A. Giakoumaki, K. Castro, J.M. Madariaga. "Field Raman Analysis to Diagnose the Conservation State of Excavated Walls and Wall Paintings in the Archaeological Site of Pompeii (Italy)". *J. Raman Spectrosc.* 2012. 43(11): 1747–1753.
42. I. Reiche, S. Pages-Camagna, L. Lambacher. "In Situ Raman Spectroscopic Investigation of the Adorning Gemstones on the Reliquary Heinrich's Cross from the Treasury of Basel Cathedral". *J. Raman Spectrosc.* 2004. 35(8-9): 719–725.
43. M.A. Ziemann. "In Situ Micro-Raman Spectroscopy on Minerals On-Site in the Grotto Hall of the New Palace,

- Park Sanssouci, in Potsdam". *J. Raman Spectrosc.* 2006. 37(10): 1019–1025.
44. Z. Petrová, J. Jehlička, T. Čapoun, R. Hanus, T. Trojek, V. Goliáš. "Gemstones and Noble Metals Adorning the Sceptre of the Faculty of Science of Charles University in Prague: Integrated Analysis by Raman and XRF Handheld Instruments". *J. Raman Spectrosc.* 2012. 43(9): 1275–1280.
 45. P. Colomban, G. Sagon, X. Faurel. "Differentiation of Antique Ceramics from the Raman Spectra of Their Coloured Glazes and Paintings". *J. Raman Spectrosc.* 2001. 32(5): 351–360.
 46. P. Colomban, A. Tournie, L. Bellot-Gurlet. "Raman Identification of Glassy Silicates Used in Ceramics, Glass and Jewellery: a Tentative Differentiation Guide". *J. Raman Spectrosc.* 2006. 37(8): 841–852.
 47. P. Colomban, V. Milande, H. Lucas. "On-Site Raman Analysis of Medici Porcelain". *J. Raman Spectrosc.* 2004. 35(1): 68–72.
 48. P. Colomban, V. Milande. "On-Site Raman Analysis of the Earliest Known Meissen Porcelain and Stoneware". *J. Raman Spectrosc.* 2006. 37(5): 606–613.
 49. B. Kirmizi, P. Colomban, B. Quette. "On-Site Analysis of Chinese Cloisonné Enamels from Fifteenth to Nineteenth Centuries". *J. Raman Spectrosc.* 2010. 41(7): 780–790.
 50. B. Kirmizi, P. Colomban, M. Blanc. "On-Site Analysis of Limoges Enamels from Sixteenth to Nineteenth Centuries: an Attempt to Differentiate Between Genuine Artefacts and Copies". *J. Raman Spectrosc.* 2010. 41(10): 1240–1247.
 51. P. Colomban. "On-Site Raman Identification and Dating of Ancient Glasses: A Review of Procedures and Tools". *J. Cult. Herit.* 2008. 9, Supplement: e55–e60.
 52. P. Colomban, A. Tournié. "On-Site Raman Identification and Dating of Ancient/Modern Stained Glasses at the Sainte-Chapelle, Paris". *J. Cult. Herit.* 2007. 8(3): 242–256.
 53. P. Ricciardi, P. Colomban, A. Tournié, V. Milande. "Nondestructive On-Site Identification of Ancient Glasses: Genuine Artefacts, Embellished Pieces or Forgeries?" *J. Raman Spectrosc.* 2009. 40(6): 604–617.
 54. S. Bowie, A. Darnley, J. Rhodes. "Portable Radioisotope X-ray Fluorescence Analyser". *Trans. Inst. Min. Metall.* 1965. 74: 361–379.
 55. R. Cox. "Assessment of Tin Ore In Situ at Cleveland Mine, Tasmania, with a Portable Radioisotope X-Ray Fluorescence Analyzer". *Inst. Mining Met., Trans. Sect. B.* 1968. 77: B109–B116.
 56. A.G. Darnley, C.C. Leamy. "Analysis of Tin and Copper Ores Using a Portable Radioisotope X-Ray Fluorescence Analyzer". In: *Radioisotope Instruments in Industry and Geophysics.* Vienna, Austria: I.A.E.A., (1966). Pp. 191–210, discussion 210–211.
 57. J.O. Karttunen, H.B. Evans, D.J. Henderson, P.J. Markovich, R.L. Niemann. "Portable Fluorescent X-Ray Instrument Utilizing Radioactive Sources". *Anal. Chem.* 1964. 36: 1277–1282.
 58. J.O. Karttunen, D.J. Henderson. "Developments in a Portable X-Ray Fluorescence Instrument Using Radioisotope Excitation Sources". *U.S.A.E.C. (1965). ORNL-IIC-5:* 154–180, discussion 180–181.
