



A multi-spectroscopic study for the characterization and definition of production techniques of German ceramic sherds[☆]



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ABSTRACT

The aim of this archaeometric study is to recover information regarding technological processes and raw materials used for the production of ceramic sherds coming from five central and Eastern German sites, between Lower Saxony and Saxony states. The ceramic fragments have been investigated by a multi-spectroscopic approach: Fourier transform infrared spectroscopy (FT-IR), micro-Raman spectroscopy and X-ray Fluorescence (XRF) were employed to characterize both ceramic bodies and glazes. Moreover the innovative application of Laser Induced Fluorescence (LIF) on ceramic findings has been proposed and evaluated. Chemical and mineralogical composition, as well as microstructure, of ceramic mixture and glaze are correlated to native material composition and firing temperature, which have become a fundamental features in archaeometric research and play a key role in understanding the provenance of the pottery and its production techniques.

The multi-spectroscopic approach applied in this work has enabled the ability to characterize the ceramic sherds and to investigate through non-destructive techniques both ceramic glaze and matrix giving information regarding the raw materials and pigments/colourants used, and regarding firing temperature and technology. The present study carried on using complementary methods suggests different raw material sources and temperature kilns. These data are in agreement with the location of ceramic sites and with data in literature. Furthermore, the interesting results suggest that non-destructive techniques, such as LIF and Raman spectroscopy, are promising methods for ceramic and glaze characterization.

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1. Introduction

The historical ceramic fragments examined in this study, dating from the late 13th to 19th century, come from five different sites between Lower Saxony and Saxony states in Germany. The studied materials are: stoneware, near-stoneware, unglazed earthenware and glazed earthenware (see Table 1). Stoneware is a type of fossil in archaeology and represents the most important synthetic artefact during the medieval and the early modern period [1]. Several ceramic types with incomplete sintered body, proto- and near-stoneware, can be considered as a preliminary stage of the development of ceramic production technique. The emergence of a dense sintered ceramic body can be traced in Germany since around 1250 [2] and a huge number of production sites were established in the subsequent periods. The majority of these workshops had traded their products primarily in Central and

North Europe and some of them reached the New World as well as the Far East [3]. These unique manufacturing conditions for ceramic materials, outstanding in medieval Central Europe, are comparable only to China, where the development of stoneware began in the middle of the second millennium BC [3].

The divergent state of research on medieval and post medieval pottery is displayed by the knowledge of the production sites from where the analysed ceramic fragments originated. In this study, five different sites have been considered: Bürgel, Brandis, Cottbus, Duingen and Peine. Duigen, with well-researched workshops, dominated the ceramic market in Lower Saxony and in parts of North Germany during the 16th and 17th century [4]. Stoneware manufacturer can be traced back until 1250 and these vessels were mainly exported in the region of the former Hanseatic League. A few of them, were also detected in the New World [4]. The information about Bürgel is derived primarily from written sources, which illustrate the conditions of the 18th until the 20th century. Production techniques, number of workshops and distribution of the products all over Central Germany were described by Rottländer [5]. On the other hand, there are only a few data about sites like Peine, Brandis and Cottbus. The excavated pottery wasters and

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Table 1
Description of the ceramic samples analysed.

Code	Origin	Description	Decoration	Category
Bu36	Bürgel, Thuringia	Basal sherd, earthenware, glazed, light yellow body	Surface with light yellow glaze, inside white dotted pattern on dark blue glaze	D
Bu43		Body sherd, earthenware, dark green slip, grey body	None	C
Bu44		Basal sherd, stoneware, glazed, greyish yellow body	Surface with cobalt-blue salt-glaze	A
Bu48		Body sherd, stoneware, dark brown salt-glaze, light grey body	None	A
Bu49		Rim sherd, high fired earthenware, brown glaze, yellowish grey body	Surface brown slip painting	D
Br08	Brandis, Saxony	Basal sherd, earthenware, dark green glaze, light yellow body	None	D
Br09		Basal sherd, earthenware, green glaze, light yellow body	None	D
Br11		Rim sherd, earthenware, light brown glaze, light yellow body	None	D
Br14		Body sherd, near-stoneware, dark purple engobe/slip, light yellow and dark grey stained body	None	B
Br19		Body sherd, earthenware, light yellow body	Surface with brown slip painting	C
Pe96	Peine, Lower Saxony	Body sherd, near-stoneware, light brown glaze, grey body	None	B
Pe98		Body sherd, high fired earthenware, dark reddish grey slip, light yellow body	None	C
Pe00		Body sherd, near-stoneware, dark purple slip, light grey and light red stained body	None	B
Co04	Cottbus, Brandenburg	Body sherd, earthenware, surface greenish grey, light red and red layered body	None	C
Co05		Body sherd, earthenware, surface light greyish red, light greyish red and light red layered body	None	C
Co06		Body sherd, earthenware, light grey surface light red flamed, light grey body	None	C
Co07		Body sherd, earthenware, grey body	None	C
Dui78	Duingen, Lower Saxony	Body sherd, high fired earthenware, light red surface, yellowish grey body	Medallion bearing, floral motif	C
Dui80		Body sherd, stoneware, dark brown salt-glaze, greyish yellow body grey coated	Medallion bearing, armorial motif	C
Dui88		Basal sherd, earthenware, brown glaze, light yellow body	None	D
Dui90		Body sherd, earthenware, glazed, light reddish yellow body	None	D

kilns imply a local established workshop and gave a first impression on the produced types and style of ceramics. Furthermore, there are no other archaeological or historical sources available and archaeometric analyses offer a new possibility to find out more about the applied technology and the distribution of the ceramic products.

In this work we propose a whole approach in the study of the archaeological and historical ceramics, considering the chemical composition associated with the provenance and production technology.

