

EVALUATION OF COMPLEMENTARY METHODOLOGIES APPLIED TO A PRELIMINARY ARCHAEOMETRIC STUDY OF GLAZED POTTERY FROM AGSU (AZERBAIJAN)

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Abstract

Agsu town is an Azerbaijan's recently excavated, important archaeological site, considered a crossroads of commercial routes since the ancient times between China, Asia Minor and Europe. For this reason, the area is rich in different typologies of artifacts with various provenances such as stone objects, glazed pottery and coins. The excavations indicated the presence of workshops specialized in various spheres of metallurgy, as well as of dye-works. A non-invasive or, at least, micro-destructive multi-technique approach was applied for the characterization of eight archaeological pottery fragments taken from Agsu Site (Azerbaijan) dated back XIX century A.D.. At different spatial scales, a combination of complementary optical microscopy (OM), scanning electron microscopy – energy dispersive spectroscopy (SEM-EDS), X-ray diffraction (XRD), and prompt gamma activation analysis (PGAA) was applied. The proposed study is aimed at addressing issues such as the characterization of raw materials, the determination of manufacturing, the reconstruction of the firing technology, the identification of the pigments used for decoration and the formulation of a first hypothesis about provenance of the artifacts considered the scarce studies about it in literature.

Keywords: Pottery; Azerbaijan; SEM-EDS; XRD; PGAA; technology.

Introduction

Each age and region has its own peculiar thought and customs that influence every human activity. In particular, the artistic works reflect and emphasize the culture of a geographical area and of an historical period. The aesthetic style, the manufacturing procedure and the materials employed are peculiar parameters for the classification of an artwork. So both the artistic and scientific contributions to the cultural heritage field provide fundamental information in order to individuate the temporal–spatial context.

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Particularly, the identification of pigments is a very charming, but complex task. Decorations and colours, as artistic and cultural expressions, have always fascinated human sensitivity and intellect. The characterization of materials and methods used for the preparation of colouring substances is a fundamental step to carry out a correct classification of artworks, because pigments composition and production techniques reflect both art and technology development typical of a population, settled in a geographical region and located in a particular historical age. Nevertheless, decorated ceramics are not easy to be analysed because of the difficulty to isolate the glazed layer from the bulk paste. In fact in the brushwork the pigment mixes with the matrix and some colouring substances can be absorbed by the earthenware. Furthermore, the recent pottery surfaces are often glazed and this makes harder the spectroscopic study because the silicates bands can mask other more interesting and peculiar contributions [1-3].

The production of ceramic wares in Azerbaijan started since Neolithic age and it is well known the use of pottery's wheel already in that period. In Medieval Age the production diversified into three groups: unglazed ceramics, glazed ceramics and construction ceramics. Bowl, dish, goblets represent the most common artefacts; usually they show an inner part decorated with geometrical, botanical or live descriptions. Construction ceramics in Middle Ages consist mainly of brick, tile and water pipes. This can be explained on the one hand with demands of domestic circumstances, on the other hand wide-spread of Islamic architecture.

Azerbaijan shows a great variety of ceramic findings beyond the local ones, due to the strategic position of the area in the most important commercial routes between Europe, Near East and Far East. Studies on provenance and technological details of the manufacture of pottery can yield important archaeological information allowing the determination of trading patterns and approximate fabrication dates of the artefacts [4].

In this regard, just recently Agsu medieval artefacts underwent systematic archaeometrical investigations. The main goal of the present study is to introduce a combined methodological approach involving and comparing different spatial regimes, based on optical microscopy (OM), scanning electron microscopy – energy dispersive spectroscopy (SEM-EDS) and prompt gamma activation analysis (PGAA) to define raw materials and pigments used for the production of some representative pottery samples. Moreover, by means of X-ray diffraction (XRD) analysis, it was possible to assess the firing temperature of the samples. The achievement of this crucial information allowed to clarify technological features about preparation processes and to collect data useful to enhance next studies focused on the provenance of the artefacts. In fact, this research represents a milestone in the archaeometric study of the pottery coming from Azerbaijan, because of the scarce documentation about the local raw materials, the production processes and the amount of foreign potteries in the area coming from especially Middle and Far East.