 59. S.H.U. Bowie. "Portable X-Ray Fluorescence Analyzers in the Mining Industry". *Mining Mag. (London).* 1968. 118: 230–231, 233, 235, 237, 239.
 60. T. Pantazis, J. Pantazis, A. Huber, R. Redus. "The Historical Development of the Thermoelectrically Cooled X-Ray Detector and its Impact on the Portable and Hand-Held XRF Industries (February (2009))". *X-Ray Spectrom.* 2010. 39: 90–97.
 61. P.T. Palmer. "Energy-Dispersive X-Ray Fluorescence Spectrometry: A Long Overdue Addition to the Chemistry Curriculum". *J. Chem. Ed.* 2011. 88: 868–872.
 62. E. Frahm, R.C.P. Doonan. "The Technological Versus Methodological Revolution of Portable XRF in Archaeology". *J. Archaeol. Sci.* 2013. 40: 1425–1434.
 63. M.S. Shackley. "Is There Reliability and Validity in Portable X-Ray Fluorescence Spectrometry (PXRF)?" *SAA Archaeol. Rec.* 2010. 17–20.
 64. A.N. Shugar. "Portable X-Ray Fluorescence and Archaeology: Limitations of the Instrument and Suggested Methods To Achieve Desired Results". In: R.A. Armitage, J.H. Burton (eds) *ACS Symposium Series.* Washington, D.C., USA: American Chemical Society, 2013, pp. 173–193.
 65. R. Jenkins, R.J. Windfordner. *X-Ray Fluorescence Spectrometry*, 2nd ed. New York, USA: Wiley, 1999.
 66. P.J. Potts, M. West. *Portable X-Ray Spectrometry: Capabilities for In-Situ Analysis.* London, UK: Royal Society of Chemistry, 2008.
 67. E. Margui, R. Van Grieken. *X-Ray Fluorescence Spectrometry and Related Techniques: An Introduction.* New York, USA: Momentum Press, 2013.
 68. K. Uhlir, M. Griesser, G. Buzanich, P. Wobrauschek, C. Strelci, D. Wegrzynek, A. Markowicz, E. Chinea-Cano. "Applications of a New Portable (Micro) XRF Instrument Having Low-Z Elements Determination Capability in the Field of Works of Art". *X-Ray Spectrom.* 2008. 37(4): 450–457.
 69. M.K. Donais, B. Duncan, S. Wojtas, A. Desmond, D. George. "Differentiation of Hypocaust and Floor Tiles at Coriglia, Castel Viscardo (Umbria, Italy) using Principal Component Analysis (PCA) and Portable X-Ray Fluorescence (XRF) Spectrometry". *Appl. Spectrosc.* 2012. 66(9): 1005–1012.
 70. Y. Abe, I. Nakai, K. Takahashi, N. Kawai, S. Yoshimura. "On-Site Analysis of Archaeological Artifacts Excavated from the Site on the Outcrop at Northwest Saqqara, Egypt, by Using a Newly Developed Portable Fluorescence Spectrometer and Diffractometer". *J. Anal. and Bioanal. Chem.* 2009. 395: 1987–1996.
 71. M.K. Donais, D. George, B. Duncan, S. Wojtas, A. Daigle. "Evaluation of Data Processing and Analysis Approaches for Fresco Pigments by Portable X-Ray Fluorescence Spectrometry and Portable Raman Spectroscopy". *Anal. Methods.* 2011. 3(5): 1061–1071.
 72. C. Colombo, S. Bracci, C. Conti, M. Greco, M. Realini. "Non-Invasive Approach in the Study of Polychrome Terracotta Sculptures: Employment of the Portable XRF to Investigate Complex Stratigraphy". *X-Ray Spectrom.* 2011. 40: 273–279.
 73. D.N. Papadopoulou, G.A. Zachariadis, A.N. Anthemidis, N.C. Tsirliganis, J.A. Stratis. "Development and Optimisation of a Portable Micro-XRF Method for In Situ Multi-Element Analysis of Ancient Ceramics". *Talanta.* 2006. 68(5): 1692–1699.
 74. A.G. Karydas. "Application of a Portable XRF Spectrometer for the Non-Invasive Analysis of Museum Metal Artefacts". *Ann. Chim. (Rome, Italy).* 2007. 97(7): 419–432.

75. V. Desnica, K. Skaric, D. Jembrih-Simburger, S. Fazinic, M. Jaksic, D. Mudronja, M. Pavlicic, I. Peranic, M. Schreiner. "Portable XRF as a Valuable Device for Preliminary In Situ Pigment Investigation of Wooden Inventory in the Trski Vrh Church in Croatia". *Appl. Phys. A: Mater. Sci. Process.* 2008. 92(1): 19–23.
