



The combined use of spectroscopic techniques for the characterisation of Late Roman common wares from Benevento (Italy)



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ABSTRACT

This paper reports the results of an archaeometric characterisation carried out on nineteen samples of Late Roman table and cooking ware by means of the combined use of spectroscopic techniques (colorimetry, FT-IR and μ -Raman). The study attempts at defining the technology adopted in the manufacturing of these ceramics, unearthed during archaeological surveys carried out within the "Ancient Appia Landscapes" project. Successful results were achieved and the reconstruction of the productive process was carried out. Second derivative profiles of IR spectra and μ -Raman analyses allowed defining the mineralogy of ceramic pastes, inferring the local provenance of raw materials and the low attention paid in their manufacturing. If good technological standards were achieved in the production of tableware, cooking ware shows colorimetric and mineralogical evidences of uncontrolled firing conditions, testifying a not-well standardized technological process.

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1. Introduction

During the last years spectroscopic techniques such as μ -Raman (μ -RS) and Fourier Transform Infrared (FT-IR) spectroscopy have been used as an innovative approach for the characterisation of archaeological objects, due to their high spectral resolution as well as the non-destructiveness and non-invasiveness [1,2]. In particular, these techniques revealed a high versatility for the characterisation of ceramic shards, providing mineralogical information on micrometric-sized mixtures, like ceramic pastes.

Over the past decades, technological improvements in the instrumentations for both techniques, measuring fundamental molecular vibrations resulting in sharp, well-resolved bands [3], increased their suitability for the mineralogical characterisation of ceramic pastes. Actually, each band provides information on chemical functional groups of crystalline and amorphous substances, based on its position, intensity and shape [4].

Within the study of ancient pottery, the main archaeological issues to infer the production processes, the evolution of technological standards, relationships and commercial trades among

ancient populations, are the provenance of pottery and related raw materials along with the technology adopted by ancient craftsmen [5].

Chemical analysis (X-ray fluorescence (XRF)) is a widespread method for provenance studies of pottery. However, chemical data should be carefully weighed for the possible compositional changes due to pre-treatments of the raw materials (e.g., levigation, tempering) [6,7]. For this reason, one of the most effective method to infer the provenance of pottery is the comparison of the most peculiar mineralogical features of a-plastic grains (e.g. temper) with mineralogical and petrological information of geological material outcropping near the production centre [6,8–14]. These features are usually achieved by polarized light microscopy (PLM) and SEM/EDS analyses. While the mineralogical and textural features of the ceramic pastes are easily recognizable by optical microscopy, the correctness of chemical composition of grains is strongly depending on accurate sample preparation (polished thin section and graphite coating) and precise calibration of EDS detector using international standards.

On the other hand, μ -Raman spectroscopy, coupled with a confocal microscope, perfectly fits such types of investigations. It enables to investigate the textural features of ceramic samples and to identify the crystalline phases by Raman measurements

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[15–17]. It also discriminates among the polymorphs of a mineral phase and provides information about the mineral chemistry of solid solutions [2,4,18]. Thus, μ -Raman spectroscopy could represent a rapid as well as non-destructive approach into the studies of provenance [19].

Another interesting aspect in the study of ancient pottery concerns the reconstruction of firing technology, which determines textural and mineralogical changes in the ceramics as a function of firing temperatures and type of atmosphere [5,20,21]. The electric and more resolved technique for the estimation of firing temperatures is represented by X-ray diffraction (XRD), which allows detecting newly-formed micro- and crypto- crystalline phases, representing important thermal indicators [21–23]. FT-IR spectroscopy, which is becoming a useful tool in the characterisation of clay-based materials [24–27], constitutes an alternative and rapid method for the definition of firing temperatures that requires a reduced amount of archaeological materials, often scarce and precious.

Finally, firing atmosphere is usually inferred by Mössbauer spectroscopy, which provides information about the oxidation state of iron oxides, function of redox conditions occurring into the kiln during firing processes [28]. Although precise and accurate, this technique requires powdered material, expensive and advanced instrumentations (a high-energy source is required) and long acquisition times. The same information (occurrence of different iron oxides, i.e. hematite-maghemite-magnetite) can be obtained by μ -Raman spectroscopy.

Hence, spectroscopic techniques turn to be suitable and advantageous for archaeometric studies and, for this reason, they were adopted to investigate mineralogical features of a set of samples of Late Roman common wares, dated back from the 4th to the 6th century AD. Ceramic potsherds were collected during archaeological surveys near the city of Benevento (Italy) within the “Ancient Appia Landscapes” project. Although FT-IR and μ -Raman spectroscopy could replace widely-used techniques for the archaeometric characterisation of ancient ceramics, if singularly considered they do not disclose sufficient information for a reliable and complete definition of ancient technology. For this reason, this paper aims at approaching the study of pottery by means of a

combined use of both spectroscopic techniques, in order to determine the technological features of ceramic artefacts produced in Benevento surroundings during the Late Roman period.

2. Brief archaeological overview and materials

The “Ancient Appia Landscapes” project started in 2011 with the scope of a topographic survey of the *Via Appia* in the segment between the city of Benevento (ancient *Beneventum*) and the so-called Ponte Appiano on the Calore River (Fig. 1).

The on-going research project also includes the reconstruction of the ancient landscape in this area, which was strongly influenced by the presence of one of the most important roman road. For this reason, the multidisciplinary approach has been achieved paying attention to the environmental events, population dynamics, settlement patterns and economic activities [29–35].

The archaeological surveys performed in the area unearthed a representative set of ceramic findings, accounting for a rural life in neighbourhoods of *Beneventum*. The typological repertoire and stylistic features of vessels, in fact, highlighted a clear predominance of presumed local pottery, also reflecting the general decrease in the penetration of imported goods into inner areas of Samnium from the 5th century [35].

One of the most important and complex aspects of the research is the quantification and classification of ceramic finds coming from archaeological surveys, which provided a spatial distribution of ceramic materials rather than a punctual information of the stratigraphic excavation.

The typological study of each ceramic sample was based on a careful description of ceramic fabric, shape, type and, if present, decorative patterns. A typo-chronological study of pottery was developed, and, comparing the ceramic assemblages with coeval regional productions, new elements on the production, circulation and consumption of pottery in this part of the territory of Benevento were provided [35].