Materials and methods

Site and samples

The ruins of the medieval Agsu town (17th-18th century) are situated 4-5 km away in the south-east from the town of Agsu, about 160 km west far from Baku the capital of Azerbaijan.

Large-scale archaeological excavations at the site of Agsu began just in 1983 and revealed an extensive town rich in architectural remains and artefacts, depicting a settlement with solid trade and cultural connections to other parts of the world. Although Agsu city was repeatedly exposed to feudal attacks, destruction, and inhabitant deportation during the 18th century, enough remained to show the features of a city that was circumscribed with fortified walls, a castle with round defensive towers, and other dwellings that were erected very close to each other with narrow streets, along with other comparatively wider central streets.

The excavations put into light artefacts as earthenware, coins and glazed potteries [5], indicative of trade and cultural relations of Agsu with a number of countries and cities of the world.

Eight fragments of pottery (Fig. 1) were taken from the medieval ruins of Agsu, but the available information such as use and historical period is scarce; probably the sherds belongs to objects for domestic uses as bowls, dishes or vessels.

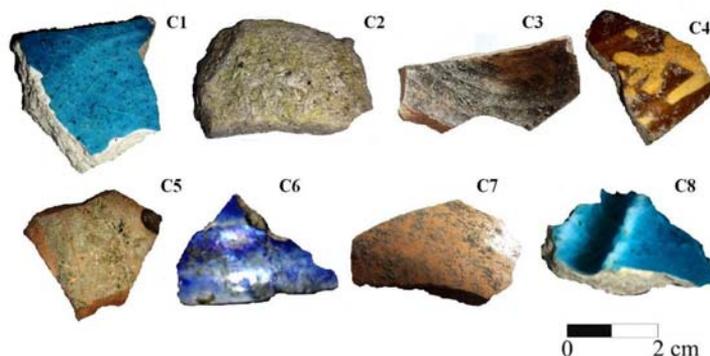


Fig. 1. Pottery fragments sampled in Agsu site.

Table 1 reports the main information about the potteries. It is possible to recognize traces of the original decoration just in sample C4. From a macroscopic analysis, the eight fragments presented a fine grained and compact ceramic body, coated by a glazed layer except the sample C2.

Table 1. Summary of the studied samples with related descriptive information.

| Sample | Typology | Description | |
|--------|----------------|--------------|--------------------|
| | | Ceramic body | Glaze |
| C1 | Faience | Whitish | Light Blue |
| C2 | Pottery | Beige | - |
| C3 | Glazed pottery | Dark beige | Black |
| C4 | Glazed pottery | Reddish | Yellow decorations |
| C5 | Glazed pottery | Reddish | Dark Yellow |
| C6 | Faience | Whitish | Blue |
| C7 | Glazed pottery | Reddish | Yellowish |
| C8 | Faience | Whitish | Light Blue |

Instrumentation

Petrographic observations were carried out by a Zeiss polarizing microscope and described according to Whitbread [6], which characterizes the microstructure, groundmass and inclusions. Micro-morphological analyses by SEM were performed to characterize the groundmass microstructure and the vitrification degree [7]. The EDS provided the chemical composition of slip and ceramic body. The analyses were performed on a FEi Quanta 200 Scanning Electron Microscope equipped with an EDaX genesis 4000.

Mineralogical analysis aimed to assess the firing temperature has been carried out by means of XRD measurements. For this purpose, it has been used a D8 Advance Bruker X-ray diffractometer, using Cu K α radiation as the X-ray source. The diffractograms were recorded in the 2 θ range of 10-80°. Measuring conditions were set at 40 kV voltage, 30mA current, 0.02° 2 θ step size, and 3.0 sec step time.