76. G. Paternoster, R. Rinzivillo, F. Nunziata, E.M. Castellucci, C. Lofrumento, A. Zoppi, A.C. Felici, G. Fronterotta, C. Nicolais, M. Piacentini, S. Sciuti, M. Vendittelli. "Study on the Technique of the Roman Age Mural Paintings by Micro-XRF with Polycapillary Conic Collimator and Micro-Raman Analyses". *J. Cult. Herit.* 2005. 6(1): 21–28.
77. A.J. Sakalis, N.A. Kazakis, N. Merousis, N.C. Tsirliganis. "Study of Neolithic Pottery from Polyplatano (Imathia) Using Micro X-Ray Fluorescence Spectroscopy, Stereoscopic Microscopy and Multivariate Statistical Analysis". *J. Cult. Herit.* 2013. 14(6): 485–498.
78. H.A. van Sprang. "Fundamental Parameter Methods in XRF Spectroscopy". *Proceedings from: Denver X-Ray Conference.* Denver, CO; (1998).
79. M. Mantler, J. Willis, G. Lachance, B. Vrebos, K.-E. Mauser, R. Kawahara, R. Rousseau, P. Brouwer. "Quantitative Analysis". In: B. Beckhoff, B. Kanngießer, N. Langhoff, R. Wedeller, H. Wolff (eds) *Handbook of Practical X-Ray Fluorescence Analysis.* Berlin, Germany: Springer, 2006, pp. 309–410.
80. P. Sarrazin, G. Chiari, M. Gailhanou. "A Portable Non-Invasive XRD-XRF Instrument for the Study of Art Objects". *Adv. X-Ray Anal.* 2009. 52: 175–186.
81. L. Beck, H. Rousseliere, J. Castaing, A. Duran, M. Lebon, B. Moignard, F. Plassard. "First Use of Portable System Coupling X-Ray Diffraction and X-Ray Fluorescence for In-Situ Analysis of Prehistoric Rock Art". *Talanta.* 2014. 129: 459–464.
82. M. Eveno, B. Moignard, J. Castaing. "Portable Apparatus for In Situ X-Ray Diffraction and Fluorescence Analyses of Artworks". *Microsc. Microanal.* 2011. 17: 667–673.
83. M. Uda. "In situ characterization of ancient plaster and pigments on tomb walls in Egypt using energy dispersive X-ray diffraction and fluorescence". *Nucl. Instrum. Methods Phys. Res., Sect. B.* 2004. 226(1–2): 75–82.
84. A. Kriznar, V. Munoz, F. de la Paz, M.A. Respaliza, M. Vega. "Portable XRF Study of Pigments Applied in Juan Hispalense's 15th Century Panel Painting". *X-Ray Spectrom.* 2011. 40: 96–100.
85. E.A.M. Kajiya, P.H.O.V. Campos, M.A. Rizzutto, C.R. Appoloni, F. Lopes. "Evaluation of the Veracity of One Work by the Artist Di Cavalcanti Through Non-Destructive Techniques: XRF, Imaging and Brush Stroke Analysis". *Radiat. Phys. Chem.* 2014. 95: 373–377.
86. D. Magrini, G. Bartolozzi, S. Bracci, R. Iannaccone, V. Marchiafava, M. Picollo. "The San Pietro Martire Triptych by Beato Angelico: Materials Characterization by Mean of Integrated Non-Invasive Spectroscopic Measurements". *Int. J. Cons. Sci.* 2013. 4(Special Issue): 673–680.
87. E. Franceschi, F. Locardi. "Strontium, a New Marker of the Origin of Gypsum in Cultural Heritage?" *J. Cult. Herit.* 2014. 15(5): 522–527.
88. G. Sciutto, P. Oliveri, S. Prati, M. Quaranta, S. Bersani, R. Mazzeo. "An Advanced Multivariate Approach for Processing X-Ray Fluorescence Spectral and Hyperspectral Data from Non-Invasive In Situ Analyses on Painted Surfaces". *Anal. Chim. Acta.* 2012. 752: 30–38.
89. V. Desnica, M. Schreiner. "A LabVIEW-Controlled Portable X-Ray Fluorescence Spectrometer for the Analysis of Art Objects". *X-Ray Spectrom.* 2006. 35(5): 280–286.
90. J. Huntley, M. Aubert, J. Ross, H.E.A. Brand, M.J. Morwood. "One Colour, (at Least) Two Minerals: A Study of Mulberry Rock Art Pigment and a Mulberry Pigment 'Quarry' from the Kimberley, Northern Australia". *Archaeom.* 2015. 57(1): 77–99.
91. A. Duran, A. López-Montes, J. Castaing, T. Espejo. "Analysis of a Royal 15th Century Illuminated Parchment Using a Portable XRF-XRD System and Micro-Invasive Techniques". *J. Arch. Sci.* 2014. 45: 52–58.
