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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.

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 wildly 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 dived 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