The knowledge of technology applied for pottery production can supply suggestions to interpret the cultural contexts as well as their interactions within the environment and with other regions. Furthermore, characterization of historical ceramics provides important information for conservation and restoration methods [6,7]. To study the production and firing technologies, spectroscopic techniques are applied to determine the chemical and mineralogical compositions, and therefore the firing temperature of the ceramic sherds through the detection of phase transformations and firing minerals that occur during the firing process [8–10]. Usually, one technique is not enough to characterize and define chemical composition and firing temperature in ceramic sherds, and in the Cultural Heritage field the use of non-destructive and non-invasive techniques is required. In this study different spectroscopic techniques were applied and the use of non-destructive methods, such as Raman and LIF, is encouraged. FT-IR, Raman and XRF spectroscopies have already been widely applied in ceramic characterization obtaining useful results [11–13], while few studies on LIF applied in ceramic characterization have been found in literature [14,15]. In this research, the potentiality of LIF technique applied in archaeological objects, such as ceramic sherds, is explored. This technique offers the advantages to be sensitive and non-destructive spectroscopic technique, remote, portable, and has been used as a diagnostic tool for artworks with successful results [16–18]. The fluorescence in minerals is sensitive to activator elements, impurity ions, defects, as well as chemical composition and crystal lattice [19,20]. LIF analyses can be useful to detect trace elements in minerals [21,22] and in the present study was applied to obtain indication of both ceramic glaze and matrix composition. LIF spectroscopy could be considered an innovative technique which provides non-destructive qualitative analyses in archaeological artworks.

2. Materials and methods

2.1. Sample description

Ceramic potsherds coming from pottery wasters of different German sites were considered and sherds which better represent the single site were selected. A total of 21 sherd samples coming from Bürgel ($n = 5$), Brandin ($n = 5$), Peine ($n = 3$), Cottbus ($n = 4$) and Duingen ($n = 4$) were studied and some of them are shown in Fig. 1. The analysed fragments reflect a wide range of ceramics in everyday life. Due to the properties of the ceramic, the pottery can be classified and the studied material can be divided into four main categories: stoneware (A), near-stoneware (B), unglazed earthenware (C) and glazed earthenware (D) (Table 1). Corresponding to the characteristics of the stoneware body, there are decorated vessels for drinking and serving as jugs (Bu44) or tankards (Dui 78, Dui 80). Near-stoneware with a slip (Br14, Pe96, Pe00) was also used for this application. Bowls (Bu49) and pots (Br08, Br09, Br11, Br19) made from unglazed or glazed earthenware were mainly served as containers for storage or cooking. All the samples that originate from pottery wasters present features of misfired pottery, as discoloured surfaces (Bu43, Co04, Co05) and inadequately fired bodies (Dui78, Dui88, Dui90). The appearance of Dui78 and Dui80 is typical for stoneware, however because of the low temperature during the firing process a dense sintered ceramic body could not occur. Those kind of porous vessels were not suitable for serving liquids and for selling, this is the reason for disposing them. The fragments Bu48 and Co06 represent a particular kind of ceramic: Bu48 was used as a stacking aid and Co06 presents a part of a kiln wall made of pots. The samples Bu49, Bu44 and Bu36, show the typical pattern applied in Bürgel in the course of the 18th until the 20th century. Since 1880 the cobalt-blue salt-glaze was replaced by a new trademark, as white dots on blue background [5]. All sherds from Brandis display the common variety of potter workshops in Central Germany during the 16th and 17th century. Ceramic material from Peine is of great interest: this engobed near-stoneware is similar to the well-known production site of Coppengrave (Lower Saxony), an important source of near-stoneware during the 13th and 14th century [23]. Furthermore, Duingen was one of the main production centres of stoneware during the early modern period and the characteristic decoration patterns of

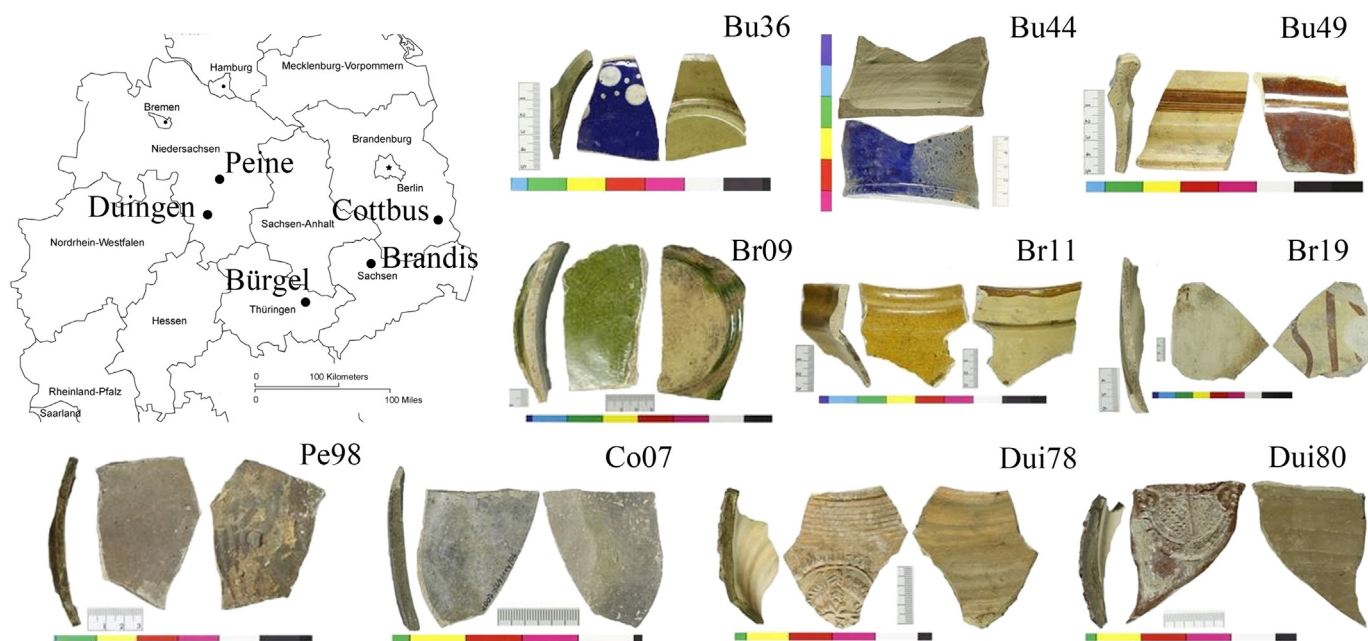


Fig. 1. Examples of ceramic sherds investigated in this work belonging to five German sites underlined in the map (on the left). Bu36: earthenware with dark blue glaze and white dots; Bu44: stoneware with cobalt-blue salt-glaze; Bu49: lead glazed earthenware with brown slip painting; Br09 and Br11: lead glazed earthenware; Br19: unglazed earthenware with brown slip painting; Pe98: high fired earthenware; Co07: earthenware; Dui78 and Dui80: misfired earthenware decorated by medallion bearing. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

stoneware produced in the 16th and 17th century were medallion bearings, as Dui78 and Dui80 show.