Middle Imperial and Late Roman pottery, in fact, revealed a remarkable morphological standardization in the ceramic production of Campania region, suggesting similar manufacturing

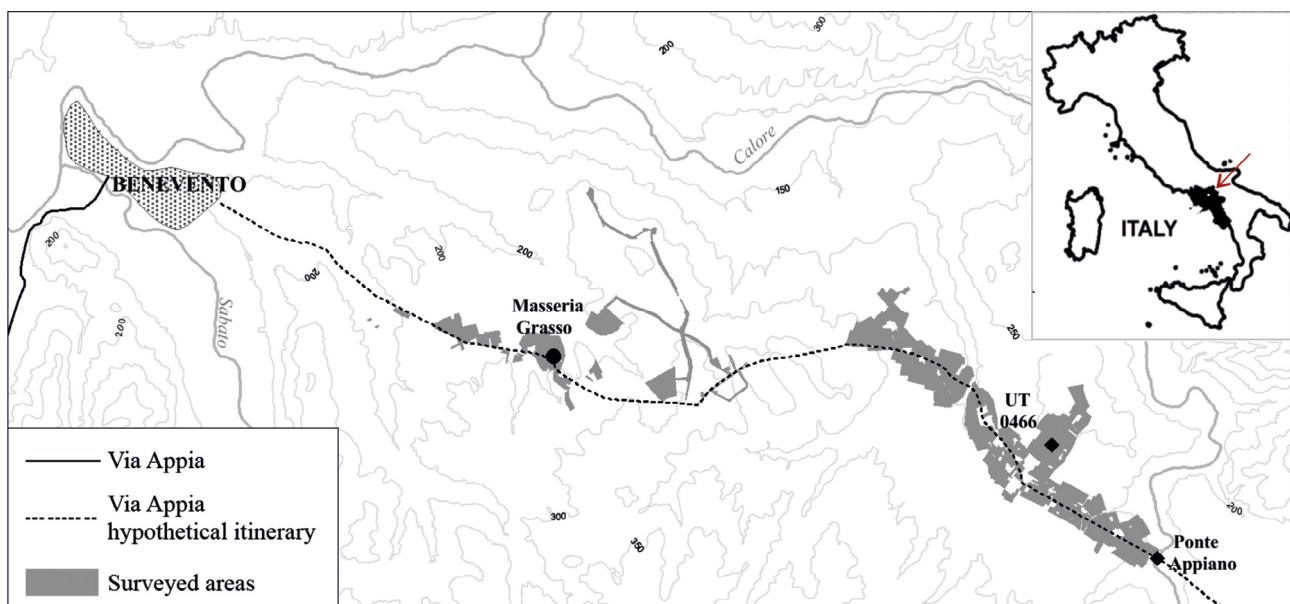


Fig. 1. Areas surveyed within the “Appia Ancient Landscapes” project (scale 1: 115,000) (modified by Santoriello and Siano [35]).

Table 1
List of the analysed samples with archaeological information and macroscopic features.

Ceramic class	Sample	Form	Type	Hardness	Texture	Coating
TW 1	BNC 3	Jug	Carminiello 90	Hard	M,R,Sp	Matte reddish slip
	BNC 15	Bowl	/	Hard	M,R,Ab	Matte reddish slip
TW 2	BNC 2	Bowl	Hayes 61	Very hard	F,R,Sp	Red polished slip
	BNC 9	Bowl	Hayes 61	Hard	F,R, Sp	Red polished slip
TW 3	BNC 4	Jug	Carminiello 90	Very hard	M,R,Ab	Matte reddish slip
	BNC 16	Jug	/	Very hard	M,R,Sp	Matte reddish slip
CW 1	BNC 7	Casserole	Carminiello 16	Very hard	F,R,Sp	Matte reddish slip
	BNC 8	Casserole	Carminiello 2 and 3	Very hard	M,R,Sp	Red polished slip
	BNC 21	Olla	Carminiello 33.1	Very hard	M,R,Ab	Matte reddish slip
	BNC 22	Olla	Carminiello 53.1	Very hard	M,R,Ab	Matte reddish slip
CW 2	BNC 5	Casserole	Carminiello 22	Very hard	M,R,Sp	Matte reddish slip
	BNC 6	Casserole	Carminiello 37.1	Very hard	F,R,Sp	Matte reddish slip
	BNC 12	Casserole	Carminiello 12	Very hard	C,R,Ab	Red polished slip
	BNC 13	Pan	Hayes 23B	Very hard	M,R,Mod	Red polished slip
	BNC 14	Casserole	Carminiello 5.1 and 5.2	Very hard	M,R,Ab	Matte reddish slip
	BNC 17	Casserole	Carminiello 39	Very hard	M,R,Mod	Matte reddish slip
	BNC 18	Pan	Hayes 23B	Very hard	M,R,Ab	Red polished slip
	BNC 19	Pan	Hayes 181	Very hard	M,R,Mod	Brownish polished slip
	BNC 23	Casserole	Carminiello 18	Very hard	M,R,Ab	Matte reddish slip

techniques adopted in Campania between the late 4th and the 6th century AD, intentionally associated with particular forms of different cultural traditions [29].

The analysed set of samples constitutes a quite representative group of Late Roman potteries unearthed during archaeological surveys [35]. Six samples of tableware and thirteen samples of cooking ware were selected for the archaeometric analyses (Table 1).

Tableware (hereafter TW), representing the least conspicuous group of ceramic finds, consists of jugs (Carminiello 90) and bowls (Hayes 61) (Table 1 and Fig. 2b), very similar, from a morphological point of view, to types well attested in Naples and Campania between the 5th and 6th century. Dense red-polished¹ or matte reddish slips cover the ceramic surfaces (Fig. 2a).

Cooking wares (hereafter CW) consist of pans imitating Hayes 23B and 181, *ollae* (Carminiello 33.1, 53.1) and casseroles (Carminiello 2, 3, 5.1, 5.2, 12, 16, 18, 22, 37.1, 39) (Table 1 and Fig. 2d) with rough-textured clay body, frequently showing a “sandwich structure”. All samples show red-polished or matte reddish or brownish coating (Table 1 and Fig. 2c), this latter applied only on the external surfaces.

3. Analytical techniques

Compositional features of ceramic pastes were investigated by means of a combined use of colorimetry, FT-IR and μ -Raman spectroscopy.

Colorimetric measurements on fresh-fractured surfaces were performed for a quantitative evaluation of the colour of the ceramic pastes, with a portable Konica Minolta CM-700d spectrophotometer. Chromatic coordinates (CIE $L^*a^*b^*$) were determined in the 400–700 nm wavelength range by selecting CIE illuminant D65 (simulating daylight with a colour temperature of 6504 K). An area of the sample of just 3 mm (8° view angle, 10° observer) in diameter was analysed. The illumination was provided by a pulsed xenon lamp with UV cut filter, while a silicon photodiode array detected and measured both incident and reflected light

[36]. When possible, colours of cores and rims were measured on zoned samples.