92. F. Bardelli, G. Barone, V. Crupi, F. Longo, D. Majolino, P. Mazzoleni, V. Venuti. "Combined Non-Destructive XRF and SR-XAS Study of Archaeological Artefacts". *Anal. Bioanal. Chem.* 2011. 399: 3147–3153.
93. M. Uda, M. Nakamura, S. Yoshimura, J. Kondo, M. Saito, Y. Shirai, S. Hasegawa, Y. Baba, K. Ikeda, Y. Ban, A. Matsuo, M. Tamada, H. Sunaga, H. Oshio, D. Yamashita, Y. Nakajima, T. Utaka. "Amarna Blue" Painted on Ancient Egyptian Pottery". *Nucl. Instrum. Methods Phys. Res., Sect. B.* 2002. 189: 382–386.
94. L. Van de Voorde, M. Vandevijvere, B. Vekemans, J. Van Pevenage, J. Caen, P. Vandenebeele, P. Van Espen, L. Vincze. "Study of a Unique 16th Century Antwerp Majolica Floor in the Rameyehof Castle's Chapel by Means of X-Ray Fluorescence and Portable Raman Analytical Instrumentation". *Spectrochim. Acta B.* 2014. 102: 28–35.
95. E. Angelini, S. Grassini, S. Corbellini, G.M. Ingo, T. de Caro, P. Plescia, C. Riccucci, A. Bianco, S. Agostini. "Potentialities of XRF and EIS Portable Instruments for the Characterization of Ancient Artefacts". *Appl. Phys. A: Mater. Sci. Process.* 2006. 83(4): 643–649.
96. Y. Hayakawa. "Portable XRF Analysis of Japanese Historical Objects". *Adv. X-Ray Anal.* 2004. 47: 36–41.
97. M. Alfeld, K. Janssens, J. Dik, W. de Nolf, G. van der Snickt. "Optimization of Mobile Scanning Macro-XRF Systems for the In Situ Investigation of Historical Paintings". *J. Anal. At. Spectrom.* 2011. 26: 899–909.
98. D. Fontana, M.F. Alberghina, R. Barraco, S. Basile, L. Tranchina, M. Brai, A. Gueli, S.O. Troja. "Historical Pigments Characterisation by Quantitative X-Ray Fluorescence". *J. Cult. Herit.* 2014. 15(3): 266–274.
99. L.G. Cecil, M.D. Moriarty, R.J. Speakman, M.D. Glascock. "Feasibility of Field-Portable XRF to Identify Obsidian Sources in Central Peten, Guatemala". In: M.D. Glascock, R.J. Speakman, R.S. Popelka-Filcoff (eds) *ACS Symposium Series.* Washington, D.C., USA: American Chemical Society, 2007, pp. 506–521.
100. N. Craig, R.J. Speakman, R.S. Popelka-Filcoff, M.D. Glascock, J.D. Robertson, M.S. Shakley, M.S. Aldenderfer. "Comparison of XRF and PXRF for Analysis of Archaeological Obsidian from Southern Peru". *J. Arch. Sci.* 2007. 34: 2012–2024.
101. E. Frahm, B.A. Schmidt, B. Gasparyan, B. Yeritsyan, S. Karapetian, K. Meliksetian, D.S. Adler. "Ten Seconds in the Field: Rapid Armenian Obsidian Sourcing with Portable XRF to Inform Excavations and Surveys". *J. Arch. Sci.* 2014. 41: 333–348.
102. A.J. Nazaroff, K.M. Pruffer, B.L. Drake. "Assessing the Applicability of Portable X-Ray Fluorescence Spectrometry

- for Obsidian Provenience Research in the Maya Lowlands". *J. Archaeol. Sci.* 2010. 37(4): 885–895.
103. F.P. Romano, G. Pappalardo, L. Pappalardo, S. Garraffo, R. Gigli, A. Pautasso. "Quantitative Non-Destructive Determination of Trace Elements in Archaeological Pottery Using a Portable Beam Stability-Controlled XRF Spectrometer". *X-Ray Spectrom.* 2006. 35(1): 1–7.
104. F. Forouzan, J.B. Glover, F. Williams, D. Deocampo. "Portable XRF Analysis of Zoomorphic Figurines, "Tokens," and Sling Bullets from Chogha Gavaneh, Iran". *J. Archaeol. Sci.* 2012. 39: 3534–3541.
105. R.A. Ikeoka, C.R. Appoloni, P.S. Parreira, F. Lopes, A.M. Bandeira. "PXRF and Multivariate Statistics Analysis of Pre-Colonial Pottery from Northeast of Brazil". *X-Ray Spectrom.* 2012. 41(1): 12–15.