2.2. Methods

Infrared spectra were obtained by FT-IR Nicolet Nexus 750 spectrometer in transmission configuration using KBr pellets (1:100-wt.% sample/KBr). Spectra were recorded in the range $4000\text{--}400\text{ cm}^{-1}$ as a ratio of 64 single-beam scans at 4 cm^{-1} resolution. The FT-IR spectra of the samples were compared with data reported in the bibliography [25–33] for a reliable attribution of the bands.

Raman analyses were carried out using a custom-made micro-Raman system, based on a single 320 mm focal length imaging spectrograph (Triax – 320 Horiba Jobin Yvon), equipped with a holographic 1800 g/mm grating and a liquid nitrogen cooled CCD detector. The excitation source was a Spectra Physics Ar⁺ ion laser (Stabilite 2017) operating at 514.5 nm. An optical microscope (Olympus BX40) equipped with three objectives, $20\times/0.35$, $50\times/0.75$ and $100\times/0.90$, was optically coupled to the spectrograph. Microscope objective $50\times$ was employed to focus on the samples and the visual camera attached to the microscope allowed the selection of different points from which to collect Raman spectra, obtained by averaging 10 scans and with $1.5\text{--}2.0\text{ cm}^{-1}$ spectral resolution. The laser power was set at 8 mW and recording time at 10 s. Peak at 520 cm^{-1} of the silicon standard was used for calibration. Potsherds were cut to obtain body-glaze cross-sections and they were polished to have flat surface.

Philips MiniPal X-ray fluorescence spectrometer was employed for XRF measurements. It was used to detect the chemical composition in the ceramic body and glaze in terms of major, minor and some trace elements. Pottery sherds were placed in the holder samples with their surface perpendicular to the detector axis. The analyses were carried out in He atmosphere, without filter, at 18 kV and in the range of 50–100 μA .

LIF analyses were carried on using a radiation source Thomsom DIVA diode pulsed Nd:YAG laser with excitation wavelength of 266 nm at a repetition rate of 20 Hz with a pulse duration of 8 ns. A laser fluence of 0.9 mJ/cm^2 was used in this case. The LIF apparatus was made at the ENEA laboratory and it is described with more details in the

references [24]. The spectrometer working range was 200–900 nm and appropriate filters were placed at the entrance of the spectrometer (Ocean Optics USB 4000) in order to avoid the backscattered radiation and the second order of the emissions at lower wavelengths. No optical elements were used to collimate the laser beam and in the present case we may infer a resolution of approximately 1 to 2 mm from the spot size on the target. The digitized spectrum was transferred to a portable computer where a LabView programme allowed the user to set experimental parameters, to control data acquisition, and to perform a preliminary data analysis.

Spectra manipulations and adjustments such as smoothing and baseline subtraction, if necessary, were performed using OriginPro9 software.

3. Results and discussion

3.1. FT-IR results and discussion

FT-IR analyses were carried out on both ceramic bulks and coating layers, when present. Obtained results on coating glazes did not give further information about pigments/colourants and composition of the glass in comparison to those obtained by other techniques. For instance, in Fig. 2 the FT-IR spectra of the glazes of Bu36, Bu44, Br08 and Br09 are reported, and they show the characteristic peaks of quartz ($1088\text{--}1032\text{ cm}^{-1}$ due to Si–O and Si–O–Si asymmetric stretching; $785\text{--}775\text{ cm}^{-1}$ and $465\text{--}457\text{ cm}^{-1}$ related to Si–O symmetric stretching and Si–O bending respectively) and a weak peak at 914 cm^{-1} ascribable to kaolinite presents as clay mineral in the ceramic body [25,26].

FT-IR spectra related to the ceramic matrix of all the samples are reported and summarized in Table 2, where the tentative vibrational assignments made on the basis of FT-IR spectra of minerals reported in literature are given [25–33]. On the basis of the FT-IR results, the ceramics may be divided in three groups.

All fragments contain quartz as the main component ($1084\text{--}1092$, $1163\text{--}1178\text{ cm}^{-1}$, characteristic doublet at $795\text{--}798$ and $777\text{--}781\text{ cm}^{-1}$, $692\text{--}694\text{ cm}^{-1}$), feldspar (731 and $628\text{--}664\text{ cm}^{-1}$) and hematite ($536\text{--}557$ and $469\text{--}472\text{ cm}^{-1}$) suggesting oxidizing kiln