FT-IR spectra were collected in transmission mode on KBr pellets, prepared by mixing potassium bromide and powdered samples in an agate mortar, pouring the mixture in a steel die and then applying a pressure of about 8 ton/cm². The spectra were recorded using a BRUKER ALPHA FTIR spectrometer, covering the 4000–400 cm⁻¹ spectral range, with a resolution of 4 cm⁻¹ and 128 scans. Opus 7.0 software was used for data processing. In the absorption spectra the main mineralogical compounds (e.g. silicates, carbonates, oxides) were preliminary detected. Then, the second derivative profiles of absorption spectra were computed to emphasize, in the spectral region between 1600 and 400 cm⁻¹, the characteristic infrared frequencies of each mineralogical phase forming the ceramic pastes, whose identification was performed by comparing data with those reported in Refs. [25,26,37].

On thin sections representative samples, selected on the basis of their colorimetric and mineralogical features, μ -Raman spectroscopy was performed using a JASCO NRS-5100 μ -Raman dispersive spectrometer equipped with near-infrared diode laser (785 nm), using a collection time of 30, 60 or 90 s, with one to three accumulations. Magnification of 100× was used for each measurement. For the calibration of laser beam, the 521 cm⁻¹ peak of a silicon standard was employed. The analyses were carried out both on a-plastic grains and ceramic matrices of zoned samples. Raman spectra collected from different spots on both cores and rims allowed describing the mineralogical heterogeneities causing the zonation. Spectra Manager II Software was used to acquire and analyse the Raman spectra, treated by smoothing and baseline correction. The identification of minerals was carried out comparing the acquired spectra with data reported in Refs. [2,18,38–41].

4. Results

4.1. Macroscopic and textural features of pottery

Different colour, hardness and texture characterise the ceramic pastes of table and cooking ware.

¹ For interpretation of color in Fig. 2, the reader is referred to the web version of this article.

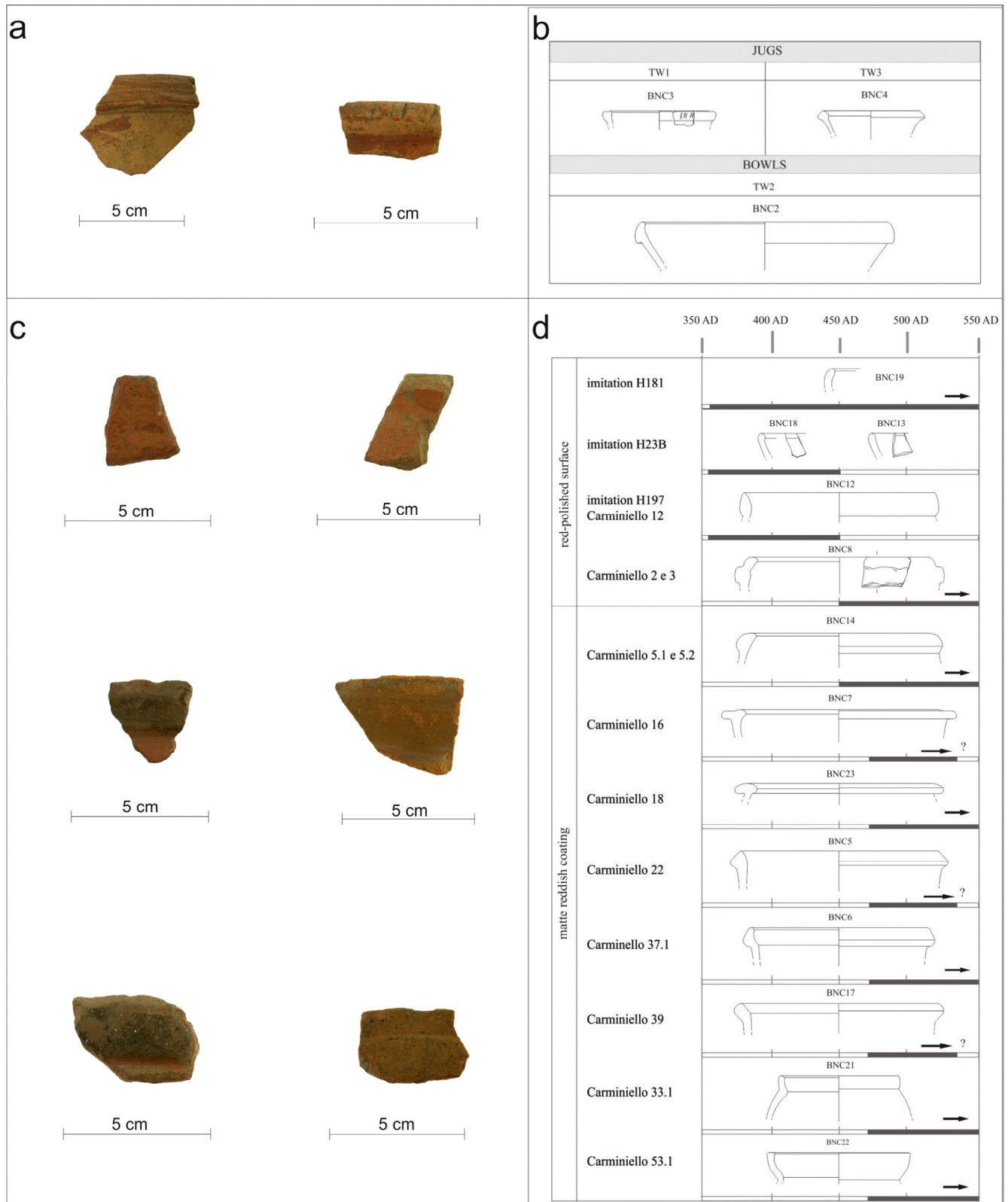


Fig. 2. Table (a) and cooking ware (c) fragments with respective ceramic shapes (b, d), reported in scale 1:6 (modified by Germinario et al. [29]).

As far as the tableware is concerned, the samples show hard or very hard pastes, with scarce rounded a-plastic grains scattered into the clayey matrix (Table 1). On the basis of the coating and macroscopic features of ceramic pastes, Germinario et al. [29] have

identified three different groups (TW 1, TW 2 and TW 3). Samples covered by a red polished slip (BNC 2, 9) (group TW 2) show finer texture if compared to samples of groups TW 1 (BNC 3, 15) and TW 3 (BNC 4, 16), characterised by a thin and matte reddish coating