106. A. Gianoncelli, G. Kourousias. "Limitations of Portable XRF Implementations in Evaluating Depth Information: An Archaeometric Perspective". *Appl. Phys. A: Mater. Sci. Process.* 2007. 89(4): 857–863.
107. T. Nagae, H. Mifune. "XRF Analysis of the Seated Shaka Nyorai Statue of Kaniman-ji at Kyoto". *ISIJ Int.* 2014. 54: 1117–1122.
108. M. Ferretti, C. Polese, C.R. Garcia. "X-Ray Fluorescence Investigation of Gilded and Enamelled Silver: The Case Study of Four Medieval Processional Crosses from Central Italy". *Spectrochim. Acta B.* 2013. 83–84: 21–27.
109. G.E. Gigante, S. Ridolfi, D. Ferro. "Diagnostic Investigations and Statistical Validation of EDXRF Mapping of the Burial Monument of Pope Sixtus IV by Antonio Pollaiuolo (1493) in the Vatican". *J. Cult. Herit.* 2012. 13(3): 345–351.
110. M. Uda, A. Ishizaki, R. Satoh, K. Okada, Y. Nakajima, D. Yamashita, K. Ohashi, Y. Sakuraba, A. Shimono, D. Kojima. "Portable X-Ray Diffractometer Equipped with XRF for Archaeometry". *Nucl. Instrum. Methods Phys. Res., Sect. B.* 2005. 239(1–2): 77–84.
111. A. Heginbotham, J. Bassett, D. Bourgarit, C. Eveleigh, L. Glinsman, D. Hook, D. Smith, R.J. Speakman, A. Shugar, R. Van Langh. "The Copper CHARM Set: A New Set of Certified Reference Materials for the Standardization of Quantitative X-Ray Fluorescence Analysis of Heritage Copper Alloys". *Archaeom.* 2015. 57(5): 856–868.
112. D. Ogburn, B. Sillar, J.C. Sierra. "Evaluating Effects of Chemical Weathering and Surface Contamination on the In Situ Provenience Analysis of Building Stones in the Cuzco Region of Peru with Portable XRF". *J. Arch. Sci.* 2013. 40(4): 1823–1837.
113. P.J. Potts, F. Bernardini, M.C. Jones, O. Williams-Thorpe, P.C. Webb. "Effects of Weathering on In Situ Portable X-Ray Fluorescence Analyses of Geological Outcrops: Dolerite and Rhyolite Outcrops from the Preseli Mountains, South Wales". *X-Ray Spectrom.* 2006. 35(1): 8–18.
114. P. Grave, V. Attenbrow, L. Sutherland, R. Pogson, N. Forster. "Non-Destructive pXRF of Mafic Stone Tools". *J. Arch. Sci.* 2012. 39(6): 1674–1686.
115. L. Bonizzoni, A. Galli, M. Gondola, M. Martini. "Comparison Between XRF, TXRF, and PXRF Analyses for Provenience Classification of Archaeological Bricks". *X-Ray Spectrom.* 2013. 42: 262–267.
116. M.K. Donais, B. Duncan, D. George, C. Bizzarri. "Comparisons of Ancient Mortars and Hydraulic Cements through In-Situ Analyses by Portable X-Ray Fluorescence Spectrometry". *X-Ray Spectrom.* 2010. 39: 146–153.
117. M.K. Donais, D. George. "Using Portable XRF to Aid in Phasing, Locus Comparisons, and Material Homogeneity Assessment at an Archaeological Excavation". In: A. Shugar, J. Maas (eds) *Handheld XRF for Art and Archaeology*. Leuven, Belgium: Leuven University Press, 2012, pp. 349–377.
118. E.G. Coronel, D.A. Bair, C.T. Brown, R.E. Terry. "Utility and Limitations of Portable X-Ray Fluorescence and Field Laboratory Conditions on the Geochemical Analysis of Soils and Floors at Areas of Known Human Activities". *Soil Sci.* 2014. 179(5): 258–271.
119. E.G. Coronel, S. Hutson, A. Magnoni, C. Balzotti, A. Ulmer, R.E. Terry. "Geochemical Analysis of Late Classic and Post Classic Maya Marketplace Activities at the Plazas of Coba, Mexico". *J. Field Archaeol.* 2015. 40(1): 89–109.
120. R.K. Gauss, J. Batora, E. Nowaczinski, K. Rassmann, G. Schukraft. "The Early Bronze Age Settlement of Fivár, Vrábce (Slovakia). Reconstructing Prehistoric Settlement Patterns Using Portable XRF". *J. Arch. Sci.* 2013. 40(7): 2942–2960.
121. L.G. Davis, S.J. Macfarlan, C.N. Henrickson. "A PXRF-Based Chemostratigraphy and Provenience System for the Cooper's Ferry Site, Idaho". *J. Arch. Sci.* 2012. 39(3): 663–671.