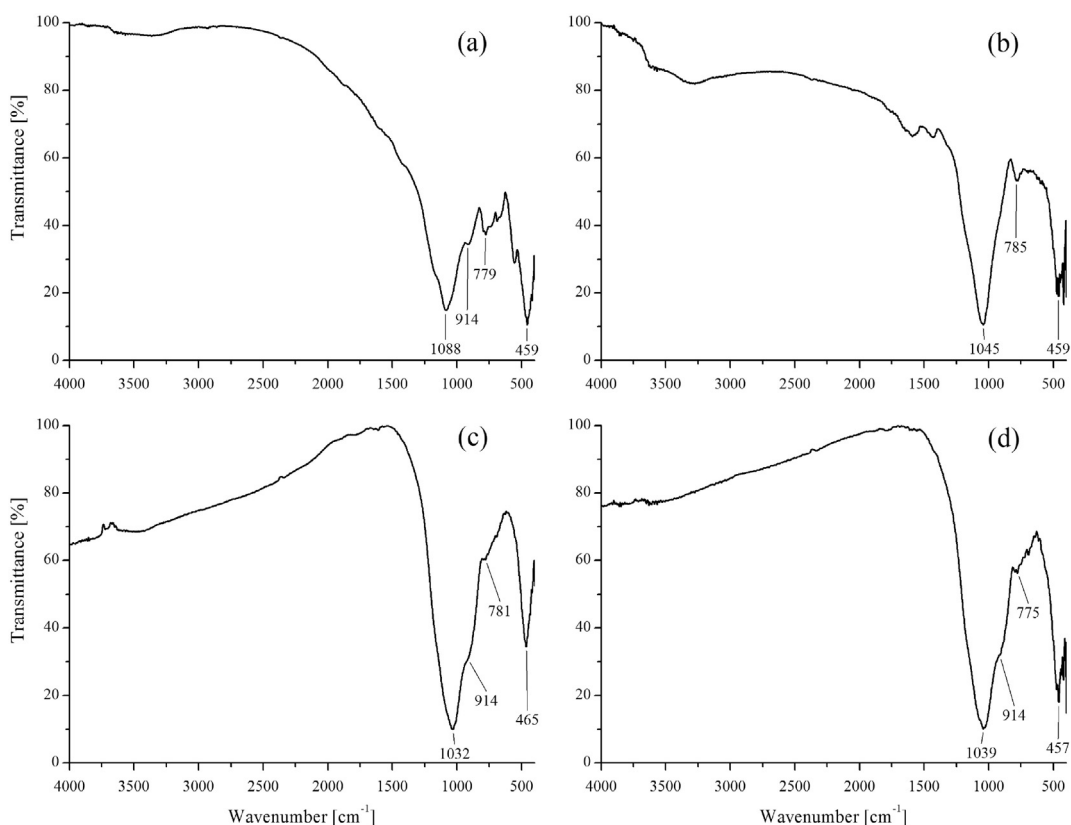


Fig. 2. FT-IR spectra of coating glazes present in the German ceramic sherds coming from Bürgel and Brandis. (a) Bu36, blue glaze; (b) Bu44, blue glaze; (c) Br08, green glaze; (d) Br09, green glaze.

condition [12,26,27]. The first group is formed by Brandis, Pe98, Cottbus, Dui78 and Dui80 samples. It is characterized by clay minerals as kaolinite (3699–3622, 1032–1036, 1005–1012 and 910–912 cm^{-1}) and smectite, probably montmorillonite (typical absorption band centred at 3400 cm^{-1} and peak at 469–471 cm^{-1}) inferred by FT-IR

spectra [27,28]. These ceramic samples show weak peaks at the range 3690–3620 cm^{-1} due to the stretching vibration of inner surface OHs and inner OH attributed to kaolinite. The relatively low intensity of these bands suggests that the dehydroxylation of kaolinite followed by a collapse of the crystalline structure is not complete. Furthermore,

Table 2

FT-IR vibrational frequency assignments of the ceramic bodies. The wavenumbers are a summary of all the ceramic bodies coming from each German site analysed in this work.

Bürgel	Brandis	Peine		Cottbus	Duingen		Tentative vibrational assignment			
		Pe96	Pe98		Dui88	Dui90			Dui78	Dui80
IR frequency with relative intensity (cm^{-1})										
	3697 w		3699 w	3660 vw			3695w		O–H str.	Kaolinite
	3622 w		3622 w				3622w		O–H str.	Kaolinite/illite/smectite ^a
	3433 bd, vw		3404 bd	3390 bd			3384 bd		O–H str.	Water/smectite ^a
1624 vw	1624 w	1626 w	1608 w	1622 vw			1631 w		O–H–O bend.	Water
			1429 vs	1444 s			1431 vw		$-\text{CO}_3^{2-}$	Calcite
1178 sh	1163 sh	1173 sh	1101 sh		1173 sh				Si–O str.	Quartz
1084 vs	1086 vs	1088 vs		1086 vs	1092 vs		1086 s		Si–O str./Al–O–Si str.	Quartz/alumino-silicates
1034 bd	1032 s, sh		1036 vs	1036 vs			1034 vs		Si–O–Si str.	Kaolinite
	1007 sh			1012 sh			1005 sh		Si–O/Si–O–Al str.	Kaolinite/muscovite
910 w	912 w		914 w	928 sh			912 w		Al–O–H	Kaolinite
			874 m	874 w					$-\text{CO}_3^{2-}$	Calcite
796 s	796 s	796 s	795 m	796 m	795 s		798 m		Si–O str.	Quartz
777 s	779 s	779 s	777 m	777 m	777 s		781 m		Si–O str.	Quartz
731 m									Al–O–Si bend.	Feldspar
			714 w	714 w					Si–O bend./ $-\text{CO}_3^{2-}$	Calcite
	649 vw		664 w	647 w			628 w			Feldspar
694 m	692 m	692 m	692 w		694 w		692 m		Si–O bend.	Quartz
548 m	536 m	557 m			542 w		540 m			Hematite
			532 m	517 w					Si–O–Al ^{IV} /Fe–O bend.	Kaolinite/muscovite/hematite
459 s	471 s	463 s	471 s	472 m	471 s		469 s		Al–O/Si–O deformation mode	Feldspar/hematite/smectite ^a
				457–418 w	422 m		420 m		Si–O mixed deformation	Silicates

s: strong; vs: very strong; w: weak; vw: very weak; m: medium; sh: shoulder; bd: broad band.

str.: stretching mode; bend.: bending mode.

^a Smectite, probably montmorillonite.

in this range are present only two peaks instead of the characteristic four peaks of kaolinite suggesting the mineral is in disordered state. The transformation from kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) to metakaolinite ($\text{Al}_2\text{Si}_2\text{O}_7 + 2\text{H}_2\text{O}$) takes place at around 600 °C but small amount of water can persist up to 750–800 °C [27,28].

Calcite (1429–1444, 874 and 714 cm^{-1}) in different relative amounts is also detected in this first group except for Brandis samples [29]. The presence of calcite in pottery may indicate: the use of carbonatic clay raw materials, calcite as the impurity of clay and/or secondary calcite due to precipitation or alteration during burial of the ceramic sherds [30]. Furthermore, the detection of calcite may allow to estimate the firing temperature. The high intensity of calcite peaks in Cottbus fragments and the non-presence of Ca-silicate phases (as gehlenite and wollastonite) suggest firing temperature below 800–900 °C [6,9,26,27,29,31]. Dui78 and Dui80 also show a low intensity calcite peak at 1431 cm^{-1} indicating low firing temperature. Duingen is located in Lower Saxony where quite rare and good quality tertiary clays were available. If these clays are composed of small amount of CaCO_3 , as shown in Dui78 and Dui80, but fired at a temperature above 950 °C, they give a simple mineralogical composition of quartz and hematite, as seen in the case of Pe96, Pe00, Dui88 and Dui90 which form the second group discriminated by FT-IR spectra [3,32,33].