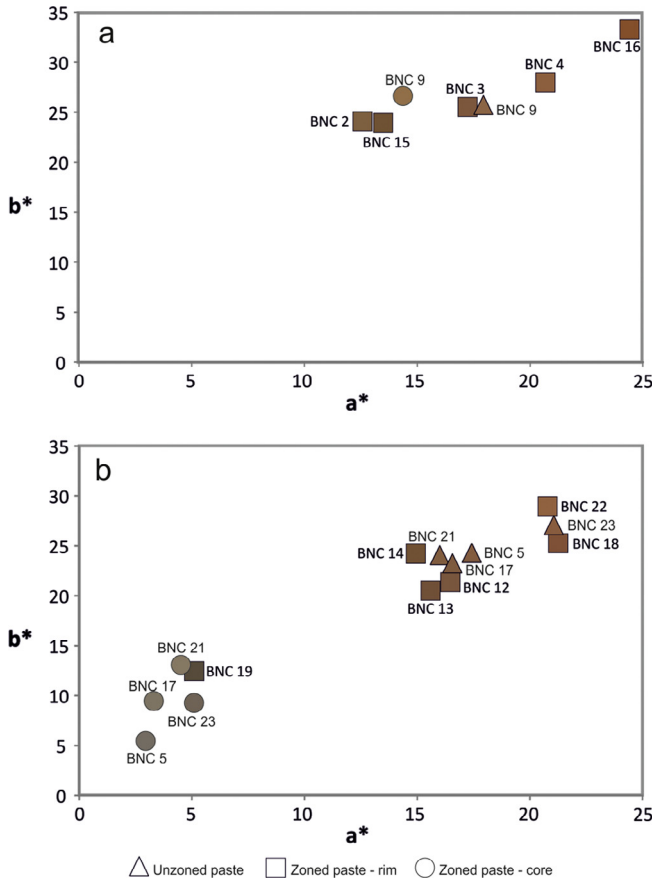


Fig. 3. Plots of colorimetric coordinates of table (a) and cooking ware (b). Colorimetric coordinates of lightness (L^*) were used to fill the symbols, attributing to each sample its real colour. For the interpretation of colours in this figure, the reader is referred to the web version of this article or, alternatively, colorimetric coordinates are reported in Table 2.

(Table 1). The coarser texture of TW 1 and TW 3 samples is due to the occurrence of siliciclastic and/or volcanic phases scattered in a light brown or red matrix, respectively. Germinario et al. [29]

observed that samples of group TW 1 are characterised by coarser quartz, feldspar, arenaceous fragments and subordinate juveniles scattered in a clayey matrix containing abundant mica; in samples of group TW 3 volcanic grains (feldspar, clinopyroxene and juveniles) are the main constituents.

Cooking ware shows hard coarse pastes, often zoned, in which abundant and rounded a-plastic inclusions are scattered. As in tableware, the fragments are characterised by two types of coating: a reddish or brownish matte coating, which covers the external surfaces of vessels, and a dense, red-polished coating, used both for internal and external surfaces. Quantity, sorting and size of grains, composed by feldspar, clinopyroxene, biotite, amphibole, olivine, juveniles and subordinate quartz and arenaceous fragments, allowed distinguishing two main fabrics (CW 1, 2) (Table 1) [29].

Group CW 1 (BNC 7, 8, 21, 22) is characterised by the occurrence of 15–20% of coarser a-plastic grains, whereas samples of group CW 2 (BNC 5, 6, 12, 13, 14, 17, 19, 23) show a higher content of inclusions (20–30%) scattered in the ceramic matrix [29].

4.2. Colour of ceramic bodies

The ceramic pastes of tableware are basically red in colour ($a^*_{med.} = 18.94$; $b^*_{med.} = 26.23$), with the exception of a dark red sample (BNC 16 - $L^*_{med.} = 49.76$; $a^* = 24.75$; $b^* = 33.38$) and the samples BNC 2 and BNC 15, showing a reddish yellow colour (Fig. 3a and Table 2). Only the sample BNC 9 shows a light zonation, with the innermost part slightly paler ($L^*_{med.} = 58.52$; $a^* = 14.35$; $b^* = 26.64$) than the external one ($L^*_{med.} = 56.43$; $a^* = 17.92$; $b^* = 25.24$) (Fig. 3a).

Cooking ware shows a wide chromatic variability, still within reddish tones. Dark red pastes, characterised by higher values of chromatic coordinates ($L^*_{med.} = 51.18$; $a^* = 21.91$; $b^* = 27.91$), differ from pale red pastes, displaying lower L^* (46.86), a^* (14.84) and b^* (21.32) average values (Fig. 3b and Table 2). Only the sample BNC 19 show a brownish colour ($L^*_{med.} = 51.18$; $a^* = 21.91$; $b^* = 27.91$) (Fig. 3b). Most samples (BNC 5, 6, 7, 8, 17, 21, 23) appear zoned, with red rims ($L^*_{med.} = 52.88$; $a^* = 18.14$; $b^* = 24.48$) and grey ($L^*_{med.} = 56.49$; $a^*_{med.} = 3.16$; $b^*_{med.} = 7.74$) or brownish grey cores ($L^*_{med.} = 56.16$; $a^*_{med.} = 4.87$; $b^*_{med.} = 11.37$) (Fig. 3b and Table 2).

Table 2
Colorimetric measurements of ceramic pastes using D65 standard illuminant. L^* : lightness, a^* and b^* : chromatic parameters.

		Unzoned pastes			Zoned pastes					
		L^*	a^*	b^*	Cores			Rims		
					L^*	a^*	b^*	L^*	a^*	b^*
TW 1	BNC 3	51.01	17.60	25.39						
	BNC 15	48.31	13.61	23.59						
TW 2	BNC 2	53.42	12.74	24.21						
	BNC 9				58.52	14.35	26.64	56.43	17.92	25.24
TW 3	BNC 4	55.05	20.82	27.51						
	BNC 16	49.76	24.75	33.38						
CW 1	BNC 5				55.31	2.98	5.61	52.95	17.70	24.11
CW 2	BNC 12	50.17	16.78	21.30						
	BNC 13	47.78	15.89	20.50						
	BNC 14	48.34	15.23	24.35						
	BNC 17				57.66	3.35	9.87	51.50	16.89	23.26
	BNC 18	50.39	21.66	25.24						
	BNC 19	43.40	5.20	12.24						
	BNC 21				60.49	4.58	13.27	53.24	16.50	23.92
	BNC 22	55.98	21.18	28.94						
	BNC 23				51.83	5.16	9.47	53.84	21.46	26.63

Table 3
Mineralogical composition of ceramic artefacts obtained by FT-IR spectroscopy.

		Quartz	Feldspar	Phyllosilicates	Clinopyroxene	Hematite
TW 1	BNC 3	*	*	*		*
	BNC 15	*	*	*		*
TW 2	BNC 2	*	*	*	*	*
	BNC 9	*	*	*	*	*
TW 3	BNC 4	*	*			*
	BNC 16	*	*			*
CW 1	BNC 7	*	*	*		*
	BNC 8	*	*	*	*	*
	BNC 21	*	*		*	*
	BNC 22	*	*	*		*
CW 2	BNC 5	*	*			*
	BNC 6	*	*	*		*
	BNC 12	*	*	*		*
	BNC 13	*	*	*		*
	BNC 14	*	*	*	*	*
	BNC 17	*	*	*	*	*
	BNC 18	*	*		*	*
	BNC 19	*	*	*		*
	BNC 23	*	*		*	*

4.3. Mineralogical composition of ceramic pastes

FT-IR and μ -Raman spectroscopy inferred the mineralogical assemblages characterising the ceramic productions.