122. A.M.W. Hunt, R.J. Speakman. "Portable XRF Analysis of Archaeological Sediments and Ceramics". *J. Arch. Sci.* 2015. 53: 626–638.
123. Y. Abe, R. Harimoto, T. Kikugawa, K. Yazawa, A. Nishisaka, N. Kawai, S. Yoshimura, I. Nakai. "Transition in the Use of Cobalt-Blue Colorant in the New Kingdom of Egypt". *J. Arch. Sci.* 2012. 39(6): 1793–1808.
124. D. Sokaras, A.G. Karydas, A. Oikonomou, N. Zacharias, K. Beltsios, V. Kantarelou. "Combined Elemental Analysis of Ancient Glass Beads by Means of Ion Beam, Portable XRF, and EPMA Techniques". *Anal. Bioanal. Chem.* 2009. 395: 2199–2209.
125. B. Dal Bianco, U. Russo. "Basilica of San Marco (Venice, Italy/ Byzantine period): Nondestructive Investigation on the Glass Mosaic Tesserae". *Journal of Non-Crystalline Solids.* 2012. 358(2): 368–378.
126. M.K. Donais, M. Redente, D. George. "Field Research and Experiential Learning with Undergraduates: Investigations of Roman Glass Tesserae by Portable X-Ray Fluorescence Spectroscopy". *Spectrosc.* 2014. 29(11): 28–33.
127. K. Tantrakarn, N. Kato, A. Hokura, I. Nakai, Y. Fujii, S. Gluscevic. "Archaeological Analysis of Roman Glass Excavated from Zadar, Croatia, by a Newly Developed Portable XRF Spectrometer for Glass". *X-Ray Spectrom.* 2009. 38: 121–127.
128. V. Van der Linden, E. Meesdom, A. Devos, R. Van Dooren, H. Nieuwdorp, E. Janssen, S. Balace, B. Vekemans, L. Vincze, K. Janssens. "PXRF, μ -XRF, Vacuum μ -XRF, and EPMA Analysis of Email Champeve Objects Present in Belgian Museums". *Microsc. Microanal.* 2011. 17: 674–685.
129. V. Van der Linden, O. Schalm, J. Houbraken, M. Thomas, E. Meesdom, A. Devos, R. Van Dooren, H. Nieuwdorp, E. Janssen, K. Janssens. "Chemical Analysis of 16th to 19th

- Century Limoges School Painted Enamel Objects in Three Museums of the Low Countries". *X-Ray Spectrom.* 2010. 39: 112–121.
130. W.L. Truett, J.P. Dybwad, G.D. Propster, C.D. Prozzo, J. Szappanos. "A Portable FTIR Spectrometer Using a Rotating Refractor". *Am. Lab. (Fairfield, Conn.)*. 1984. 16: 115–120.
131. W.F. Herget. "Analysis of Gaseous Air Pollutants Using a Mobile FTIR system". *Am. Lab. (Fairfield, Conn.)*. 1982. 14: 72–78.
132. S. Weiner, P. Goldberg. "On-Site Fourier Transform-Infrared Spectrometry at an Archaeological Excavation". *Spectrosc.* 1990. 5: 46–50.
133. P. Nel, C. Lonetti, D. Lau, K. Tam, R.S. Sloggett. "Analysis of Adhesives Used on the Melbourne University Cypriot Pottery Collection Using a Portable FTIR-ATR Analyzer". *Vib. Spectrosc.* 2010. 53: 64–70.
134. C. Conti, J. Striova, I. Aliatis, C. Colombo, M. Greco, E. Possenti, M. Realini, L. Brambilla, G. Zerbi. "Portable Raman Versus Portable Mid-FTIR Reflectance Instruments to Monitor Synthetic Treatments Used for the Conservation of Monument Surfaces". *Anal. Bioanal. Chem.* 2013. 405: 1733–1741.
135. R.S. Williams. "On-Site Non-Destructive Mid-IR Spectroscopy of Plastics in Museum Objects Using a Portable FTIR Spectrometer with Fiber Optic Probe". *Mater. Res. Soc. Symp. Proc.* 1997. 462: 25–30.
136. D. Magrini, G. Bartolozzi, S. Bracci, R. Ionnaccone, V. Marchiafava, M. Picollo. "The San Pietro Martire Triptych by Beato Angelico: Materials Characterization by Means of Integrated Non-Invasive Spectroscopic Measurements". *Int. J. Cons. Sci.* 2013. 4(Special Issue): 673–680.