The third group consists on ceramic coming from Bürgel. In addition to quartz and hematite, FT-IR spectra show characteristic peaks of kaolinite as raw clay material used but the absence of FT-IR bands in the range between 3690 and 3620 cm^{-1} is attributed to firing temperature above 900 °C.

Other minerals, such as muscovite and illite, could be identified in the samples but their IR absorption peaks could be interfered by quartz and feldspar, however, the presence of both muscovite and illite is confirmed by Raman spectroscopy (Fig. 3).

3.2. μ -Raman results and discussion

Micro-Raman spectroscopy played an important role in the identification and discrimination of some minerals and in the study of glaze coating in potteries from Bürgel and Brandis. Micro-Raman system provides punctual analyses and more than 10 points for each ceramic sample were considered. Representative micro-Raman spectra are given in Fig. 3. A very intense and narrow signal at 466 cm^{-1} associated with peaks at 143, 206, 355 and 394 cm^{-1} is due to quartz (Fig. 3 (e)),

found in all the investigated samples, and typical for quartz in free and isolated form [6,34]. Brandis samples show weak peaks at 807 and 961 cm^{-1} attributed to dehydroxylated kaolinite not completely transformed into metakaolinite, which has disordered structure and a broad and weak Raman signal [35]. Raman signals at 505, 665 and 832 cm^{-1} may be attributed to Al–Si–O and Al–OH bending assigned to feldspar and smectite (as montmorillonite) present in these samples [6]. Hematite (225, 292, 410, 608 cm^{-1}), rutile (241, 442, 609 cm^{-1}), anatase (143, 393, 513, 637 cm^{-1}) and the coexistence of anatase–rutile phase (Fig. 3(d) and Fig. 4) were also detected in Brandis samples by micro-Raman technique [6,31,36]. The Raman technique is able to discriminate these different titanium oxides which may give information about firing condition. The pure phase of rutile can be obtained only at firing temperature above 900 °C but the transition anatase–rutile can be also influenced by other minerals in the ceramic matrix and it could be possible that TiO_2 was applied as rutile phase, giving then an uncertain estimation of thermal treatment [37,38]. Br09 has a green glaze and the Raman spectrum of this layer shows a broad band around 940–945 cm^{-1} . Bu36 and Bu44, decorated by blue glaze (see Fig. 1), have Raman bands in the spectral range between 970 and 1070 cm^{-1} . These data, associated with lead glassy phases, are connected with firing temperature of the glaze. As reported in the literature [39], the broad band around 940 cm^{-1} is related to glaze fired between 600 and 900 °C and the second range is related to higher temperatures presumably above 950 °C. Bu36 and Bu44 Raman spectra of the glaze (Fig. 3(b)) show two peaks at 194 cm^{-1} and 509 cm^{-1} attributed to cobalt blue or cobalt(II) aluminate (CoAl_2O_4). Bu44 shows in addition a broad band at 825 cm^{-1} , attributable to cobalt silicate, which result from the reaction of cobalt oxides and silica matrix at high temperature [15,37,40]. Cobalt blue is a very stable pigment and has been used since ancient Egypt and re-evaluated during the Ming Dynasty (1271–1425) as colouring in Chinese porcelain [41]. For the first time at the beginning of XIX century, cobalt blue as a pure alumina-based pigment was synthesized by Louis-Jacques Thenard. Afterward the pigment was produced in France, Norway, Bohemia and Germany, where Saxony mining industries had a revival and had the finest specimens of cobalt produce [42–44]. Bu36 glaze show a weak peak at 438 cm^{-1} attributed to zinc oxide present in the blue decoration as glaze flux in the middle- and higher-temperature ranges [45,46]. The weak Raman signal of ZnO may be due to a low concentration of the compound and/or to the fact that the ZnO is a weak scatterer [47]. Peaks at 626, 708 and 774 cm^{-1} found in Bu36

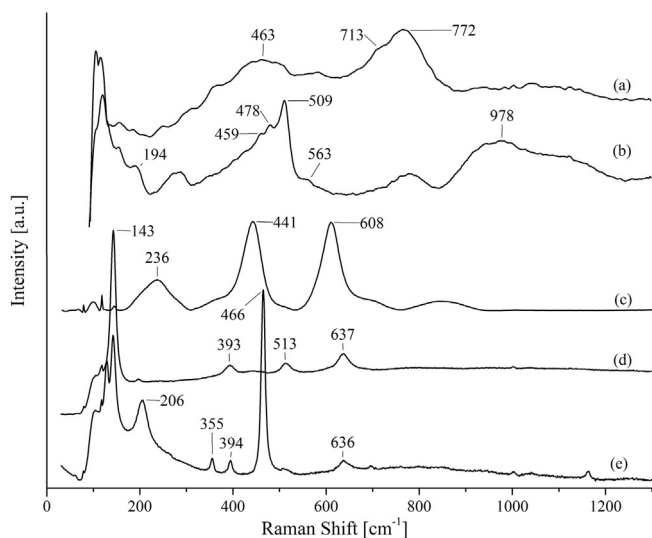


Fig. 3. Representative micro-Raman spectra recorded in different points of the German sherds. (a) Illite Raman spectrum in Dui80; (b) spectrum of Bu36 glaze which shows the presence of cobalt blue; (c) spectrum of rutile in Bu44 ceramic body; (d) and (e), respectively anatase and quartz spectra in Br09 ceramic body.