FT-IR absorption spectra of tableware highlighted the ubiquitous presence of phyllosilicates, quartz, feldspar and hematite (Table 3).

Absorption bands at around 3441 and 1630 cm^{-1} (Fig. 4a), shared with the hygroscopic water adsorbed by KBr used to prepare pellets, are due to the O–H stretching and H–O–H bending vibration of water from phyllosilicates. Their occurrence is attested by peaks at around 990, 873, 560 and 481 cm^{-1} observed on second derivative profiles of fingerprint area (1600–400 cm^{-1}) (Fig. 4b–d).

Quartz and feldspar predominate into ceramic pastes. Absorption bands at 797 (Si–O–Si stretching), 778 and 694 cm^{-1} (Si–O bending) are diagnostic of quartz, whereas the peaks at ca. 1045, 730, 645 and 575 cm^{-1} are associated to feldspars. According to De Benedetto et al. [25], the typology of feldspars could be nicely inferred by means of the second derivative, which suggests that both alkali feldspar and plagioclase occur (Fig. 4b–d).

The ubiquitous peak at ca. 460 cm^{-1} (Fig. 4), linked to the Fe–O stretching vibration, is due to the hematite that determines the reddish colour of the ceramic bodies.

As far as the second derivative profiles are concerned, it is worth noting the occurrence of absorption peak at ca. 1067, 965, 915, 861, 670 and 630 cm^{-1} in samples of TW 2 (Fig. 4c). They likely suggest the occurrence of diopside, a newly-formed Ca-pyroxene, which was not detected in the volcanic a-plastic grains of this group samples [29].

Raman spectra of coarser grains confirmed the occurrence of quartz and feldspar (Fig. 5a and b) as main a-plastic components. Both alkali feldspar and plagioclase were also recognized, in agreement with IR results. The chemical composition of feldspar grains can be inferred by evaluating the position of the two main characteristic peaks (502–516 cm^{-1} (peak I_a) and 470–490 cm^{-1} (peak I_b)) [18]. Most of them are alkali-feldspar (orthoclase-microcline-sanidine group) (Fig. 6) and subordinate plagioclase (andesine-labradorite), except for the sample BNC 2, where some crystals of anorthitic plagioclase are present (Fig. 6); worth noting is the

coarser garnet occurring in this sample (Fig. 5c). Diopside crystals (Fig. 5d) were found as coarser grains in samples of group TW 3, also detected as phenocrysts in vesicular juvenile volcanics. Scattered into ceramic matrices, micrometric-sized crystals of hematite and anatase were also observed.

As far as cooking ware is concerned, IR spectra of both zoned and unzoned samples revealed a similar mineralogical assemblage, constituted by quartz, feldspar, hematite, phyllosilicates and subordinate diopside (Table 3).

The occurrence of phyllosilicates, except in few samples (BNC 5, 18, 21, 23), is highlighted by IR absorption bands at around 3440 and 1630 cm^{-1} (Fig. 7a) and peaks at ca. 990, 564 and 480 cm^{-1} on second derivative profiles (Fig. 7b–e and Table 3).

The weak shoulder at 1165 cm^{-1} and absorption peaks at around 799, 778 and 695 cm^{-1} are due to the quartz, whereas the bands at ca. 1045 and 647 cm^{-1} suggest the ubiquitous presence of feldspar (Fig. 7a). Second derivative profiles show the signatures of K-feldspar (microcline/orthoclase (1050, 1040, 1010, 728, 646, 580 cm^{-1}), sanidine (840 cm^{-1})) and albite (760, 741, 425 cm^{-1}) (Fig. 5b–d), whereas sample BNC 18 differs for the occurrence of only sanidine (840, 640, 583, 543, 426 cm^{-1}) with subordinate albite (Fig. 7e). Feldspar also occurs as coarser a-plastic grains, as testified by μ -Raman spectroscopy, highlighting the presence of both alkali feldspar (orthoclase-microcline-sanidine group) and plagioclase, this latter with sodic, calcic or intermediate composition (Fig. 6).

Other volcanic phases also occurred in ceramic pastes. Diopside (ca. 1007, 665, 390, 350, 320 cm^{-1}) (Fig. 5d), also detected in IR spectra (Fig. 7b–e), calcic amphibole (ca. 1003, 661, 524, 296, 227, 156 cm^{-1}), olivine (Fig. 5e) and juvenile volcanics were observed as coarser grains.

Along with anatase (ca. 636, 513, 394, 143 cm^{-1}) (Fig. 5g) and rutile (ca. 610, 445, 144 cm^{-1}) (Fig. 5h), analysed by μ -Raman spectroscopy, widespread hematite (Fig. 5f) was scattered in the ceramic pastes, as confirmed by peak at ca. 460 cm^{-1} in FT-IR spectra (Fig. 7a).

μ -Raman spectroscopy on ceramic matrices revealed the occurrence of magnetite in zoned pastes. If unzoned red pastes (BNC 18, BNC 22) show a homogeneous mineralogical composition, given by