PGAA was chosen to non-invasively quantify all the major components and some important trace elements. In principle, PGAA enables to detect all the chemical elements, but the sensitivities for different elements vary within a wide range, mainly determined by the neutron-capture cross-section of various elements. It is worth remarking that although other, more wide-spread, techniques such as X-ray Fluorescence (XRF) or Instrumental Neutron Activation Analysis (INAA), allow for the identification of a wider range of trace elements, PGAA allows quantifying sodium and also offers the unique possibility to determine some light elements, like hydrogen or boron. Furthermore, since neutrons can penetrate more centimetres in silica-based material, one can obtain an average composition of the bulk irradiated volume of the investigated object. Using an external neutron beam for PGAA, one can avoid sampling of valuable cultural heritage objects. Not to mention that owing to the relatively low intensity neutron beam, no significant induced radioactivity or any damage can be observed following the analysis.

Both PGAA and SEM-EDS detect major elements useful to obtain information on composition of artefacts and technology of preparation. In this regard, the results were compared to evaluate probable differences considering that PGAA is a bulk analysis unlike SEM-EDS that allows selecting the area to analyse; this can be helpful in the glazed potteries where glaze and ceramic body are distinct. Moreover, PGAA provides minor and trace elements essential in the provenance studies about pottery [8-14]. In fact the chemical composition along with these elements of a pottery is strongly related to the source clay from which it is prepared [14].

PGAA has been performed on all fragments at the Budapest Neutron Centre [15]. The experimental station is located at the end of a horizontal guided beam of cold neutrons at the 10 MW Budapest Research Reactor. After the upgrade of horizontal neutron guides in 2006, the thermal equivalent neutron flux at the target position is approximately $10^8 \text{ cm}^{-2} \text{ s}^{-1}$. The neutron beam is collimated to a maximum area of $20 \times 20 \text{ mm}$. If necessary, the beam size can be reduced to a few mm^2 spot. The quantitative analysis is based on the detection of prompt- and decay γ -photons, emitted in the (n, γ) reaction [16, 17]. The elements are identified by the characteristic γ -energies, while the quantitative data result from the peak intensities. The standardization is based on a prompt k_0 -library [18]. The spectroscopic data libraries were developed at the Budapest Research Reactor [19].

The composition was determined using the methods described by Révay [20], the uncertainties of the concentration values were determined according to Révay [21]. From the point of the owner of the objects, it is essential that the radioactive products usually decay within a few days. The method has been successfully applied to analyse archaeological stone objects [16, 17] as well as fragments of archaeological pottery [14].

For each measurement, the acquisition time varied between 2600 and 54000s, depending on the sample size. The γ -photons from the bulk material were detected by a calibrated HPGe-BGO detector system in Compton suppressed mode [22], and the spectra were collected by 16k multichannel analyzer. The spectrum fit was done by HYPERMET PC software [23]. ProSpeRo 3.2.4 software package was used for calculation of elemental concentrations and their uncertainties.

Results and discussion

Petrographic analyses

Textural and compositional features of ceramic fragments were determined undergoing thin sections to optical microscopy according to Whitbread [6]. The study allowed to distinguish two different petrographic groups.

The Group 1 (Fig. 2a) includes the samples C2, C3, C4, C5 and C7. The microstructure in the sample C4, C5 is characterized by mesovoids ($500\text{-}50\mu\text{m}$) and vesicles. The inclusions

are double-spaced with a slight preferred orientation. The mica-rich groundmass appears moderately homogeneous with a reddish colour in plane polarized light (PPL) and crossed nicol (CN). The optical activity varies from being absent to low with a stipple speckled fabric.

Inclusions show a ratio c:f:v (coarse:fine:voids) of about 30:50:20 and are constituted by predominant quartz, common plagioclase and opaque oxides. The grain-size distribution is bimodal and varies from fine to very fine ranged between 200-100 μm and 50-10 μm . The amorphous concentration features (Acf) are commonly impregnate.

The samples, except C2, show a superficial vitrified slip about 100 μm thick. Besides an intermediate layer 40 μm thick was identified between the ceramic body and the glaze, probably an engobe. It shows a glassy aspect, a less compactness than slip and rare inclusions of very fine quartz. This layer is well visible in C4, C5 and C7.