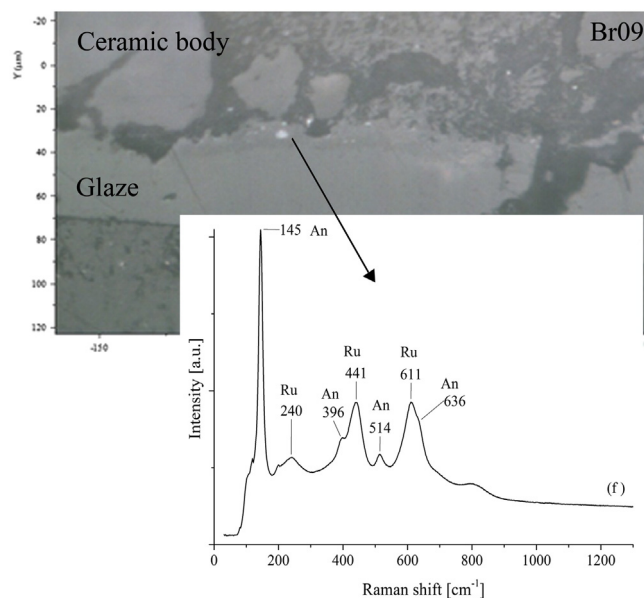


Fig. 4. Photo of Br09 sample (obj. 20×) and Raman spectrum (f) of anatase–rutile phase in the body/glaze interface. Ru = rutile, An = anatase.

glaze are attributed to cassiterite (SnO₂) as pigment in the white dots. Ceramic matrix of Bürgel samples show the presence of quartz, Al–Si–O bending (510, 831 cm⁻¹) and rutile (236, 441, 608 cm⁻¹). Illite was identified in the Raman spectrum at 463, 713 and 772 cm⁻¹ of the sample Dui80 (shown in Fig. 3(a)). The presence of this clay mineral indicates a firing temperature below 850 °C, a temperature at which the skeleton of illite crystal collapses [6].

3.3. XRF results and discussion

Elementary analyses carried out by XRF were able to confirm some consideration about the chemical composition of ceramic matrix and glaze in particular. Semi-quantitative XRF analyses of major and minor elements detected in the German sherds are reported in Table 3. XRF results of Bu36 and Bu44 glaze show Co as a component of the blue colourant. Zn was found only in Bu36 and not in Bu44 glaze, confirming the data obtained by Raman analyses. Cu in Br08 and Br09 was detected. Copper in the decorated layer is attributed to so-called *ramina*, copper oxide (CuO) which produces an intense green coloration, as these two samples from Brandis show [48]. Al, Si, K, Pb, Ca, Ti and Fe were detected in all coating layers of the samples from Bürgel and Brandis. The presence of Pb (18–66 wt.%) indicates the use of lead-glaze, aluminium oxide as stabilizing oxide for silica and calcium oxide as fluxe. Ti in XRF results of all the samples is due to the minerals rutile and anatase (TiO₂), also detected in Raman spectra (Fig. 3(c and d)), used in both glaze, to nucleate the crystal in a low-viscosity glaze, and ceramic body [37]. Anatase/rutile are often present as accessory minerals in clays and they may contain Fe, which is present in all the analysed ceramic bodies with around 10 ± 4 wt.% in average, as shown in the XRF semi-quantitative results [49]. XRF results show similar relative amount of Ti in the samples from Duingen and Peine (in average 3.83 ± 0.95 wt.% and 3.64 ± 0.48 wt.% respectively) and in the binary diagrams (Fig. 5) the distinction among the potteries coming from the different sites is observed. In TiO₂ vs. SiO₂ and TiO₂ vs. Fe₂O₃ plots, shown in Fig. 5(a) and (b), it is possible to isolate the Cottbus samples, characterized by a low content of Ti, and samples from Brandis, with high relative amount; furthermore, Duingen and Peine potteries seem

almost overlapped. FT-IR results also propose a similar mineralogical composition of the raw materials used in Duingen and Peine ceramics suggesting the provenance of the clays from Lower Saxony, but different technological production among the two sites. High relative content of Ca (24–52 wt.%) is present in all the Cottbus samples, suggesting the use of naturally Ca-rich clays or clay tempered with calcite. Cottbus group is also well discriminated by binary plots reported in Fig. 5(c) and (d), where the samples are disposed with about the same trend.

3.4. 3.3 LIF results and discussion

The German ceramic fragments were also investigated by LIF technique, already used as a diagnostic tool in the field of cultural heritage [16,50]. Furthermore, at the ENEA laboratory in Frascati (Rome) has been developed and patented a LIF scanning system [50], which is capable to collect hyperspectral fluorescence images scanning large areas for applications to cultural heritage surfaces. LIF spectroscopy is used in this research to explore the potentiality of this technique to investigate ceramic materials exploiting the mineral luminescence and carrying on fast analyses in a non-destructive and non-invasive way. Luminescence in minerals and glaze ceramic depends on activator elements, such as impurity ions and lattice defects, on composition and structure of the glass [20,51]. It has to be considered that interpretation of LIF spectra can be difficult due to the characteristic fluorescence broad bands and the lack of studies regarding its application on archaeological and historical ceramic and glass materials. In Fig. 6 the main spectra acquired on glazes and ceramic bodies are shown. The LIF spectra of blue glaze in both Bu36 and Bu44 sherds (Fig. 6(a)) show bands in UV, blue and green regions may be due to Pb²⁺ doped silicas [15]. In the UV region the fluorescence may be also due to Al³⁺, Li⁺, K⁺ and Na⁺ doped SiO₂ [20]. LIF band at ~450 nm can be attributed to cobalt blue pigments, which shows a characteristic fluorescence signal at 442 nm [52]. The spectrum of Bu36 blue glaze in Fig. 6(a) shows two more bands in UV and red regions ascribed to ZnO, also detected by XRF and Raman spectroscopy in this samples and absent in Bu44 [22,53]. Fluorescence spectrum of white glaze in Bu36 (Fig. 6(a)) can be attributed to SnO,

Table 3

Semi-quantitative XRF analyses on the bulk and glaze of the German sherds given as normalized % concentration (wt.%).

