Research Article

Mobile Spectroscopy in Archaeometry: Some Case Study

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We provide an overview of recent results obtained by the innovative application of mobile spectroscopy for in situ investigation in archaeometry. Its growing relevance is linked to the great advantages of avoiding the transport and eventual damage of precious artifacts and of allowing the analysis of those specimens that are, for example, built into infrastructures or in some way permanently affixed. In this context, some case studies of combined instrumental approaches, involving X-ray fluorescence (XRF) and Raman spectroscopy, integrated by infrared thermography (IRT), are, in particular, discussed: the archaeological site of Scifì (Forza d'Agrò, province of Messina, Italy) and the Abbey of SS. Pietro e Paolo d'Agrò (Casalvecchio Siculo, province of Messina, Italy). In the first case, the elemental composition, as obtained by XRF, of two types of mortars belonging to two different chronological phases, dated back between the 3rd and the 5th century AD, allowed us to hypothesize a same origin area of their raw materials and a different production technique. Again, the combined use of XRF and Raman spectroscopies, supported by IRT technique, on pottery fragments of Greek-Hellenistic age and late imperial period, furnished important information concerning the receipts for the pigmenting agents of the finishing layer, allowing in some cases their unambiguous identification. In the second case, XRF data collected on bricks and stones from the external facade of the abbey allowed us to make some hypothesis concerning the provenance of their constituents materials, supposed to be in the area of valley of the river Agrò.

1. Introduction

Archaeometry is a multidisciplinary research area, involving skills varying from physics to chemistry, from material science to geology and biology, called to give help in open problems of humanistic sciences such as archaeology and anthropology.

The essential need to preserve valuable works of art imposes the use of specific techniques that can simultaneously furnish much valuable information minimizing the risk of damage. Then, the best experimental approach consists in applying complementary noninvasive or, at least, microdestructive methodologies. In this sense, a big step forward is represented by in situ investigation [1–4], in which
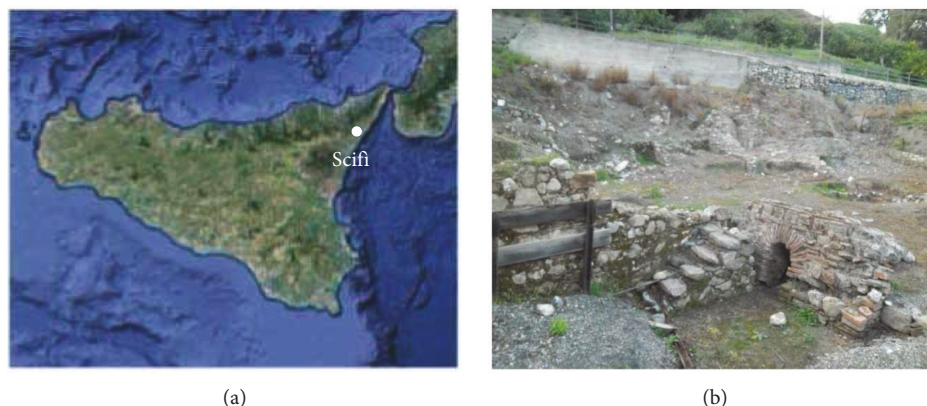
(a)

(b)

Figure 1: (a) Map of Scifì (Forza d'Agrò, province of Messina, Italy). (b) The archaeological site of Scifì.

the spectrometer can be carried onto the site, museum, or whatever, considerably reducing any risk of damage.

These direct studies [5, 6] can be performed by

(i) *transportable instrumentation*: spectrometers can be easily carried from one site to another in cars or vans. After transporting, some installation and, eventually, alignment is required;

(ii) *mobile instrumentation*: instruments whose high stability, when designed, allows for mobility without any internal adjustment, such as alignment or calibration procedures;

(iii) *portable instrumentation*: mobile spectrometers that can be carried into the site by a single person. They generally do not have moving parts, are battery operated, and can fit in a suitcase;

(iv) *handheld instruments*: instruments that can be held in one hand by the operator. For this reason, measurements are generally short, and sometimes a support, such as a tripod, can be used;

(v) *palm equipments*: instruments of new generation are so small to fit in the palm of one's hand.

In this paper, we focus in particular on the potentialities of mobile and handheld instrumentation to perform noninvasive spectroscopic investigation at elemental scale, by X-ray fluorescence spectroscopy, and at molecular level, by Raman technique, on cultural heritage objects in order to face questions related to provenance, dating, and manufacture technology. In addition, the integration of these spectroscopic techniques with transportable infrared thermography (IRT) equipment for nondestructive in situ analysis is also presented.

Nevertheless, it is worth remarking that they constitute only a part of the analytical techniques that archaeometry can include. As an example, geophysical methods revealed powerful in all those questions linked to landscapes, prospection, and reconstruction and successfully integrated also the information reported here [7, 8].

We will highlight some case studies, namely mortars, potteries, bricks, and stones coming from the archaeological site of Scifì (Forza d'Agrò, province of Messina, Italy) and

from one of the most valuable monuments of the Norman period in Sicily, the Abbey of SS. Pietro e Paolo d'Agrò (Casalvecchio Siculo, province of Messina, Italy). The site of Scifì and the Abbey of SS. Pietro e Paolo d'Agrò are located on the opposite banks of the river "Fiumara d'Agrò," few kilometers far from each other.

We finally want to underline that the data presented here are part of a wide investigation performed in the framework of the National School "Science and Cultural Heritage: from Non-Invasive Analysis to 3D Reconstruction" (19–23 September 2016, Messina-Valle d'Agrò, Italy), organized by the Department of Mathematical and Computer Sciences, Physical Sciences and Earth Sciences of the University of Messina, in cooperation with the Department of Geosciences of the University of Malta and in agreement with the Regional Order of Geologists of Sicily.

2. The Archaeological Contexts

2.1. The Archaeological Site of Scifì (Forza d'Agrò, Province of Messina, Italy). The archaeological site of Scifì belongs to the community of Forza d'Agrò, in the province of Messina, Sicily (Figure 1). The site occupies a dominant position in the confluence of the river "Fiumara d'Agrò" and one of its tributaries, the river Munafò, in the middle stretch of the valley that takes its name from the broad stream. The area has been the subject of three short excavation works carried out in the last century by the Superintendence of Cultural and Environmental Heritage of Messina (1987, 1995, and 1997) and an excavation in extension carried out between 2001 and 2002 by the University of Messina. The excavations brought to light numerous late-old masonry structures, some of which in excellent state of preservation, articulated at different levels to adapt to the natural slope and belonging to two chronological phases following one another, between the end of the 3rd and 5th century AD [9].