The samples C2 and C3 exhibit some differences as a brownish groundmass and the presence of secondary calcite as clasts and as recrystallization rims on the voids walls.

In the second group (Fig. 2b), including the samples C1, C6 and C8, the microstructure is characterized by mesovoids; the distribution of inclusions is open-spaced without any preferred orientation. The matrix is quartz-rich, probably because of the different raw material employed, i.e. a quartzite, or to the addition of quartz as temper in the ceramic body during the production process. The matrix is scarcely homogeneous and optically active with a crystallitic fabric; its aspect is cloudy and slightly coloured with shades from yellowish in PPL to greyish-brown in CN. The ratio c:f:v is about 10:70:20.

Quartz represents the predominant phase in the inclusions. The grain-size is fine and unimodal ($\sim 100\mu\text{m}$); whereas the Acf are impregnative. A slip $\sim 200\mu\text{m}$ thick is present on the ceramic body.

All the samples show a yellowish (in PPL) superficial deposit with a variable thickness (150 - 20 μm) probably of secondary origin.

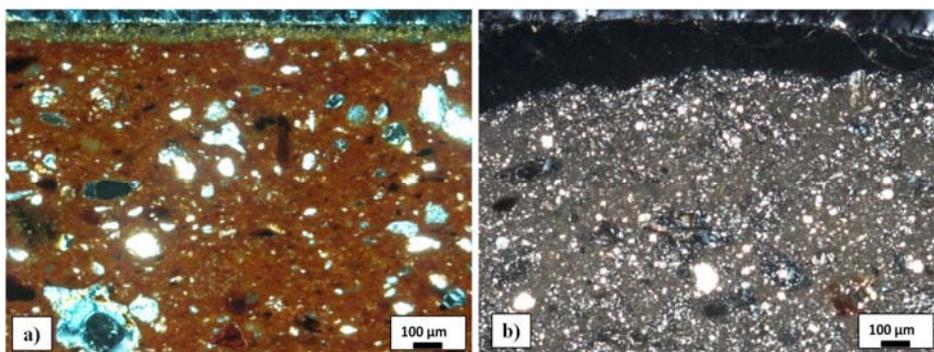


Fig. 2. Thin section microphotos in CN show sample C7 related to Group 1(a) and sample C8 to Group 2(b).

SEM-EDS analyses

The morphological analyses carried out by SEM point out the high degree of vitrification of the slip and the sharp contact with the ceramic body in the samples of the first group (C2, C3, C4, C5, C7) (Fig. 3a).

The group 2 (C1, C6, C8) is characterized by a very extensive vitrification of the matrix showing almost an amorphous aspect; the glaze is also vitrified; its contact with the ceramic body is clear-cut but irregular (Fig. 3b).

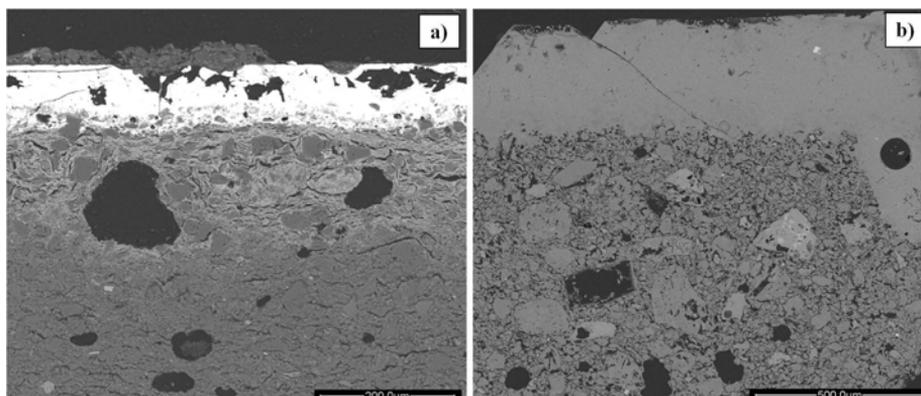


Fig. 3. SEM micromorphological details of glaze and ceramic body in sample C4 (a) and C6 (b), respectively from Group 1 and 2.