Sample		Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	ZnO	PbO	CoO	CuO	tot
Bu36	Bulk	30.73	61.13	2.57	0.37	2.14	1.31	0.23	0.67	–	–	99.15
	Glaze	6.32	28.46	–	18.18	1.58	2.45	3.95	38.14	0.88	–	99.97
Bu43	Bulk	22.64	44.64	11.95	7.92	4.15	7.83	–	0.87	–	–	100.00
	Slip	18.63	37.97	4.70	6.03	3.90	7.71	–	18.99	–	–	97.93
Bu44	Bulk	28.23	51.84	9.26	1.36	4.79	4.53	–	–	–	–	100.00
	Glaze	17.67	43.85	3.85	6.59	4.18	5.30	–	17.67	0.74	–	99.84
Bu48	Bulk	28.41	52.91	7.10	0.89	4.97	5.52	–	–	–	–	99.80
Bu49	Bulk	18.46	46.86	17.75	5.11	5.11	4.87	–	1.85	–	–	100.00
Br08	Bulk	23.92	53.54	4.44	1.14	6.72	9.20	–	–	–	–	98.97
	Glaze	20.12	39.67	1.98	6.52	10.48	12.92	–	7.37	–	0.94	100.00
Br09	Bulk	24.85	49.56	3.88	1.55	8.91	9.55	–	0.80	–	–	100.00
	Glaze	9.74	19.47	0.13	1.09	1.69	1.95	–	61.40	–	4.54	100.00
Br11	Bulk	26.07	46.23	8.22	2.23	7.45	7.80	–	0.79	–	–	98.78
	Glaze	2.20	18.56	0.00	2.20	1.93	7.91	–	66.20	0.11	–	99.10
Br14	Bulk	25.48	45.38	5.95	3.40	7.44	9.32	–	–	–	–	96.97
	Slip	8.21	39.80	9.70	6.47	2.74	30.85	–	–	–	–	97.76
Br19	Bulk	25.62	52.41	4.08	0.93	7.42	8.60	–	–	–	–	99.06
Pe96	Bulk	18.61	59.81	3.99	2.47	4.18	10.96	–	–	–	–	100.00
Pe98	Bulk	23.18	55.36	4.77	2.59	3.27	9.09	–	–	–	–	98.27
Pe00	Bulk	22.66	57.72	3.46	1.55	3.46	9.24	–	–	–	–	98.09
Co04	Bulk	5.52	19.64	3.31	51.92	0.95	16.08	–	–	–	–	97.42
Co05	Bulk	11.10	33.58	8.32	26.57	1.46	18.83	–	0.13	–	–	100.00
Co06	Bulk	9.11	26.72	6.31	40.32	1.03	14.09	–	0.24	–	–	97.81
Co07	Bulk	13.14	37.37	5.11	24.09	1.46	18.83	–	–	–	–	100.00
Dui78	Bulk	24.87	52.51	4.01	2.35	3.45	10.05	–	–	–	–	97.24
Dui80	Bulk	25.67	55.49	4.40	1.34	3.18	9.79	–	0.12	–	–	100.00
Dui88	Bulk	14.71	54.34	5.15	3.93	3.43	12.77	–	–	–	–	94.33
Dui90	Bulk	16.07	57.25	3.79	3.43	5.24	9.70	–	–	–	–	95.48

Note that other elements (as Mn, S, P, Ba, Ni, V) at low concentration occur but are not shown in this table.

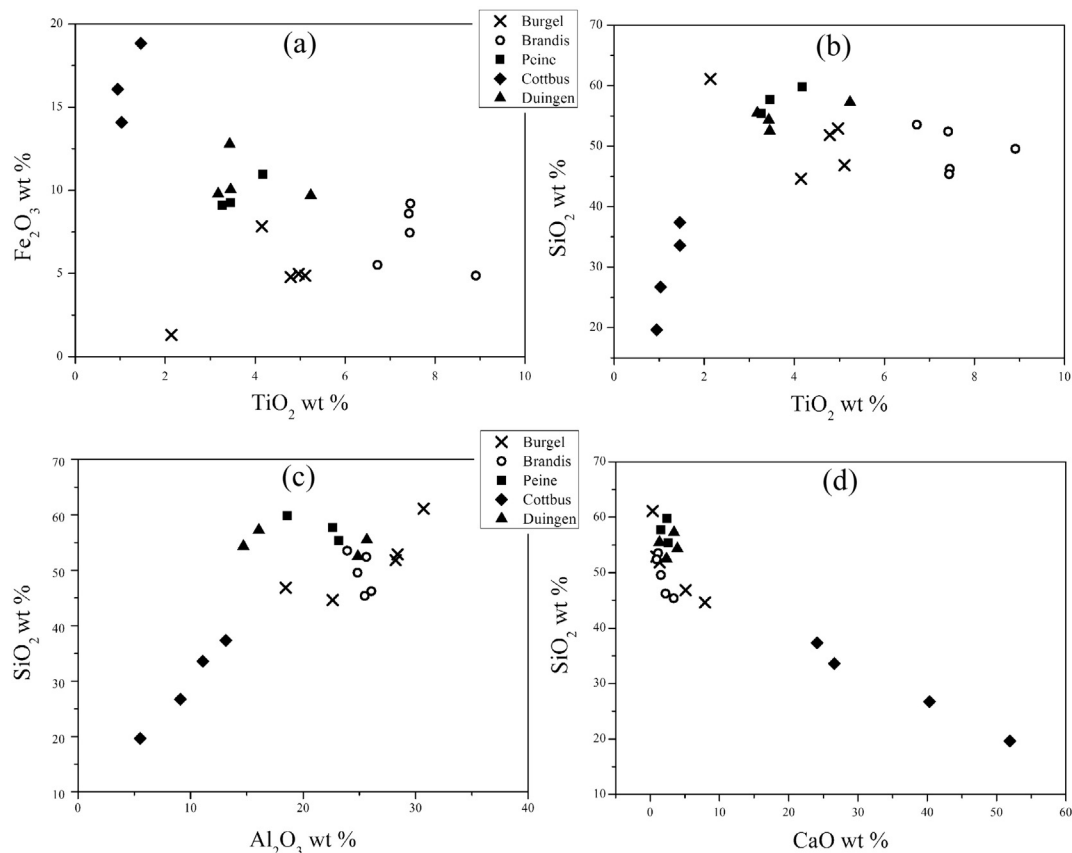


Fig. 5. Binary diagrams of selected major and minor oxides obtained by XRF semi-quantitative analyses in weight percent (wt.%) of all the ceramic sherds. (a) Fe₂O₃ vs. TiO₂; (b) SiO₂ vs. TiO₂; (c) SiO₂ vs. Al₂O₃; (d) SiO₂ vs. CaO.

