

# SPECTROSCOPIC AND POROSIMETRIC ANALYSES OF ROMAN POTTERY FROM AN ARCHAEOLOGICAL SITE NEAR MOŠNJE, SLOVENIA

## SPEKTROSKOPSKE IN POROZIMETRIČNE PREISKAVE RIMSKE LONČENINE Z ARHEOLOŠKEGA NAJDIŠČA PRI MOŠNJAH, SLOVENIJA

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*Prejem rokopisa – received: 2014-07-16; sprejem za objavo – accepted for publication: 2014-07-31*

doi:10.17222/mit.2014.110

This study deals with spectroscopic and porosimetric analyses of pottery from a Roman villa rustica near Mošnje, Slovenia. Samples of coarse ware and fine ware, which according to archaeological considerations have been recognised as local or perhaps regional products, were investigated using FTIR spectroscopy, scanning electron microscopy, mercury-intrusion porosimetry and gas sorption. Based on their FTIR spectra, the pottery sherds can be divided into two main groups, depending on the presence or absence of calcite. The firing temperature was estimated according to the presence of an absorption band at around 3630 cm<sup>-1</sup>, associated with hydroxyl groups of minerals that are persistent up to 800 °C. The differences among the coarse and fine ware sherds related to the pore morphology and the pore volume in the matrix were observed, as was the extent of the vitrification. In general, the total porosity of the pottery sherds with coarse-grained calcite inclusions was lower than that of the fine pottery sherds. The fine ware samples also exhibited a significantly higher BET surface area than the coarse ware samples.

Keywords: Roman pottery, archaeological ceramics, FTIR, porosimetry, Mošnje

V prispevku so predstavljeni rezultati spektroskopskih in porozimetričnih analiz lončenine iz rimske vile rustike pri Mošnjah (Slovenija). Vzorce grobe in fine keramike, ki naj bi bila glede na arheološke raziskave lokalnega ali regionalnega izvora, smo preiskali s spektroskopijo FTIR, vrstično elektronsko mikroskopijo, živosrebrovo porozimetrijo in plinsko sorpcijo. Glede na spektre FTIR lahko lončenino razdelimo v dve skupini, odvisno od tega, ali vsebuje kalcit. Temperatura žganja je bila ocenjena glede na prisotnost absorpcijskega traku hidroksilnih skupin pri okoli 3630 cm<sup>-1</sup>, ki je obstojen do 800 °C. Med grobo in fino keramiko so opazne razlike v obliki in volumnu por ter obsegu vitrifikacije. Na splošno je celotna poroznost lončenine z dodatkom debelozrnatega kalcita nižja kot pri fini keramiki. Slednja ima v primerjavi z grobo keramiko tudi občutno višjo specifično površino BET.

Ključne besede: rimska lončenina, arheološka keramika, FTIR, porozimetrija, Mošnje

## 1 INTRODUCTION

Analyses of the potteries that represent one of the most abundant types of archaeological find reveal information regarding the daily life and culture of ancient societies.<sup>1,2</sup> The mineralogical and chemical characterisation of pottery provides evidence for the technology involved in the manufacturing process and potentially the provenance of the raw material used.<sup>3-6</sup> Besides the raw materials, the nature and quality of the pottery depend on the firing temperature, the firing atmosphere or the kiln conditions, as well as the technical skill of the potter.<sup>7</sup>

Thermal transformations in clay materials during firing provide a means with which to estimate the firing temperature of the artefacts.<sup>8</sup> FTIR spectroscopy is considered as an important tool in the analysis of clay minerals and mineral transformation due to thermal effects, with the infrared spectra of the pottery revealing both the type of clay and the firing temperature.<sup>8-10</sup> An SEM examination of the pottery provides information

regarding not only the internal morphology that developed during the original firing in antiquity, but also the extent of the vitrification (the glassy phase) and the pore structure.<sup>11,12</sup>

Porosity is a fundamental attribute of pottery and can provide information about many aspects of archaeological manufacturing technologies, including the firing temperature, the type of clay and tempering materials, and the manufacturing and forming techniques employed, which all contribute to the degree of ceramic porosity exhibited.<sup>13</sup> Porosity also influences a wide range of ceramic use-related properties, such as strength, permeability, thermal insulation, as well as resistance to abrasion and thermal shock.<sup>14</sup>