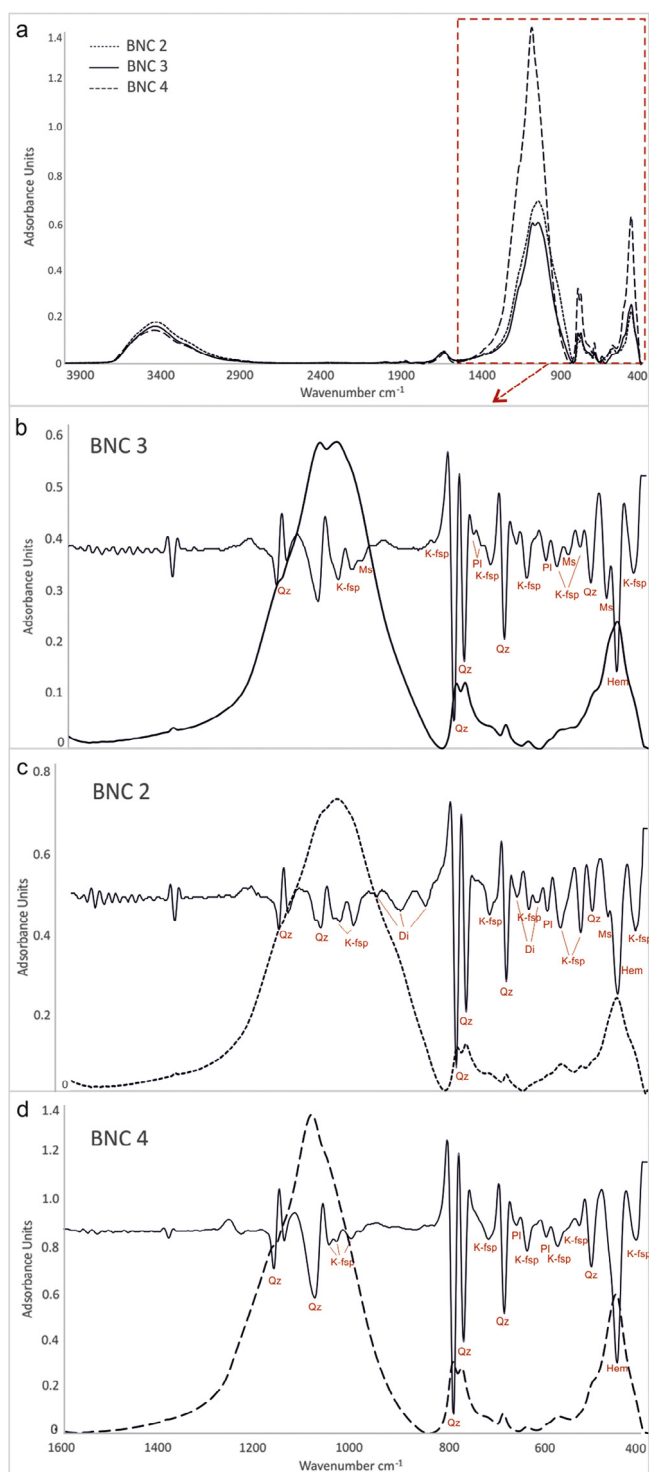


Fig. 4. IR spectra of representative tableware samples. (a) Absorbance IR spectra; (b, c, d) Absorbance IR spectra and second derivative profiles of spectral region between 1600 and 400 cm^{-1} . Abbreviations [42]: Qz = quartz; K-fsp = K-feldspar; Pl = plagioclase; Hem = hematite; Ms = muscovite; Di = diopside.

hematite (ca. 224, 294, 410, 608 cm^{-1}), quartz (ca. 460 cm^{-1}), feldspar (ca. 508 cm^{-1}) and anatase (ca. 143 cm^{-1}) (Fig. 8a), zoned samples (BNC 6, BNC 7, BNC 17, BNC 23) highlighted significant mineralogical differences between cores and rims. Red rims have

mineralogical compositions very similar to those of the unzoned pastes (Fig. 8b), while grey and brownish matrices at cores, are characterised by slight different mineralogical assemblages. They both show the occurrence of quartz, anatase and magnetite (Fe_3O_4), suggested by peaks at around 302 and 680 cm^{-1} (Fig. 8c); in brownish core of sample BNC 23 hematite and feldspar were also detected (Fig. 8d).

5. Discussions

Mineralogical features obtained by spectroscopic measurements shed light on the manufacture of vessels, emphasizing differences between table and cooking wares, belonging to well-standardized morphological and typological repertoire circulating in inner and coastal territories of Campania region between the late 4th and the 6th century [29,43].

Tableware production accounts for good technological standards achieved by workers, in particular for the production of bowls of group TW 2 (BNC 2, 9), whose fine texture and decoration recall to the Imperial fine decorated wares (e.g. *Red Slip Ware*), widely exported in the Mediterranean area [44]. The technological features inferred by firing process and the presence of the red-polished slip testify the higher accuracy in their manufacturing. In fact, high firing temperatures were hypothesized, as suggested by the bulk mineralogical composition of vessels, obtained by second derivative profiles of FT-IR spectra. In particular, the occurrence of newly-formed diopside, developed in high-CaO clays by the interaction between carbonates and fired clays, suggests temperatures higher than 900 °C [21–23].

TW 1 and TW 3 group samples, on the other hand, showed mineralogical signatures that account for different clayey raw materials adopted for their production, as well as different firing conditions suffered by ceramic artefacts. As far as raw materials are concerned, the absence of absorption bands of calcite and/or of Ca-silicates (e.g. gehlenite and diopside) allowed supposing that they were made with carbonate-free clays [45]. The occurrence of residual phyllosilicates and newly formed hematite also allowed estimating firing temperatures. Hematite, which starts forming at about 700 °C [23,46] was observed in all samples (Table 3), suggesting firing temperatures ranging between that value but never exceeding 900 °C in samples in which residual phyllosilicates still occur [21]. By contrast, for samples not showing residual phyllosilicates (BNC 4 and BNC 16) (Table 3), firing temperatures could have exceeded 900 °C [21,22].

As far as the cooking ware is concerned, FT-IR and μ -Raman analyses highlighted similar mineralogical ceramic bodies, made of free-carbonates clays, as testified by the lack of calcite and/or newly-formed Ca-silicates, along with coarser siliclastic (quartz and feldspar) and volcanic phases (clinopyroxene, calcic amphibole, garnet, olivine). The rougher texture and colour zoning of pastes testify a not-well standardized production, in terms of manufacture and firing conditions.

Actually, ceramic samples certainly experienced variable firing temperatures: lower than 900 °C for samples showing IR bands of residual phyllosilicates (Table 3), higher (>900 °C) for those lacking [21–23].

Colorimetric measurements well evidenced the occurrence of both unzoned and zoned pastes, these latter showing a clear sandwich structure, due to uncontrolled reducing/oxidising conditions of the firing atmosphere. μ -Raman analysis performed on ceramic matrices detected different Fe-oxides, which allowed inferring the changes of redox conditions [2,28,47].