To the first phase (named as "phase I"), dating between the late third and the first half of the 4th century AD, belong findings that can be ascribed to a quite extensive building, of which at least six rooms were recognized, perhaps destroyed because of an earthquake (which might be a well-known one dating back to 365 AD quoted by the sources). The remains are made of blocks, stones, and bricks that are worked with

Figure 2: The Abbey of SS. Pietro e Paolo d'Agrò.

a quite accurate technique and abundant use of mortar. In particular, a square structure can be distinguished, with input and arched window of bricks and concrete cover, that, due to its vertical development, has been referred to as "the tower."

After a definitely short time period ("phase II"), the building had to be reconstructed and partly reused, and flanked by at least another building, with a slightly different exposure and a less accurate masonry technique, in stones of varying size and with little use of bricks. Even these newer structures were arranged on sloping levels and suffered a violent destruction probably around the middle of the 5th century AD, followed by a long period of abandonment. Regarding the destination of the structures, it has been suggested the hypothesis of a small villa (villula) or a rural settlement, or even a way station (statio).

The hypothesis of the villa seems more plausible—perhaps of "fortified" type, because of the alleged tower—significantly placed in this large tract and well exposed of the valley named Valle d'Agrò, that, in a rough landscape like that of the Ionian coast of Messina, could represent an important route of penetration into the interior, other than a connection with the Tyrrhenian side.

2.2. Abbey of SS. Pietro e Paolo d'Agrò (Casalvecchio Siculo, Province of Messina, Italy). The Abbey of SS. Pietro e Paolo d'Agrò (Figure 2) is one of the most important architectural works of the whole valley of the river "Fiumara d'Agrò," from which it is named, and one of the most important of all Sicily. The original church was presumably about 560 AD. It was later completely destroyed by the Arabs and then rebuilt in 1117 AD by Ruggero II Norman. Definitively restructured in 1172 AD, it came to us practically intact and without substantial retrofits. It is a fortified church, whose appearance and crowning of barges undoubtedly indicate the function of fortress that it has had to support over the centuries. Its architectural style can be retained the synthesis of Byzantine, Arab, and Norman architecture.

It has a spectacular polychrome facade thanks to the wise alternation of bricks and stones. The interior is characterized by absolute austerity, with no decorations or frescoes.

The abbey has been the subject of numerous studies over the years [10, 11]. It has recently been officially proposed to UNESCO to include this monument in the list of human heritage assets.

3. Materials and Methods

3.1. Materials

3.1.1. Samples from the Archaeological Site of Scifì. Two types of mortars of the visible building, respectively, belonging to "phase I" and "phase II," have been investigated by XRF spectroscopy. At first inspection, they appear similar, and the analysis was aimed at establishing if the compositional homogeneity is maintained also at elemental level. Furthermore, four pottery fragments of different typology, labelled SC1, SC2, SC3, and SC4, belonging to a set of shards excavated from this archaeological site were analysed by XRF, Raman, and IRT techniques. All samples are dated back to the late imperial period, and precisely to the 4th-5th century AD, with the exception of the SC1 fragment, which is of Greek-Hellenistic age, about 3rd century BC. No archaeometric data exist on these samples, so their characterization was a prerequisite for their cataloguing. In addition, a brick from the "tower," for which a local production is reasonable, has been also analysed by XRF spectroscopy.

All the information relative to the investigated samples are reported in Table 1.

Regarding the pottery fragments, the colour of their ceramic body and coating is described according to Munsell soil colour chart, whereas their photos are shown in Figure 3.

3.1.2. Samples from the Abbey of SS. Pietro e Paolo d'Agrò. We performed an XRF investigation of bricks and stones from the facade of the abbey. In particular, data have been collected on a red brick and on black, white, and yellow stones (Table 2).

The photo of the analysed samples is reported in Figure 4. The goal of the investigation was to make some hypothesis concerning the local production of the used materials and to support archaeological and/or geological classification.

3.2. Methods

3.2.1. X-Ray Fluorescence (XRF) Spectrometry. As is well known, XRF is an atomic spectroscopic technique that can provide both qualitative and quantitative information regarding the elemental composition of a sample. In recent years, a number of portable XRF (PXRF) spectrometers have become commercially available, and PXRF analysis, also combined with other analytical techniques, has been representing one of the most powerful tool for the study of archaeological findings such as manuscripts, paintings, and ceramic artifacts, other than for the investigation of other types of materials including metallic objects, bronze statuettes, coins, and gold artifacts [12–14].

The increasing interest in PXRF technique is connected with the several advantages that this nondestructive analysis can provide. Indeed, this method can be performed in situ,

TABLE 1: Information relative to the investigated samples from the archaeological site of Scifì.

| Sample	Sampling area	Typology	Colour (Munsell soil colour chart)	Performed analysis
Ancient mortar, "phase I"	Room 6, northern wall	—	—	XRF
Ancient mortar, "phase II"	Wall 18	—	—	XRF
SC1	No information	Black-painted askòs hem	7.5YR 6/4 (ceramic body)–2.5Y 3/1 (coating)	XRF, Raman, IRT
SC2	Lombardo property	Fragment of sealed Italic pottery	2.5YR 4/6 (ceramic body)–2.5YR 6/6 (coating)	XRF, Raman
SC3	Lombardo property	Fragment of sealed African D pottery	2.5YR 6/8 (ceramic body)–10R 5/8 (coating)	XRF, Raman, IRT
SC4	Lombardo property	Fragment of sealed African D pottery	10R 6/8 (ceramic body)–10R 6/8 (coating)	XRF, Raman
Brick	"The tower"	—	—	XRF

(a)

(b)

(c)