Chemical compositions obtained by quantitative EDS on ceramic bodies and glazes are listed in Table 2.

Table 2. Major element compositions (in wt%) determined by EDS microanalyses respectively for ceramic body, glaze and probable engobe. Each data is mean value of three determinations.

| Sample | Na ₂ O | MgO | Al ₂ O ₃ | SiO ₂ | PbO ₂ | SO ₃ | Cl ₂ O | K ₂ O | CaO | TiO ₂ | Fe ₂ O ₃ | CuO | TOT |
|--------------|-------------------|------|--------------------------------|------------------|------------------|-----------------|-------------------|------------------|------|------------------|--------------------------------|-------|--------|
| Ceramic body | | | | | | | | | | | | | |
| C1 | 5.06 | 1.13 | 15.12 | 76.12 | - | - | - | 1.00 | 1.38 | - | 0.20 | - | 100.00 |
| C2 | 2.51 | 2.85 | 16.58 | 60.30 | 0.79 | - | - | 1.73 | 9.42 | 0.63 | 5.20 | - | 100.00 |
| C3 | 2.41 | 2.57 | 15.04 | 65.56 | - | - | - | 2.40 | 7.85 | 0.34 | 3.84 | - | 100.00 |
| C4 | 1.04 | 2.46 | 21.06 | 63.03 | - | - | - | 3.26 | 2.51 | 0.92 | 5.73 | - | 100.00 |
| C5 | 1.34 | 2.27 | 20.00 | 65.31 | - | - | - | 3.14 | 1.17 | 0.85 | 5.92 | - | 100.00 |
| C6 | 5.86 | 1.51 | 14.31 | 74.75 | - | - | - | 1.33 | 2.24 | - | - | - | 100.00 |
| C7 | 1.10 | 2.69 | 22.90 | 59.63 | - | - | 0.13 | 3.45 | 2.34 | 1.14 | 6.62 | - | 100.00 |
| C8 | 5.08 | 0.97 | 13.28 | 77.41 | - | - | - | 1.24 | 2.03 | - | - | - | 100.00 |
| Glaze | | | | | | | | | | | | | |
| C1 | 14.78 | 1.63 | 5.05 | 67.39 | - | 0.38 | 1.25 | 1.43 | 2.93 | 0.24 | 1.04 | 3.91 | 100.00 |
| C3_a | - | - | - | 0.74 | - | - | - | - | - | - | 99.26 | - | 100.00 |
| C3_b | - | - | 2.56 | 2.16 | - | - | - | - | 1.16 | - | - | 94.12 | 100.00 |
| C4 | 0.94 | 0.86 | 6.75 | 32.98 | 56.11 | - | - | 0.51 | 0.81 | 0.34 | 0.73 | - | 100.00 |
| C5 | 0.60 | 0.90 | 5.45 | 26.48 | 63.91 | - | - | 0.30 | 0.46 | - | 1.92 | - | 100.00 |
| C6 | 13.44 | 2.58 | 4.73 | 67.29 | - | 0.66 | 0.44 | 2.25 | 2.68 | 0.32 | 1.44 | 2.18 | 100.00 |
| C7 | 2.11 | 1.25 | 10.14 | 39.14 | 41.90 | - | - | 1.23 | 0.87 | 0.71 | 2.67 | - | 100.00 |
| C8 | 12.64 | 1.53 | 5.37 | 69.71 | - | 0.54 | - | 2.07 | 2.13 | 0.21 | 0.85 | 4.95 | 100.00 |
| Engobe | | | | | | | | | | | | | |
| C4 e | 1.23 | 1.63 | 20.85 | 58.99 | 7.94 | - | - | 4.15 | 1.00 | 1.54 | 2.69 | - | 100.00 |
| C5 e | 1.31 | 1.80 | 16.40 | 60.71 | 11.36 | - | - | 2.58 | 0.89 | - | 4.98 | - | 100.00 |

The samples C4, C5 and C7 show a typical lead glaze constituted by a mixture of PbO₂ and silica [24, 25] whereas the underlying yellow is related to Fe³⁺ oxides [25-28].