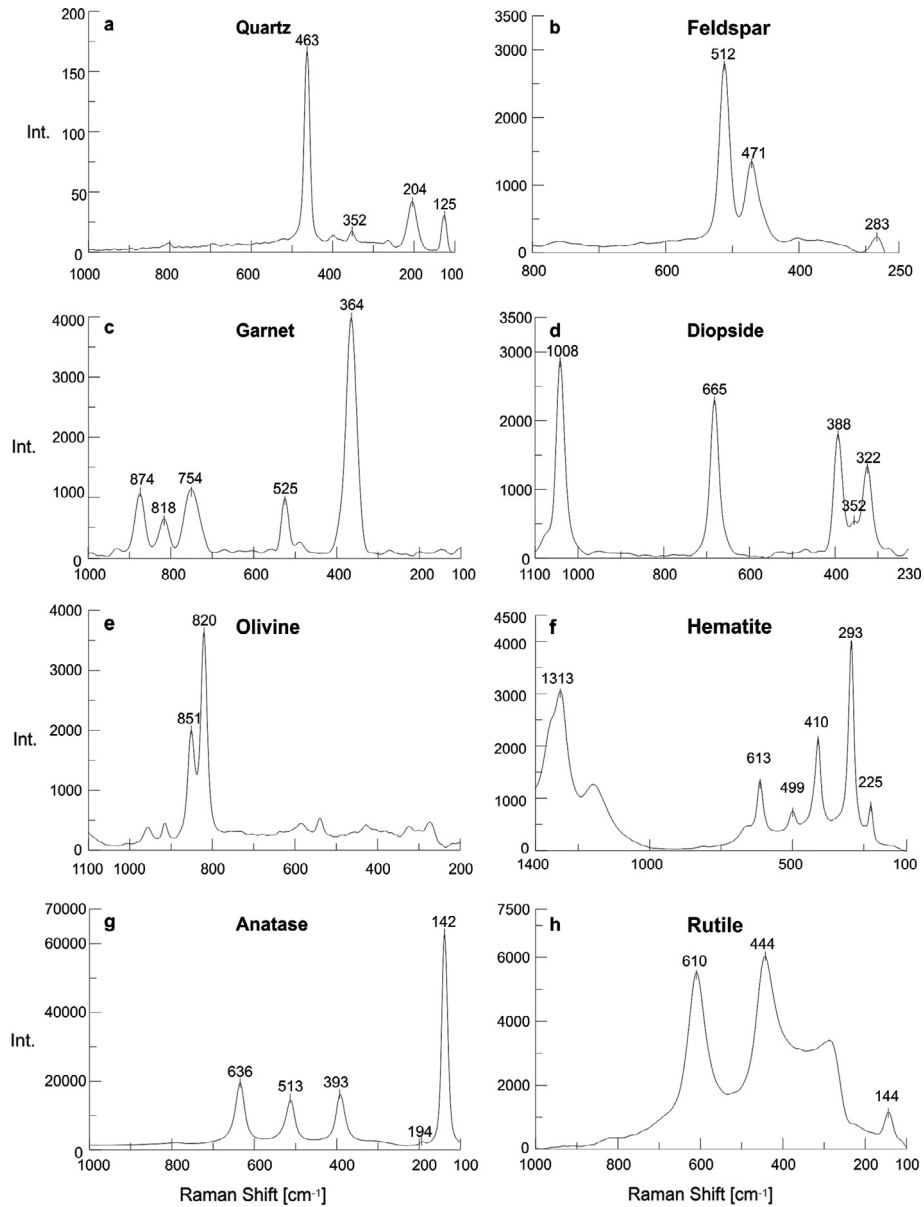


Fig. 5. Raman spectra of main mineralogical phases detected in ceramic pastes. (a) Sample BNC 3, (b) Sample BNC 6, (c) Sample BNC 2, (d) Sample BNC 4, (e) Sample BNC 22, (f) Sample BNC 7, (g) Sample BNC 4, (h) Sample BNC 7.

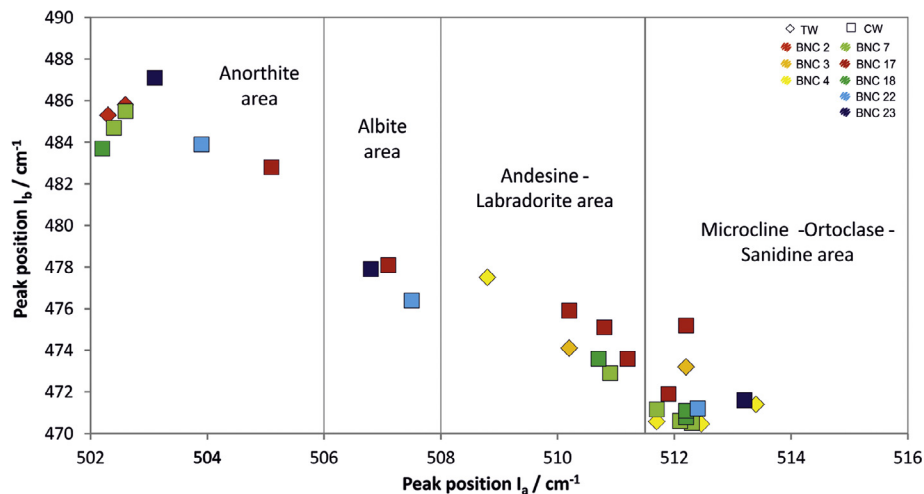


Fig. 6. Discrimination diagrams of feldspar grains composition. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

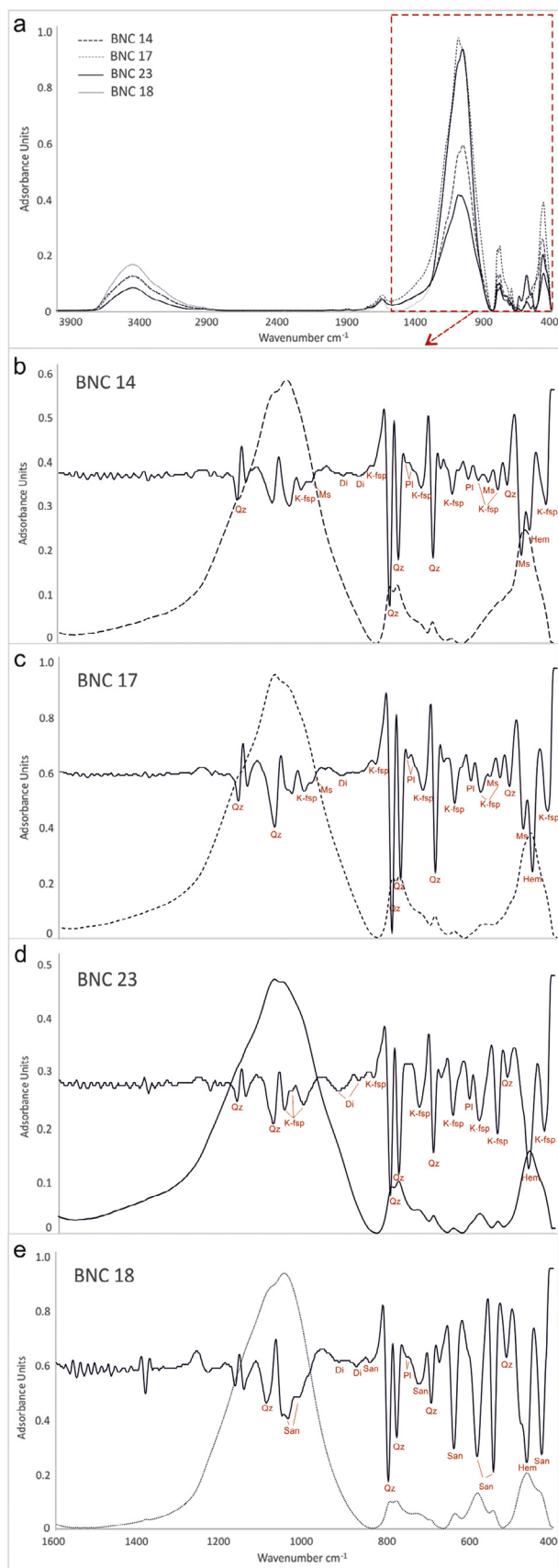


Fig. 7. IR spectra of representative cooking ware samples. (a) Absorbance IR spectra; (b, c, d, e) Absorbance IR spectra and second derivative profiles of spectral region between 1600 and 400 cm^{-1} . Abbreviations [42]: Qz = quartz; K-fsp = K-feldspar; San = sanidine; Pl = plagioclase; Hem = hematite; Ms = muscovite; Di = diopside.