(d)
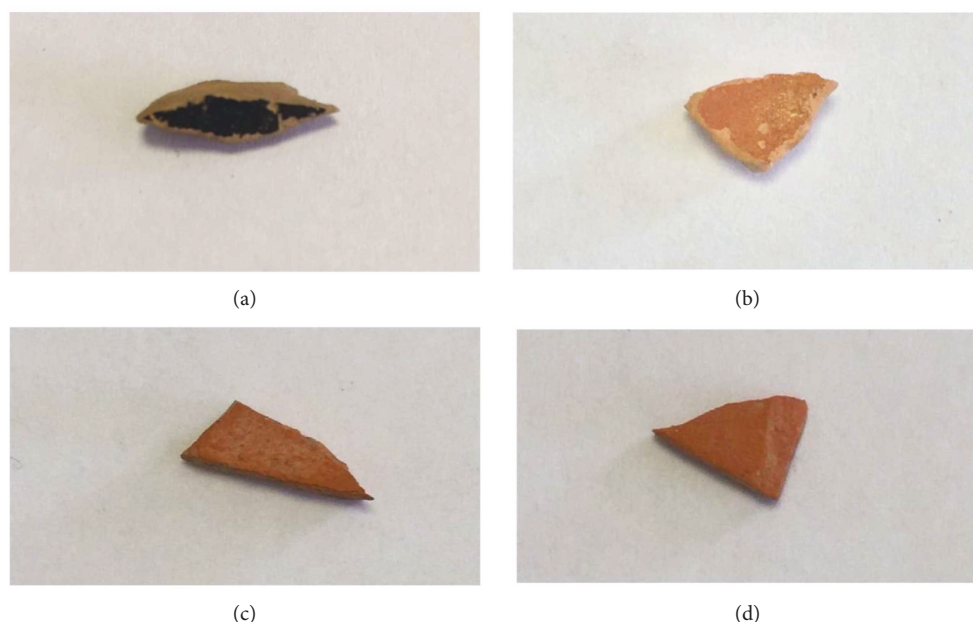
FIGURE 3: Photo of the investigated pottery fragments from the archaeological site of Scifì: (a) SC1, (b) SC2, (c) SC3, and (d) SC4.

TABLE 2: Information relative to the investigated samples from the Abbey of SS. Pietro e Paolo d'Agrò.

Sample	Area	Performed analysis
Red brick	Facade right side	XRF
Black stone	Facade right side	XRF
White stone	Facade right side	XRF
Yellow stone	Facade right side	XRF

no sample preparation is required, and no alteration of the material occurs; furthermore, low costs and short analysis time are additional assets. In many studies, nondestructive PXRF technique was employed as preliminary surface analysis of samples. In these cases, the elemental composition obtained by XRF measurements was used to choose some areas of samples to more deeply analyze through other nondestructive and/or microdestructive analytical techniques [15–17]. The potentiality of this nondestructive technique was tested for the identification of the production centers of a set of archaic transport amphorae was already proved [18]. Its application to the characterization of mortars and bricks represents a relatively new approach. Again, when applied to the pigments analysis, PXRF furnishes an indirect identification of pigments through evidence of key elements. For example, the simultaneous presence of Hg and S, found by PXRF analyses on a red pigment, indicates the use of cinnabar (HgS). On the other hand, being an element-specific technique, insensitive to the chemical state and/or the molecular environment in which the elements are present, PXRF is often not specific enough to identify the pigments with certainty, especially when dealing with pigments of the same or similar colours or containing the same main elements. For instance, the detection of Cu can indicate the presence of several pigments (azurite, malachite, etc.). Hence, it is not always possible to identify the nature of the pigment, but only its class. In these cases, the elemental characterization needs to be completed by the complementary description of the molecular structures of the pigmenting agents, as achieved by Raman spectroscopy.
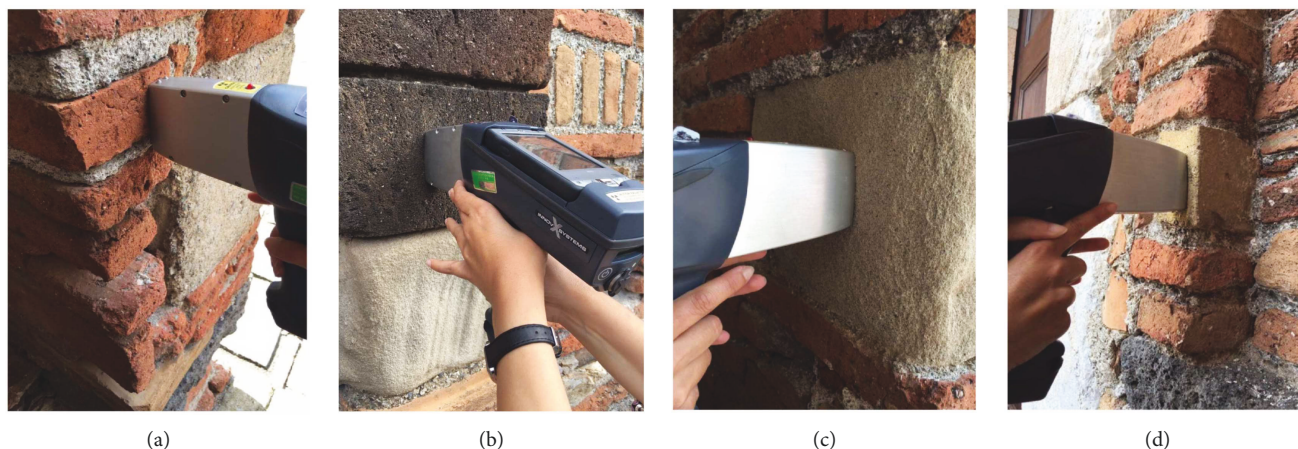
FIGURE 4: Red brick (a) and black (b), white (c), and yellow (d) stones from the facade of the Abbey of SS. Pietro e Paolo d'Agrò.

In our study, XRF measurements were performed by using a portable XRF "alpha 4000" (Innovex-X system) analyzer that allowed the detection of various chemical elements having an atomic number (Z) between phosphorus and lead.

The apparatus was equipped with a Ta anode X-ray tube excitation source and a high-resolution Si PIN diode detector with an active area of $170 \, mm^2$. The instrument operated in "soil" mode and two sequential tests were performed on each sample. The operating conditions were $40 \, kV$ and $7 \, \mu A$ for the first run and $15 \, kV$ and $5 \, \mu A$ for the second one, for a total spectrum collection time of $120 \, s$. The two sequential measurements allowed us to detect elements from P to Pb. A Hewlett-Packard iPAQ Pocket PC was used to control the instrument and data storage. The calibration was performed by soil LEAP II and was verified using alloy certified reference materials produced by Analytical Reference Materials International.