The sample C3 is characterized by two different pigmented glazes, respectively an iron-based black and another rich in CuO, probably a blue; however it is difficult to determine this latter one because the glaze is seriously damaged and present just in few points.

The composition of ceramic body suggests a clay rich in alumina e silica as raw material with low percentages of calcium and other oxides. The probable engobe identified in the

potteries shows a similar composition of the ceramic body; moreover, the little amount of lead detected in C4 and C5 engobe comes from the glaze above (see Table 2).

It is worth specifying that there is no data or information in literature about the probable local production of pottery in Azerbaijan and it could be necessary to increase the amount of samples studied and the analysis to carry out both on potteries and local clays. In this context it is difficult to express any hypothesis about provenance of raw materials. The data gathered could just suggest two probable source area: Islamic Near East or Chinese one: the presence and the amount of lead and silica in glaze could suggests an Islamic provenance of the artifacts [29], on the other hand the absence of tin, an important component used as opacifier in this typology of potteries, does not confirm this hypothesis. Moreover, it is well known in literature that ancient Islamic ceramics are mainly made of calcareous clay with high lime contents (usually higher than 10% CaO), whereas there is a dearth of calcareous clays in China, so they were seldom used in pottery making in ancient China [30]. Therefore, it is traditionally thought that lime and alumina can be regarded as the two major characteristic oxides that allow distinguishing approximately the two provenances [31, 32], although further analysis i.e. on isotopes and trace elements would be useful. So it could be more probable a Chinese provenance such as preliminary hypothesis.

The glaze in Group 2 is coated by a glassy layer with a slightly different composition respect the previous group, i.e. richer in SiO₂, Na₂O or CaO. CuO was identified as main pigment chromophore providing the blue color in C1, C6 and C8. The analyses performed on the ceramic body suggest the probable addition of quartz as temper in a silica clay employed as raw material.

XRD analyses

XRD was used to determine mineralogical composition of the ceramic body and to evaluate firing temperatures [33]. Identified mineralogical phases are listed in Table 3.

Table 3. Mineralogical composition (relative abundances of phases were estimated on the basis of the intensity of reflections in the diffraction patterns) of the ceramic body detected by XRD. Legend: Qtz = quartz; Pl = plagioclase; Feld= Feldspar; Hem = hematite; Cal = calcite; Di = diopside; CM = total clay minerals. ++++ = very abundant; +++ = abundant; ++ = common; + = scarce.

| Sample | Qtz | Pl | Feld | Hem | Cal | Di | CM |
|--------|------|-----|------|-----|-----|----|----|
| C1 | ++++ | +++ | | | | + | |
| C2 | +++ | +++ | | + | + | ++ | + |
| C3 | +++ | +++ | | + | + | ++ | + |
| C4 | ++++ | +++ | ++ | + | | + | |
| C5 | ++++ | +++ | ++ | + | | + | + |
| C6 | ++++ | +++ | | | | + | |
| C7 | +++ | +++ | ++ | + | | + | |
| C8 | ++++ | +++ | | | | + | |

Quartz and plagioclase are ubiquitous in all samples; the Group 1 (C2, C3, C4, C5, C7) shows a more heterogeneous composition because of the presence feldspar, hematite and clay fraction. In addition, C2 and C3 contain calcite probably related to secondary crystallization processes as reported in petrographic analysis. On the other hand, the mineralogical phases in Group 2 are constituted essentially by predominant quartz and subordinated plagioclase.

The XRD analysis revealed the occurrence of diopside (CaMgSi₂O₆) as neoformation phase in all samples, suggesting that the original calcareous clay was fired at temperatures higher than 850°C [7, 34, 35].