that shows luminescence at ~450 and ~510 nm when cassiterite is activated by W and Ti [54,55]. LIF spectra of Cottbus, Dui88, Dui90 and Pe98 ceramic bodies (Fig. 6(b)) show different signals in the blue, green and red regions. Dui88 and Dui90 present blue (~350 nm) and red (~700 nm) fluorescence bands probably connected to plagioclase with Mn²⁺ activator element, Ti³⁺ and/or Fe³⁺ in the Al³⁺ tetrahedral sites of feldspar lattice [22,56]. Pe98 and all Cottbus samples have bands at ~430, 500 and 680 nm. Previous studies carried out by the authors [57] suggest the attribution to the intrinsic fluorescence of calcite mineral is due to crystal defects, Fe²⁺ and Mn²⁺ in the Ca²⁺ sites [18,21,58,59]. The presence of calcite in these ceramic fragments is confirmed by FT-IR analyses as discussed in Table 2. LIF spectra of these samples do not show other fluorescence emission bands of silicates probably due to the quenching effects of Fe²⁺ activator element in calcite [59].

4. Conclusion

The archaeometric study carried out on German ceramic sherds by a multi-spectroscopic approach suggests different production technologies in terms of firing temperature and different raw material sources.

Samples from Brandis represent homogenous group showing similar chemical and mineralogical composition. The ceramic matrix consists of quartz, hematite, feldspar, anatase/rutile, smectite and kaolinite, in accordance with kaolinite-rich clay in Sachsen mines [60]. The presence of these clay minerals in the final products suggests firing temperature lower than 900 °C. This datum is confirmed by Raman analyses of the glaze layer present in two of these samples (Br09 and Br11). Sherds from Cottbus, Dui78, Dui80 and Pe98 show similar composition to Brandis sherds but in addition the presence of illite and calcite, clearly detected by FT-IR analyses, confirm the

low firing temperature (≤ 800 °C) and different raw material source is shown. In Dui88 and Dui90 fragments, it was not possible find out particular clay minerals and, as well as in Pe96 and Pe00, the ceramic matrix appears to be formed mainly by quartz, hematite and anatase/rutile, in accordance with tertiary clays source in Lower Saxony and higher kiln temperature (>950 °C). Only a few deposits of tertiary clays are known and they can be found near to villages like Duingen and Coppengrave, indicating that the raw materials used for Peine ceramics have been taken near to these villages [33]. The different composition among Duingen sherds proposes different fabric and use; in fact, Dui78 and Dui80 fired at lower temperature are the typical beer tankards.

The obtained data from Bürgel sherds show a chemical and mineralogical composition which allows the affirmation that the ceramics were fired at higher temperature, above 950 °C. LIF and Raman analyses gave more information about the lead-glaze composition presents in Bu36 and Bu44. In Bu36 cobalt-blue, cassiterite and white zinc were found, while Bu44 seems to be the typical Bürgel stoneware with cobalt-blue salt-glaze (*Smaltebewurf*), formed by throwing salt into the kiln during the firing process [3].

In conclusion, the multi-spectroscopic approach using complementary methods provided the ability to obtain information about composition, firing condition and production techniques used in ceramic materials.

FT-IR analyses give more information about the chemical composition of the ceramic body, whereas the interesting results obtained by LIF and Raman spectroscopies suggest that these non-destructive techniques, are promising methods for ceramic and especially for glaze characterization. Laser induced fluorescence enables to investigate the lead glazes and the pigments used. The successful results obtained encourage its application in other archaeological and historical glaze ceramics. Moreover, thanks to its characteristics, such as portability and the

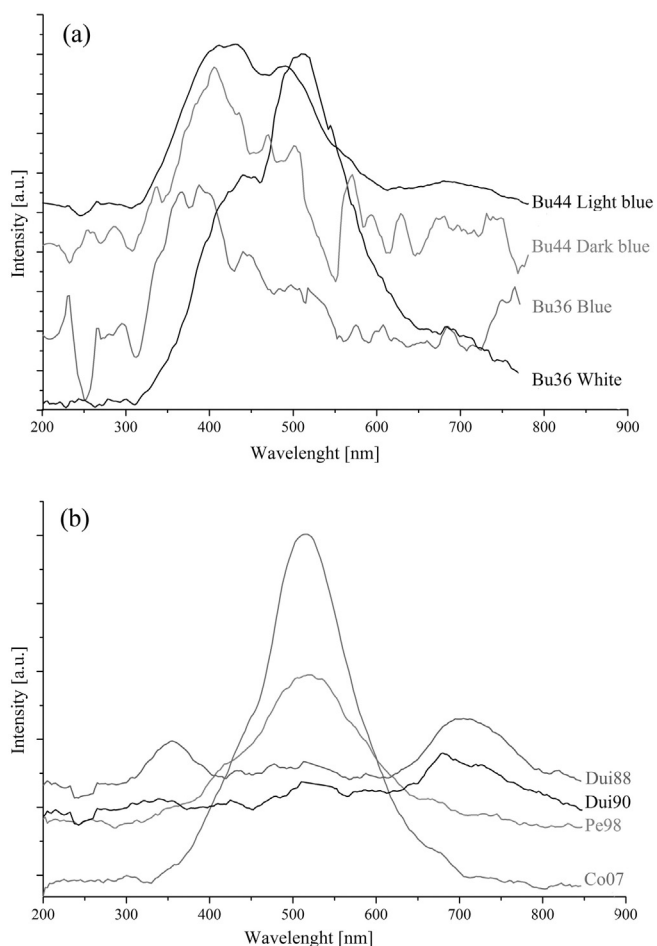


Fig. 6. : (a) LIF spectra of ceramic glaze of two sherds coming from Bürgel (Bu36 and Bu44); (b) LIF spectra of ceramic body of sherds from Cottbus, Duingen and Peine.

possibility to collect hyperspectral fluorescence images by the scanning setup, LIF system could be capable to analyse artefacts of large dimension such as glass windows and mosaics with glass tessera.

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