The fluorescence signal was collected for about $60 \, s$ per run in order to increase the statistics. For all the investigated samples, the lines detected ~8.15 keV and ~9.34 keV are attributed to the L_{α} and L_{β} transitions of Ta anode. When Cu is present, the L_{α} line of Ta is superimposed to the K_{α} line of Cu.

In the case of mortars, bricks, and stones, because of their heterogeneity both in compositional and dimensional terms, we decided to proceed in the following way: we selected only samples that, at a visual inspection, appeared similar (i.e., in colour, granulometry, and absence of macroscopic inhomogeneities). For each sample, several measurements (~50) on many different points were performed. Almost the 80% of the collected data turned out to be reproducible (the reported spectra are, for each specimen, representative of this class of data). The remaining 20%, very different from each other and also with respect to the first class, can be ascribed to the presence of inhomogeneities nonmacroscopic or not present on the surface.

3.2.2. Raman Spectroscopy. Raman spectroscopy is a suitable technique for the identification of organic and inorganic chemical compounds, providing information on the vibrational transitions of molecules according to the specific selection rules that govern the Raman scattering [19]. Nowadays, this last methodology became very appreciated for the investigation of cultural heritage objects, thanks to the advantages offered by the fact that it does not require a sample preparation, its nondestructive character, provided the laser power is kept sufficiently low, its possibility to collect molecular spectra of both organic and inorganic particles down to micrometer scale, and its speed of analysis. For all these reasons, it has been successfully applied to a vast array of materials, including ceramics [20], gemstones [21], manuscripts [22], and paintings [23]. The main disadvantage is represented by fluorescence emission from the molecules or other trace compounds in the sample that can cause interference during the analysis. Recently, thanks to the development of miniaturized devices, mobile Raman instruments have been produced that allow in situ investigation of art objects [24–26]. The feasibility of fibre optic approach led to the development of portable fibre optic Raman equipments specifically designed for art analysis that revealed successful in investigating pigments of paintings [27]. The evolution of mobile Raman instrumentation in archaeometry research has been already reviewed [5, 25], and a description of all different features that are of importance when selecting a mobile Raman instrument for the in situ analysis of art samples has been reported [24]. Nevertheless, it is worth remarking that, generally, when this technique is used in situ, the large impact of fluorescence becomes an issue difficult to be overcome, since portable and handheld Raman equipments do not have confocal attitude and microhead. This imposes limits to the application of Raman spectroscopy in art and archaeology. For this reason, new handheld Raman spectrometers have been very recently optimized for mitigating fluorescence and proved to be a very powerful tool for the analysis of works of art [28].

Raman measurements presented here have been performed by using a portable 'BTR 111 Mini-RamTM' (B&W Tek, USA) spectrometer with an excitation wavelength of 785 nm (diode laser), 280 mW maximum laser power at the excitation port, and a charge-coupled device (CCD) detector (thermoelectric cooled, TE). In addition, the laser output power can be continuously adjusted by allowing to maximize

the signal-to-noise ratio minimizing the integration time. The system is equipped with a fibre optic interface for convenient sampling. The excitation laser emits from the probe's end where the Raman signal is then collected from the sample. The spot size is 85 μm at a working distance of 5.90 mm.

For our measurements, the maximum power at the samples was ~55 mW. Spectra have been registered in the 60–3150 cm^{-1} wavenumber range, by using an acquisition time of 40 s and a resolution of 8 cm^{-1}, adding several scans for each spectrum in order to improve the signal-to-noise ratio. An accurate wavelength calibration was performed by using an instrument from B&W Tek. Anyway, the optimal performance of the instrument was guaranteed by a calibration procedure before each measurement using the peak at 520.6 cm^{-1} of a silicon chip. Each spectrum has been processed by subtracting the blank spectrum; in addition, a baseline correction and a smoothing process have been performed by using the BWSpec 3.27 software. The collected Raman spectra have been compared with data from databases and the literature [29, 30].

3.2.3. Infrared Thermography (IRT). IRT is a noninvasive methodology recently extensively applied in cultural heritage, also thanks to the possibility to perform in situ analysis [31]. In particular, active IRT monitors the evolution, versus time, of emitted infrared radiation at the surface of the artifact after its artificial heating, usually induced by the absorption of light emitted by lamps, lasers, or other sources. In this way, this technique provides qualitative information on the surface features of the artifact as well as quantitative information on the thermal properties of the constituting material. The technique has been applied to the study of library objects, archaeological findings, and works of art such as paintings, fresco plasters, and bronze sculptures [32].

In our study, the shooting was carried out using a FLIR ThermoVision 695 telemeter, equipped with a PCMCIA data-saving card and the scanned images were processed in postproduction using a PC equipped with open-source FIJI software. The results of the processing have been reported in a point dispersion chart. Four incandescent (tungsten) lamps with 60 W red power screen oriented at 45° with respect to the vertical axis and at a distance of 50 cm from the working surface. The telethermographic station was set in order to have a thermal window from 17°C to 32°C. The shots were taken in a special room with an ambient temperature stabilized at 20°C, relative humidity of 50%, and ventilation less than 0.1 m/s. Irradiation and cooling time were 600 s and 40 min, respectively.

4. Results and Discussion

4.1. The Archaeological Site of Scifi

4.1.1. XRF Results on the Mortars. In Figures 5 and 6, the XRF spectra collected for the two ancient mortars belonging to "phase I" and "phase II" are, respectively, reported.