PGAA analyses

PGAA was able to quantify all the major components, such as H₂O, Na₂O, MgO, Al₂O₃, SiO₂, K₂O, CaO, and Fe₂O₃ with sufficient precision. Following a well-established convention

in geochemistry, major components are given in oxide forms. Since oxygen is one of the worst detectable element, the amount of oxides are calculated, based on the oxidation numbers of the elements. In addition, it was also possible to identify some geologically important minor and trace elements, such as B, S, Cl, Sc, V, Sm, Gd, with extremely high sensitivities for B and some rare-earth elements [10] helpful for next provenance studies. In fact, at the present stage of research, no geological or geochemical reference data, crucial in discriminating the source area of the raw materials, are available.

For all the investigated samples, the detailed concentration data and their precision are summarized in Table 4, where concentration values for both the major and the trace components are expressed in wt%. The relative uncertainties of the major components are typically around 1 to 3%, while the trace elements are occasionally detected with 5 to 10% relative uncertainties.

Table 4. PGAA data for pottery samples. Major and traces elements are expressed in wt%. (<D.L.= under Detection Limit).

| Sample | H ₂ O | B ₂ O ₃ | Na ₂ O | MgO | Al ₂ O ₃ | SiO ₂ | SO ₃ | Cl | K ₂ O | CaO | Sc ₂ O ₃ |
|--------|------------------|-------------------------------|-------------------|-----|--------------------------------|------------------|-----------------|--------|------------------|------|--------------------------------|
| C1 | 0.78 | 0.1175 | 6.56 | 1.1 | 13.4 | 73.4 | 0.25 | 0.144 | 1.22 | 1.7 | <D.L. |
| C2 | 2.37 | 0.0243 | 2.04 | 2.2 | 14.3 | 58.0 | 0.26 | 0.107 | 2.77 | 10.6 | 0.0032 |
| C3 | 1.62 | 0.0274 | 2.26 | 3.1 | 14.8 | 57.8 | 0.28 | 0.092 | 2.77 | 10.2 | 0.0019 |
| C4 | 1.11 | 0.0223 | 1.13 | 2.5 | 17.5 | 61.4 | <D.L. | <D.L. | 3.40 | 2.2 | 0.0025 |
| C5 | 1.22 | 0.0241 | 1.43 | 2.1 | 16.7 | 62.1 | <D.L. | 0.0041 | 3.19 | 1.1 | <D.L. |
| C6 | 0.45 | 0.1349 | 6.74 | 2.7 | 12.1 | 70.3 | 0.66 | 0.181 | 1.71 | 2.9 | <D.L. |
| C7 | 1.30 | 0.0272 | 0.96 | 2.5 | 17.8 | 61.2 | <D.L. | 0.0015 | 3.55 | 2.5 | 0.0026 |
| C8 | 0.49 | 0.1730 | 7.21 | 1.5 | 11.6 | 72.4 | 0.37 | 0.073 | 1.56 | 2.5 | <D.L. |

| Sample | TiO ₂ | V ₂ O ₅ | MnO | Fe ₂ O ₃ t | CuO | Nd ₂ O ₃ | Sm ₂ O ₃ | Gd ₂ O ₃ | PbO | TOT |
|--------|------------------|-------------------------------|-------|----------------------------------|-------|--------------------------------|--------------------------------|--------------------------------|-------|--------|
| C1 | 0.104 | 0.003 | 0.022 | 0.75 | 0.42 | 0.0018 | 0.00015 | 0.00017 | <D.L. | 100.00 |
| C2 | 0.710 | 0.032 | 0.169 | 6.44 | <D.L. | 0.0030 | 0.00046 | 0.00056 | <D.L. | 100.00 |
| C3 | 0.712 | 0.038 | 0.164 | 6.18 | <D.L. | 0.0038 | 0.00042 | 0.00052 | <D.L. | 100.00 |
| C4 | 1.29 | 0.025 | 0.140 | 7.59 | <D.L. | 0.0070 | 0.00067 | 0.00078 | 1.6 | 100.00 |
| C5 | 0.826 | 0.027 | 0.130 | 6.85 | <D.L. | 0.0051 | 0.00060 | 0.00071 | 4.3 | 100.00 |
| C6 | 0.166 | 0.0085 | 0.037 | 0.93 | 1.03 | 0.0023 | 0.00018 | 0.00020 | <D.L. | 100.00 |
| C7 | 1.31 | 0.029 | 0.129 | 7.62 | <D.L. | 0.0064 | 0.00066 | 0.00080 | 1.1 | 100.00 |
| C8 | 0.118 | 0.002 | 0.034 | 0.81 | 1.26 | 0.0034 | 0.00018 | 0.00018 | <D.L. | 100.00 |