137. C. Miliani, F. Rosi, I. Borgia, P. Benedetti, B.G. Brunetti, A. Sgamellotti. "Fiber-Optic Fourier Transform Mid-Infrared Reflectance Spectroscopy: A Suitable Technique for in Situ Studies of Mural Paintings". *Appl. Spectrosc.* 2007. 61(3): 293–299.
138. K.Y. Yamamoto, D.A. Cremers, M.J. Ferris, L.E. Foster. "Detection of Metals in the Environment Using a Portable Laser-Induced Breakdown Spectroscopy Instrument". *Appl. Spectrosc.* 1996. 50: 222–233.
139. W. Pierce, S.M. Christian, M.J. Myers, J.D. Myers, C.R. Hardy, J.A. Myers, R. Gadson, W. Younis. "Field-Testing for Environmental Pollutants Using Briefcase Sized Portable LIBS System". *Proceedings from: LIBS (2004) 3rd Int. Conf. Laser Induc. Plasma Spectrosc. Appl. Malaga, Spain; (2004)*, 1–14.
140. F.C. DeLucia, A.C. Samuels, R.S. Harmon, R.A. Walters, K.L. McNesby, A. LaPointe, R.J. Winkel, A.W. Miziolek. "Laser-Induced Breakdown Spectroscopy (LIBS): a Promising Versatile Chemical Sensor Technology for Hazardous Material Detection". *IEEE Sensors J.* 2005. 5: 681–689.
141. J. Rakovsky, P. Cermak, O. Musset, P. Veis. "A Review of the Development of Portable Laser Induced Breakdown Spectroscopy and its Applications". *Spectrochim. Acta B.* 2014. 101: 269–287.
142. I. Gobernado-Mitre, A.C. Prieto, V. Zafropoulos, Y. Spetsidou, C. Fotakis. "On-Line Monitoring of Laser Cleaning of Limestone by Laser-Induced Breakdown Spectroscopy and Laser-Induced Fluorescence". *Appl. Spectrosc.* 1997. 51(8): 1125–1129.
143. F.J. Fortes, J. Cuñat, L.M. Cabalín, J.J. Laserna. "In Situ Analytical Assessment and Chemical Imaging of Historical Buildings Using a Man-Portable Laser System". *Appl. Spectrosc.* 2007. 61(5): 558–564.
144. L.M. Osorio, L.V.P. Cabrera, M.A.A. Garcia, T.F. Reyes, I. Ravelo. "Portable LIBS System for Determining the Composition of Multilayer Structures on Objects of Cultural Value". *J. Phys.: Conf. Ser.* 2011. 274: 012093/012091–012093/012096.
145. R. Gaudiuso, M. Dell'Aglio, O. De Pascale, S. Loperfido, A. Mangone, A. De Giacomo. "Laser-Induced Breakdown Spectroscopy (LIBS) of Archaeological Findings with Calibration-Free Inverse Method: Comparison with Classical LIBS and Conventional Techniques". *Anal. Chim. Acta.* 2014. 813: 15–24.
146. M. Ferretti, G. Cristoforetti, S. Legnaioli, V. Palleschi, A. Salvetti, E. Tognoni, E. Console, P. Palaia. "In Situ Study of the Porticello Bronzes by Portable X-Ray Fluorescence and Laser-Induced Breakdown Spectroscopy". *Spectrochim. Acta, Part B.* 2007. 62B: 1512–1518.
147. K. Melessanaki, A. Mastrogiannidou, S. Chlouveraki, S.C. Ferrence, P.P. Betancourt, D. Anglos. "Analysis of Archaeological Objects with LMNTI, a New Transportable LIBS Instrument". *Springer Proc. Phys.* 2005. 100: 443–449.
148. L. Pardini, A. El Hassan, M. Ferretti, A. Foresta, S. Legnaioli, G. Lorenzetti, E. Nebbia, F. Catalli, M.A. Harith, D. Diaz Pace, F. Anabitarte Garcia, M. Scuotto, V. Palleschi. "X-Ray Fluorescence and Laser-Induced Breakdown Spectroscopy Analysis of Roman Silver Denarii". *Spectrochim. Acta, Part B.* 2012. 74–75: 156–161.
149. P. Westlake, P. Siozos, A. Philippidis, C. Apostolaki, B. Derham, A. Terlix, V. Perdikatsis, R. Jones, D. Anglos. "Studying Pigments on Painted Plaster in Minoan, Roman and Early Byzantine Crete. A Multi-Analytical Technique Approach". *Anal. Bioanal. Chem.* 2012. 402(4): 1413–1432.
150. S. Guirado, F.J. Fortes, V. Lazić, J.J. Laserna. "Chemical Analysis of Archaeological Materials in Submarine Environments Using Laser-Induced Breakdown Spectroscopy. On-Site Trials in the Mediterranean Sea". *Spectrochim Acta Part B.* 2012. 74–75: 137–143.