From a first inspection of the figures, chemical features appear similar: the presence of calcium (Ca), iron (Fe),
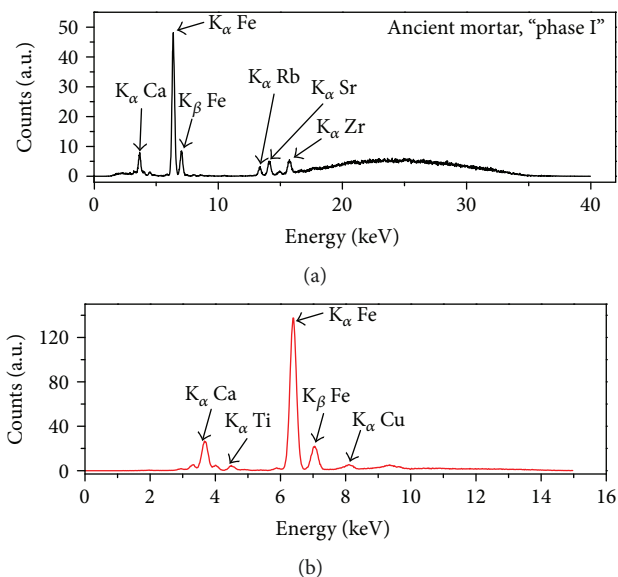

FIGURE 5: XRF spectra, in the 0–40 keV range (a) and 0–16 keV range (b), of an ancient mortar of "phase I."
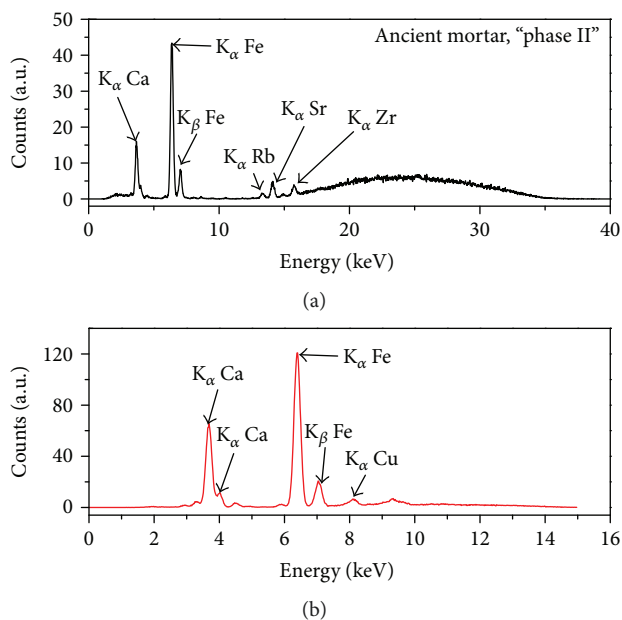

FIGURE 6: XRF spectra, in the 0–40 keV range (a) and 0–16 keV range (b), of an ancient mortar of "phase II."

rubidium (Rb), strontium (Sr), manganese (Mn), zirconium (Zr), nickel (Ni), chromium (Cr), and copper (Cu) is revealed for both the ancient mortars. For both the analysed samples, the lines K$_\alpha$ (6.39 keV) and K$_\beta$ (7.03 keV) of Fe appear much more intense than the peaks associated to the other elements.

The chemical nature of minor and trace elements and their relative concentrations suggests that there is a not a significant compositional difference between the two studied mortars. Therefore, it is possible to hypothesize that their raw materials have the same origin area. Nevertheless, an important difference between the two architectural phases
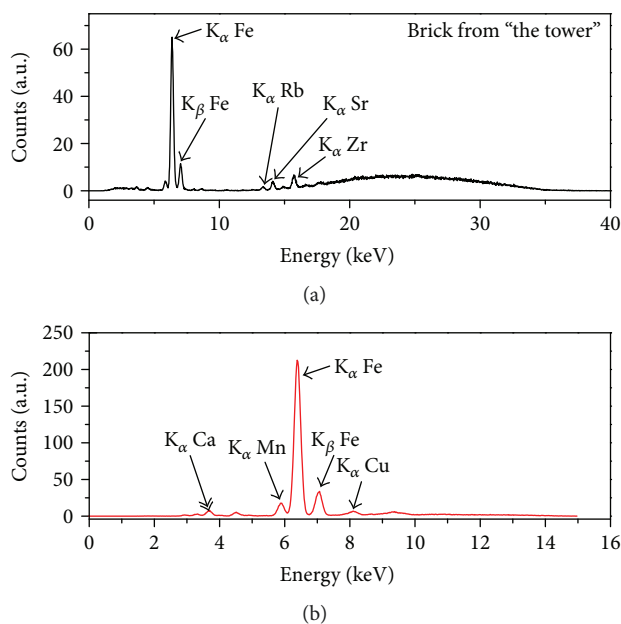
(a)

(b)

FIGURE 7: XRF spectra, in the 0–40 keV range (a) and 0–16 keV range (b), of a brick from "the tower."

concerns calcium: the associated peak, revealed at ~3.68 keV with moderate intensity in the XRF spectrum of the mortar of the "phase I," exhibits a significant increasing in intensity in the case of the mortar of the "phase II," indicating an increasing of Ca concentration. Calcium is a major constituent of mortars in various forms such as calcite, dolomite, and gypsum, so its presence was expected. Nevertheless, this difference in Ca content is surprising and could be due to a different kind of paste that could be ascribed to a different production technique.

4.1.2. XRF Results on the Brick from "the Tower." A brick from "the tower" was also analysed by XRF. The collected spectra are shown in Figure 7. It is worth remarking that Si is expected to be the main element of bricks, but unfortunately, the detection starts from P, just above it. So, in our case, Fe is the element detected in the highest amount and then, in the order, Ca, Mn, Cu, Zr, Sr, and Rb.

Detected minor and trace elements can be ascribed to different raw materials eventually present, which are not known, since destructive analyses have not been performed. The chemical composition of the brick of "the tower," of safe local production, was investigated in order to be used as reference to be compared with that of the red brick of the facade of the Abbey of SS. Pietro e Paolo d'Agrò, in order to make some hypothesis concerning the provenance, supposedly from the area of valley of the river Agrò, of the constituents materials of the latter.

4.1.3. XRF, Raman, and IRT Results on the Pottery Fragments. In the case of the pottery fragments, XRF data were collected on the painted surface of each sample. The elemental composition, as obtained by the spectral analysis, is reported in Table 3.

TABLE 3: Summary of the XRF results obtained for the investigated pottery fragments from the archaeological site of Scifì.