μ -Raman spectroscopy performed on unzoned pastes detected diffuse hematite, suggesting a complete oxidizing atmosphere during the firing/cooling process, whereas zoned matrices revealed the occurrence of Fe-oxides in both oxidation states (hematite and magnetite), accounting for rapid changes in $f\text{O}_2$ in the furnace [28].

Grey cores are due to the presence of magnetite, whereas red rims are given by diffuse hematite. Therefore, the sandwich structure of the ceramic bodies, characterised by red oxidized rim and grey reduced cores, testifies a reducing step during the firing, which allowed the development of magnetite [28], partially re-oxidized at rims, where hematite occurs.

The inhomogeneous re-oxidation of ceramic bodies is further confirmed by the detection in the samples with brown core (BNC 23) of both magnetite and hematite bands, testifying an incomplete transformation process of magnetite to hematite in oxidizing atmosphere [2,47].

As far as the provenance of the pottery is regarded, some striking information come from the composition of the coarser volcanic fraction, analysed by μ -Raman spectroscopy. The occurrence of volcanic phases (alkali feldspar, plagioclase, clinopyroxene, calcic amphibole, garnet, olivine) along with siliciclastic grains suggests the use of a temper, likely a sand, naturally composed of volcanic and sedimentary grains mixed together [29]. Since morphological and typological features accounted for local-produced artefacts, we can suppose that exploited sources of temper grains were located in the Benevento area, where pyroclastic deposits, widely adopted as temper grains in pottery as well as aggregate in mortar-based materials [10,13,48], crop out along with sedimentary rocks [49].

6. Conclusions

The combined analytical approach by means of colorimetry, FT-IR and μ -Raman spectroscopy provided successful results for the definition of the technology adopted for manufacturing ceramic artefacts during the Late Roman period in Benevento neighbourhood, confirming the suitability of coupled spectroscopic techniques in archaeometric studies.

Vibrational spectroscopy, increasingly widespread in the field of Cultural Heritage, is ongoing alongside to the common techniques (e.g. PLM, XRF, XRD, SEM/EDS) performed on archaeological materials. This “customary” approach provides detailed and complete mineralogical, textural and compositional information, sometimes necessary to satisfy and complete most archaeological issues, albeit demanding sample preparation, long acquisition times and higher costs are required.

Conversely, spectroscopic techniques turned out to be very advantageous in terms of quantity of material required, sample preparation and acquisition times, representing a viable alternative, mostly when the availability of archaeological material is limited. The high sensitivity and spatial resolution, the accuracy of the measurements, even with an extremely low amount of material (e.g. few milligrams for FT-IR acquisition), are the main features that recently increased the potential of vibrational spectroscopy in the archaeometric researches.

This study confirmed the importance of combining FT-IR and μ -Raman spectroscopy that taken individually could not yield comprehensive results in the characterisation of ancient ceramics.

This jointed approach represents a useful tool for disclosing the mineralogical composition of ceramic bodies and often provides valuable measurements (e.g., oxidation state of iron oxides) that would not be possible to obtain from the “customary” approach, but that are important for a more complete reconstruction of the technological processes of pottery production.

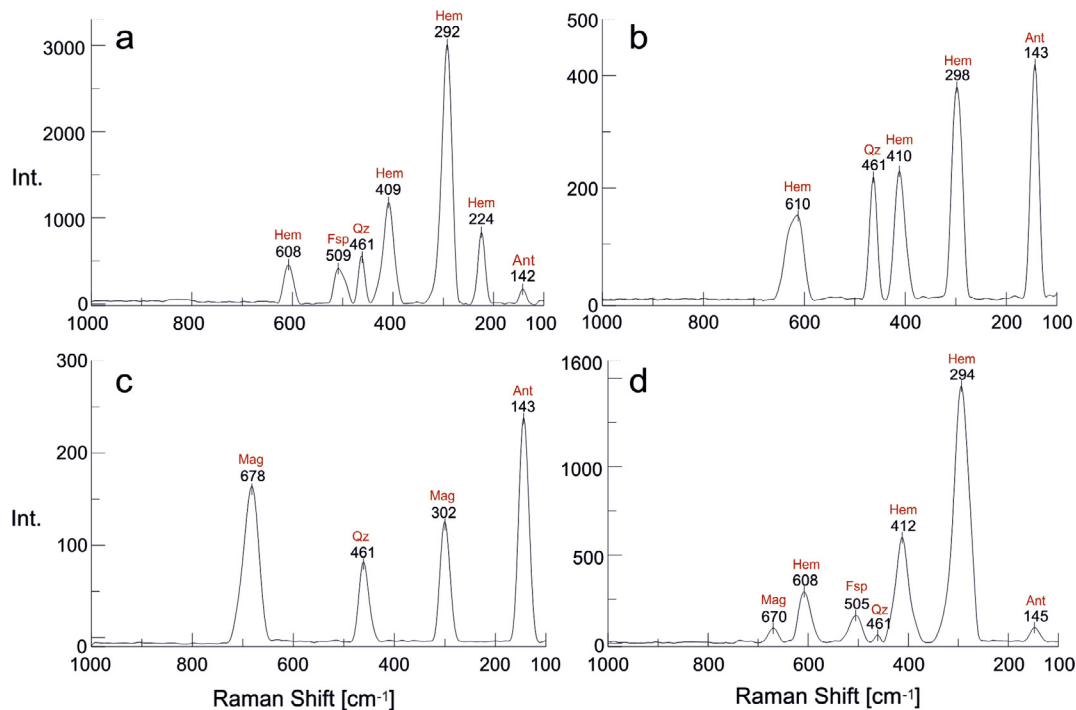


Fig. 8. Representative Raman spectra of ceramic matrices. (a) Sample BNC 18; (b) Sample BNC 17, red rim; (c) Sample BNC 17, black core; (d) Sample BNC 23, brown core. Abbreviations [42]: Qz = quartz; Fsp = Feldspar; Hem = hematite; Mag = magnetite; Ant = anatase.

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