As expected, SiO₂ is the prevailing major component, ranging from ~ 58 up to ~ 73 wt%, indicative of certain heterogeneity. The other major components are present in low amounts: Al₂O₃ varies between 12wt% and 18wt%; Na₂O and Fe₂O₃ reaches 7wt%; MgO, K₂O CaO do not exceed 4wt%, just CaO is about 10wt% in C2 and C3; TiO₂ is lower than 1wt% and MnO than 0.2wt%.

In addition to the typical components of clay, some elements constitute the pigments of the glazes how described in EDS results previously.

CuO is about 1% and represents the chromophore producing blue pigment in C1, C6, C8, conforming how reported in literature [36, 37]. PGAA was not able to detect CuO in C3 because of the worst conservation of the pigmented layer how observed in SEM morphological analysis.

Overall it is difficult to establish the kind of blue both by SEM-EDS and PGAA. In fact the samples presented a glassy coating and the clear identification of pigments is tricky due to contributions coming from the silicate compounds or the underlying ceramic body [38].

Fe₂O₃ amount is higher in C3, C4, C5, C7 where this oxide represents both a chromophore and a component of the ceramic body how suggested also by EDS.

PbO detected in C4, C5, C7 is lower than 5wt% and is related to the composition of the lead glaze [25].

The amount of trace elements is very scarce, for example, the ranges vary respectively between 0.0018 and 0.0070wt% for Nd₂O₃; 0.00015 and 0.00067wt% for Sm₂O₃; 0.00017 and 0.00080wt% for Gd₂O₃.

Overall, the comparison between EDS and PGAA data suggest how the composition obtained by PGAA is very similar to ceramic body analyzed by EDS in terms of both elements identified and wt%. Moreover PGAA provides traces elements useful for next provenance studies. On the other side, there is a scarce conformity about glaze and engobe compositions. In this regard PGAA, being a bulk analysis, is not able to discriminate probable layers, such as glaze or engobe, highlighted instead by SEM-EDS from a morphological and compositional point of view.

Data collected from the PGAA bulk analysis and SEM-EDS on the ceramic body provide information about the clay used as raw materials: the chemical characterization highlighted the alumina and silica based composition of the clay used in the production processes of the pottery. The data related to major and trace elements will be applied in next studies where geological clay samples will be undergone the same analysis campaign to evaluate the local or different provenance of the raw materials.

Conclusions

The work demonstrated the importance of an archaeometric approach to characterize specimens of potteries to increase the available historical information. Moreover, this research highlighted the advantage to apply complementary methodologies as PGAA and SEM-EDS aimed to determine the chemical composition of the samples.

The glazed potteries coming from Agsu were distinguished in two main groups based on different petrographic and compositional features of the samples. It suggests the probably presence of different production technologies and raw materials explicable partly with the site position as crossroad of commercial routes. In particular, two types of clay were identified: a more heterogeneous clay rich in quartz, plagioclase, feldspar and hematite employed in Group 1; a more selected clay constituted essentially by quartz and plagioclase used in Group 2.

XRD analysis suggested the reaching of similar firing temperatures higher than 850°C thanks to the “fingerprint” diopside in both groups.

Data collected are not sufficient at the moment to identify the probable provenance of the artifacts, only Group 1 would show compositional features probably related to the Chinese production. However this hypothesis needs to be enhanced increasing the amount of samples studied and the analysis to carry out both on potteries fragments and local clays.

In conclusion, the work gathered a good background to consider as a milestone in future archaeometric studies about this area, promoting further sampling campaigns about both archaeological and geological specimens in order to reconstruct the provenance of the artifacts.

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