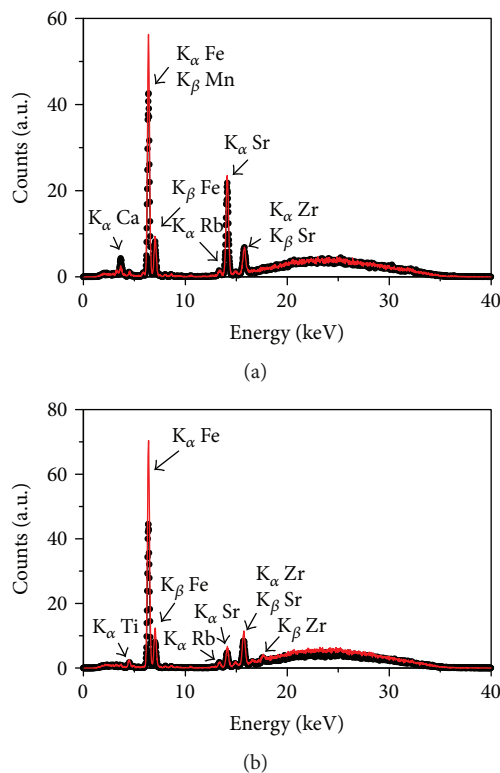| Sample	XRF
SC1	Fe, K, Ca, Ti, (Mn, Ba, Sr, Zr, Cr, Zn, Rb, Cu, Pb)
SC2	Fe, Ca, Mn, K, Ti, (Ba, Sr, Zr, Rb, Cr, Zn, Cu, Pb)
SC3	Fe, K, Ti, Ca, (Ba, Cr, Zr, Sr, Zn, Mn, Rb, Cu, Pb)
SC4	Fe, K, Ti, Ca, (Ba, Cr, Zr, Sr, Zn, Mn, Rb, Cu, Pb)

(a)

(b)

FIGURE 8: XRF spectra, in the 0–40 keV range, of SC2 (a) and SC4 (b) pottery fragments. Black circles refer to the back of each fragment, and red lines refer to its finishing layer.

Nevertheless, since, as well known, the X-ray source has a penetration depth of the order of few micrometers, the XRF signal will generally reflect not only the contribution coming from the pigmented layer, but also the one due to the preparation substrate. This latter is principally constituted by calcite and contributes to the high fluorescence lines of Ca and Sr. In order to overcome this difficulty and unambiguously identify the key elements responsible for the pigmenting agents, we also performed measurements on the back of the fragments that have been used for comparison.

As examples in Figures 8(a) and 8(b), we, respectively, report the XRF spectra collected on the reddish-brown finishing layer of the surface and on the back of SC2 fragment and on the reddish finishing layer of the surface and on the back of SC4 sample.

As can be seen from an inspection of the figure, in both cases, the XRF spectra collected on the surface of the sample exhibit a higher Fe K_{α} line with respect to the measurement performed on the back. In the case of SC2 fragment, for
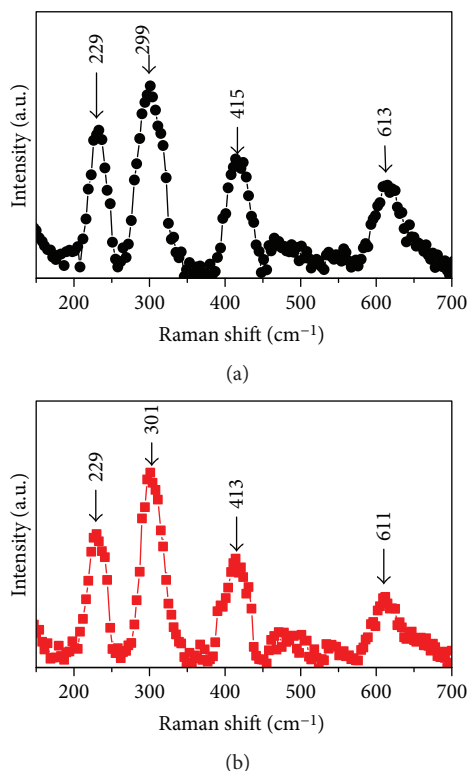
(a)

(b)

FIGURE 9: Raman spectra, in the 150–700 cm^{-1} range, of SC3 ((a): black circles) and SC4 ((b): red squares) pottery fragments. The peaks corresponding to the main features of haematite are also indicated.

(a)

(b)

FIGURE 10: Thermographs of samples SC1 (a) and SC3 (b) during heating.

which Mn is also detected in high amount, the Fe K$_\alpha$ line is superimposed to the Mn K$_\beta$ line, so its enhancement can be also ascribed to a higher Mn concentration on the surface with respect to the back of the sample. The observed increasing of the Fe K$_\alpha$ line allows to hypothesize, for both the analysed fragments, a Fe-based red pigment, such as an earth (inorganic pigment of differently hydrated iron oxide). In addition, in the case of SC2 fragment, the observation of Mn can support the hypothesis of the use of umber (combination of iron oxide, manganese oxide, and clay). XRF spectral features of SC3 sample appear very similar to those of SC4 fragment, indicating a comparable elemental composition starting from which, taking also into account their common archaeological classification, similar receipts for the pigmenting agents of the finishing layer can be supposed. Finally, as far as SC1 fragment is concerned, the observation in the XRF spectrum (data not shown) of Fe as key element indicated a Fe-based pigment for the black surface, probably magnetite (Fe_3O_4), whose use in Greek-Hellenistic potteries is already reported in literature [33].

The molecular composition of the pigments was attempted by Raman spectroscopy. Unfortunately, in the case of SC1 and SC2 fragments, no reliable data were obtained, mainly because of fluorescence, but also as a consequence of the heterogeneity of the surface and the deposited contamination. On the other side, the Raman spectra collected for samples SC3 and SC4 are reported in Figures 9(a) and 9(b), respectively.
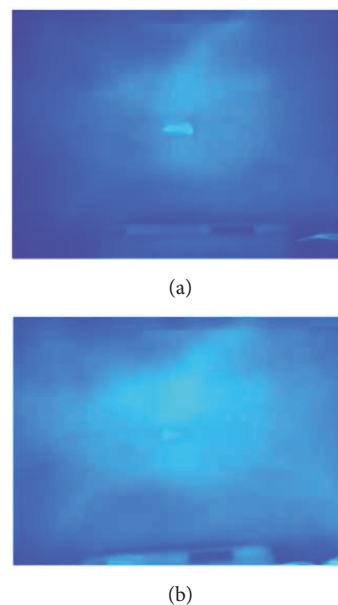
In both cases, haematite (α-Fe_2O_3) is clearly identified, by the observation of its characteristic peaks centered, on average, at ~229 cm^{-1} (stretching Fe-O), ~300 cm^{-1} (bending O-Fe-O), ~414 cm^{-1} (bending O-Fe-O), and ~612 cm^{-1} (stretching Fe-O) [34]. Finally, SC1 and SC3 fragments were also subjected to a thermographic preliminary test. The purpose was to highlight, if there were any, different behaviors of the surface pigments in relation to the absorption of thermal energy and its subsequent release. Ordinarily, these differences are reflected in a different slope of the curves describing the upward (heating phase) or the descent (cooling phase) of temperature, corresponding to a different emissivity value linked to the constituent materials at the surface.