151. G. Verri, C. Clementi, D. Comelli, S. Cather, F. Piqué. "Correction of Ultraviolet-Induced Fluorescence Spectra for the Examination of Polychromy". *Appl. Spectrosc.* 2008. 62(12): 1295–1302.
152. A. Romani, C. Clementi, C. Miliani, B.G. Brunetti, A. Sgamellotti, G. Favaro. "Portable Equipment for Luminescence Lifetime Measurements on Surfaces". *Appl. Spectrosc.* 2008. 62(12): 1395–1399.
153. M. Gil, M.L. Carvalho, S. Longelin, I. Ribeiro, S. Valadas, J. Mirão, A.E. Candeias. "Blue Pigment Colors from Wall Painting Churches in Danger (Portugal 15th to 18th Century): Identification, Diagnosis, and Color Evaluation". *Appl. Spectrosc.* 2011. 65(7): 782–789.
154. A. Lerwill, J.H. Townsend, H. Liang, J. Thomas, S. Hackney. "A Portable Micro-Fading Spectrometer for Versatile Lightfastness Testing". *e-Preserv. Sci.* 2008. 5: 17–28.
155. F. Rosi, R. Harig, C. Miliani, R. Braun, D. Sali, A. Daveri, B.G. Brunetti, A. Sgamellotti. "Mid-Infrared Hyperspectral

- Imaging of Painting Materials". *Proc. SPIE.* (2013). 8790: 87900Q/87901-87900Q/87910.
156. C. Miliani, F. Rosi, B.G. Brunetti, A. Sgamellotti. "In Situ Noninvasive Study of Artworks: The MOLAB Multitechnique Approach". *Accounts of Chemical Research.* 2010. 43(6): 728–738.
157. A. Sgamellotti, C. Miliani, B.G. Brunetti. "Non Invasive Multi-Technique Analysis of Historical Architecture for Monitoring and Conservation Purposes". *Proceedings from: 10th International Study Forum on Life of Traders.* Aversa, Italy; May 31–June 1 (2012), 118–123.
158. "CHARISMA: Cultural Heritage Advanced Research Infrastructures Synergy for a Multidisciplinary Approach to Conservation/Restoration". <http://www.charismaproject.eu/> [accessed Apr 13 2015]
159. B.G. Brunetti, M. Matteini, C. Miliani, L. Pezzati, D. Pinna. "MOLAB, a Mobile Laboratory for In Situ Non-Invasive Studies in Arts and Archaeology". *Proceedings from: Lasers in the Conservation of Artworks.* Viena, Austria; September 21–25 (2005), 453–460.
160. M.K. Donais, D. George, S. Roberts, J. Roberts, E. Wu. "Analyses of Ancient Roman Pigments by Portable X-Ray Fluorescence and Raman Spectroscopies". Paper presented at: *Conference of the Federation of Analytical Chemistry and Spectroscopy Societies.* Louisville, KY; October 19 (2009).
161. K.S. Andrikopoulos, S. Daniilia, B. Roussel, K. Janssens. "In Vitro Validation of a Mobile Raman–XRF Micro-Analytical Instrument's Capabilities on the Diagnosis of Byzantine Icons". *J. Raman Spectrosc.* 2006. 37(10): 1026–1034.
162. X. Zhu, T. Xu, Q. Lin, Y. Duan. "Technical Development of Raman Spectroscopy: From Instrumental to Advanced Combined Technologies". *Appl. Spectrosc. Rev.* 2013. 49(1): 64–82.
163. M. Hoehse, D. Mory, S. Florek, F. Weritz, I. Gornushkin, U. Panne. "A Combined Laser-Induced Breakdown and Raman Spectroscopy Echelle System for Elemental and Molecular Microanalysis". *Spectrochim. Acta, Part B.* 2009. 64(11–12): 1219–1227.
164. I. Osticioli, N.F. Mendes, A. Nevin, A. Zoppi, C. Lofrumento, M. Becucci, E.M. Castellucci. "A New Compact Instrument for Raman, Laser-Induced Breakdown, and Laser-Induced Fluorescence Spectroscopy of Works of Art and Their Constituent Materials". *Rev. Sci. Instrum.* 2009. 80(7): 076109.
165. I. Osticioli, M. Wolf, D. Anglos. "An Optimization of Parameters for Application of a Laser-Induced Breakdown Spectroscopy Microprobe for the Analysis of Works of Art". *Appl. Spectrosc.* 2008. 62(11): 1242–1249.
166. R. Bruder, V. Detalle, C. Coupry. "An Example of the Complementarity of Laser-Induced Breakdown Spectroscopy and Raman Microscopy for Wall Painting Pigments Analysis". *J. Raman Spectrosc.* 2007. 38(7): 909–915.