In Figures 10(a) and 10(b), thermographs of samples SC1 and SC3 during heating are reported.

Again, in Figure 11, we report the two experimental curves describing the behaviour of the intensity versus time. As can be seen, they exhibit a similar trend.

This occurrence indicates a comparable specific heat and emissivity for the two samples; slight differences can be attributed to their different mass. Nevertheless, in correspondence of the same time of exposure to the heat source, different temperatures are achieved by the two samples. This interesting result will be deepened and compared with those that will be obtained by the other fragments. The analysis is, at the moment, in progress.

4.2. The Abbey of SS. Pietro e Paolo d'Agrò

4.2.1. XRF Results on Bricks and Stones from the Facade. First of all, we collected the XRF spectrum on a red brick from the external facade of the abbey. It is reported in Figure 12.

Data indicated Fe as key element and then Ca, Cu, Zr, and Sr. A comparison of these spectral profiles with those
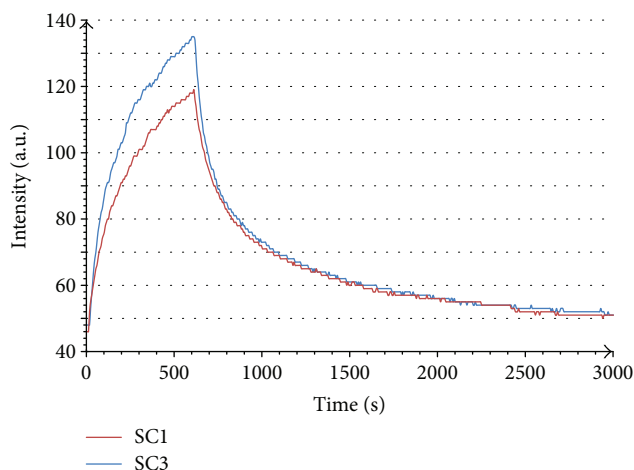
FIGURE 11: Plot of the intensity as a function of time, as obtained from thermographic analysis performed on SC1 and SC3 fragments.
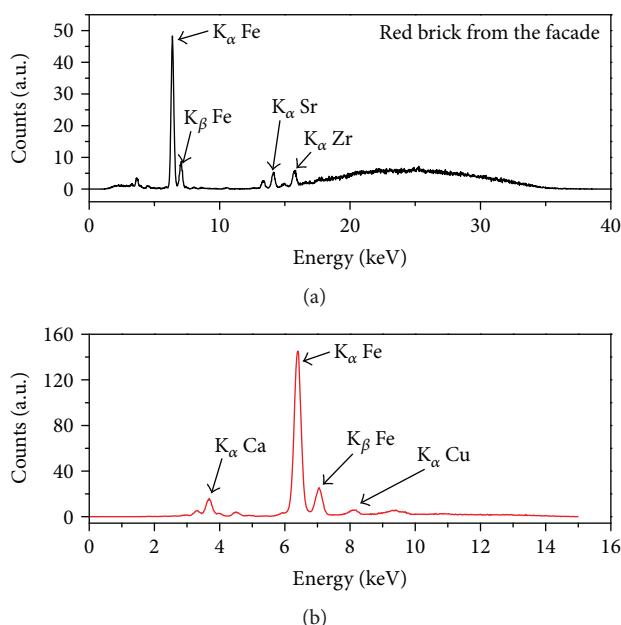

(a)

(b)

FIGURE 12: XRF spectra, in the 0–40 keV range (a) and 0–16 keV range (b), of a red brick from the facade of the Abbey of SS. Pietro e Paolo d'Agrò.
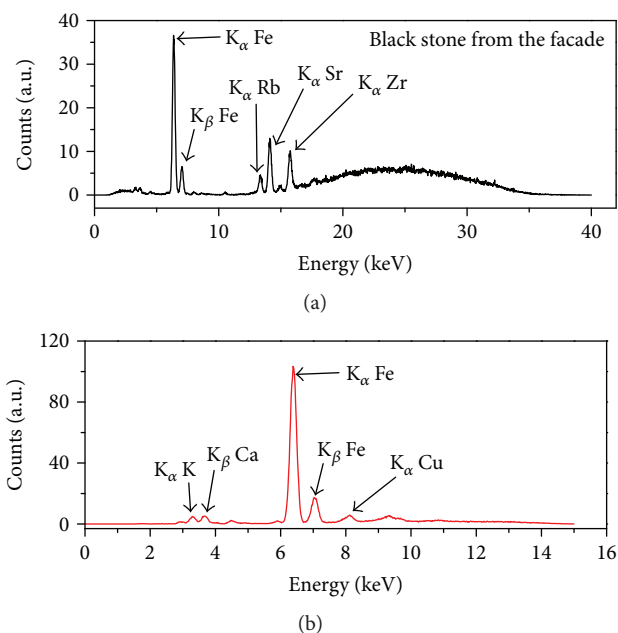

(a)

(b)

FIGURE 13: XRF spectra, in the 0–40 keV range (a) and 0–16 keV range (b), of a black stone from the facade of the Abbey of SS. Pietro e Paolo d'Agrò.
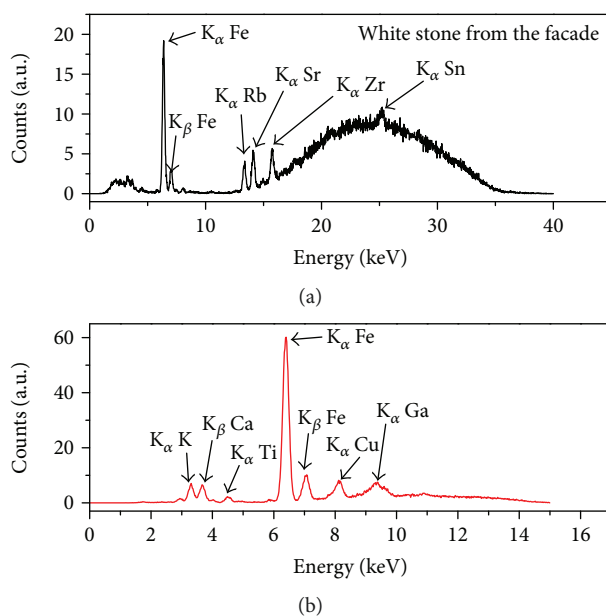

(a)

(b)

FIGURE 14: XRF spectra, in the 0–40 keV range (a) and 0–16 keV range (b), of a white stone from the facade of the Abbey of SS. Pietro e Paolo d'Agrò.

obtained for the brick from "the tower" of the archeological site of Scifì, reported in Figure 7, evidenced a similar elemental composition. It is then reasonable to suppose that the raw materials used in the manufacture of bricks in the two cases were the same. One reason is, most likely, a similar chemical composition of the soil, because the archaeological sites are geographically close to each other. Another reason could be that the bricks were produced in the same way and that the same fuel in the kilns was used. In any case, any confirmation can be achieved only by means of mineralogical and petrographic analysis that anyway are destructive methods. As far as the black stone is concerned, it was already supposed that black stones of the facade are volcanic rocks of provenance from Mt. Etna (Sicily, Italy). In our case, the collected

XRF spectrum, plotted in Figure 13, compared with the geochemical characterization of volcanic rocks from Mt. Etna [35], confirms the archaeological hypothesis.

The XRF spectra collected for the white and the yellow stones are reported in Figures 14 and 15, respectively.

In this case, the use of a local sandstone is hypothesized, and a comparison with local reference materials would allow for an unambiguous identification.
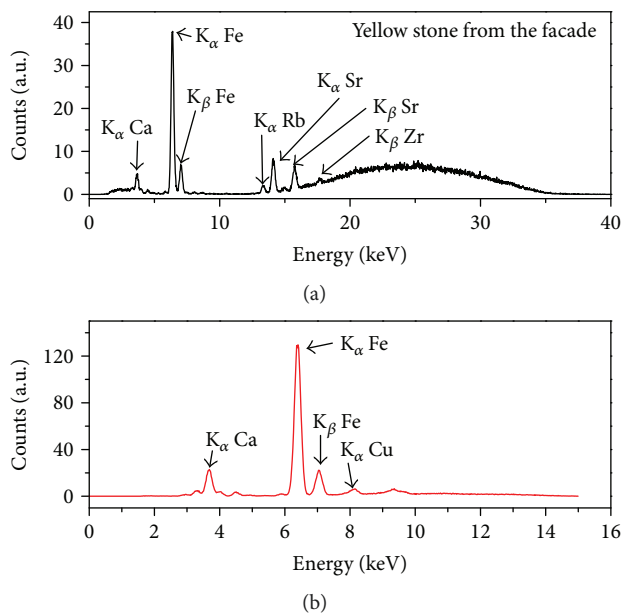
(a)

(b)

FIGURE 15: XRF spectra, in the 0–40 keV range (a) and 0–16 keV range (b), of a yellow stone from the facade of the Abbey of SS. Pietro e Paolo d'Agrò.

5. Conclusions

The use of mobile instrumentation becomes crucial in art and archaeology when specific archaeometric requirements need to be satisfied on objects that cannot be moved into the laboratory.

In this paper, we put into evidence how powerful can reveal a multitechnique in situ investigation in order to gain complementary information in view of an exhaustive characterization of the objects without the necessity of removal or sampling.

As a case study of in situ application of mobile equipments, the archaeological site of Scifì (Forza d'Agrò, province of Messina, Italy) and the Abbey of SS. Pietro e Paolo d'Agrò (Casalvecchio Siculo, province of Messina, Italy) are presented.

In the archaeological site of Scifì, XRF spectra were collected on two types of ancient mortars belonging to two different chronological phases, namely "phase I" (3rd-4th century AD) and "phase II" (4th-5th century AD), in order to understand if the compositional homogeneity observed at visual inspection was maintained also at elemental level. From the analysis of the chemical nature and the relative concentrations of minor and trace elements, a same origin area of the raw materials was argued. Nevertheless, an increase of Ca concentration was observed for the mortars of "phase II" that can be due to a different kind of paste probably ascribed to a different production technique. Furthermore, by using XRF, Raman, and IRT techniques, pottery fragments excavated in this site and dated back 3rd century BC and 4th-5th century AD were for the first time characterized from the archaeometric point of view, as prerequisite for their cataloguing. In particular, the use of magnetite, umber,

and haematite was, respectively, hypothesized for the black-, reddish-brown-, and reddish-painted sherds.

As far as the Abbey of SS. Pietro e Paolo d'Agrò is concerned, XRF results collected on a red brick from the external facade were compared to those obtained for a brick from "the tower," a square structure of the archeological site of Scifì of reasonable local production. The elemental composition turned out to be similar, suggesting the use of the same raw materials in their manufacture. The similar chemical composition of the soil could explain this occurrence, being the two sites not far from each other. Another hypothesis could be the production of the bricks in the same way and using the same fuel in the kilns.

Again, from XRF spectra, the black stones of the facade were supposed to be volcanic rocks of provenance from Mt. Etna (Sicily, Italy), whereas for the white and yellow stones, the use of a local sandstone was hypothesized.

It is to be expected that, by combining the different skills of archaeologists, chemists, physicists, geologists, on the one side, and instrument manufacturers, on the other side, this approach will continue to gain an always increasing interest over time in archaeometry, as well as in all those areas in which "in field" studies are mandatory, such as geosciences and forensic science.
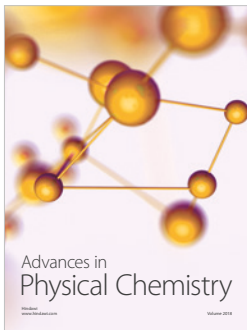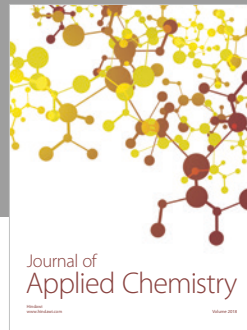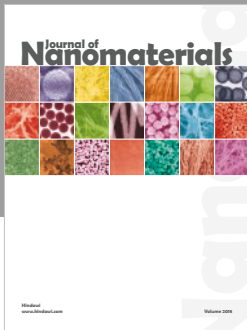
Conflicts of Interest

The authors declare that they have no conflicts of interest.

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