Most pottery sherds found at the archaeological site near Mošnje, Slovenia date from the Augustian period (27 BC to 14 AD) to the 2<sup>nd</sup> Century, thus providing additional confirmation that the Roman villa rustica was built in the first half of the 1<sup>st</sup> Century and was in use

until the end of the 2<sup>nd</sup> Century, at the latest. The discovery of pottery fragments dating to prehistory, together with a number of bronze finds from the Early and Late Iron Ages, indicates settlement of the area prior to the arrival of the Romans. Furthermore, the presence of Late Roman pottery on the site that confirms the continuity of settlement somewhere nearby the villa, which by this time had already been abandoned.

It is widely known that both coarse ware and domestic tableware are usually of local manufacture and that such forms are typically not chronologically very sensitive.<sup>15</sup> The selected pottery samples, which according to the archaeological analysis have been recognised as local or perhaps regional products (i.e., not imported/terra sigillata), differ in their mineralogical and chemical composition, reflecting a variation in the manufacturing technology and the type of clay material used.<sup>16,17</sup> The sherds were classified into two distinct groups: (i) Group 1 – sherds made from clay with a high plasticity (calcite-tempered ware), containing abundant calcite and smaller amounts of quartz; (ii) Group 2 – sherds with a predominantly fine silicate fabric, part of the original clay, calcite-free and containing abundant quartz and illite/muscovite. Group 1 sherds are fairly homogenous, indicating that the technology of manufacture changed only slightly with time. The mineralogy and geochemistry of these sherds are also similar, suggesting that they must have been produced from the same source of raw materials, although the greater amount of quartz observed in two Late Roman sherds suggests a possible different clay-mass source in use at this time. In contrast, the Group 2 samples are highly heterogeneous, indicating the use of various sources of raw materials.

In the present study, samples of Roman coarse ware and fine ware from the archaeological site of Mošnje were chosen for spectroscopic and porosimetric analyses. FTIR spectroscopy, scanning electron microscopy, mercury-intrusion porosimetry and gas sorption were applied in order to characterise the porosity and estimate the firing temperature of the pottery.

## 2 EXPERIMENTAL

### 2.1 Materials

Seven samples – four of coarse ware and three of fine ware – previously studied with respect to their mineralogical and geochemical characteristics<sup>16,17</sup> were selected for the investigation. Information regarding the micro-location, type, surface colour and probable date of the pottery samples is provided in **Table 1**.

### 2.2 Methods

Samples were analysed via Fourier-transform infrared spectroscopy (FTIR) using a Perkin Elmer Spectrum 100 spectrometer. Sixty-four signal-averaged scans were acquired. Powder pellets were pressed from a mixture of sample and KBr at a ratio of about 1 : 200. The FTIR spectra were recorded with a spectral resolution of 4 cm<sup>-1</sup> in the range 4000–400 cm<sup>-1</sup>.

Freshly fractured surfaces of the pottery as well as polished thin sections were examined using the back-scattered electron (BSE) image mode on a scanning electron microscope (SEM) at low vacuum (between 10 Pa to 15 Pa), coupled to an energy-dispersive X-Ray (EDS) analyses, using JEOL 5500 LV equipment.

The pore systems of the samples were further investigated by means of mercury-intrusion porosimetry (MIP) and gas-sorption isotherms. Small representative fragments, approximately 1 cm<sup>3</sup> in size, were dried in an oven for 24 h at 105 °C and then analysed on a Pascal 240 porosimeter within the range from 0 MPa to 200 MPa. N<sub>2</sub> sorption isotherms were obtained at 77 K on a Micromeritics ASAP 2020 analyser under continuous adsorption conditions. Prior to these measurements, chip samples were heated at 200 °C for 2 h and outgassed to 1.33 · 10<sup>-3</sup> mbar using a Micromeritics Flowprep equipment. Gas-adsorption analysis across the relative pressure range of 0.05 to 0.3 was used to determine the total specific area or Brunauer–Emmet–Teller (BET) surface area of the samples.<sup>18,19</sup> The sample total pore volume and the micropore volume were calculated using a t-plot analysis, with the Barret–Joyner–Halenda (BJH) method employed to obtain the pore-size distribution curves.<sup>20</sup>

**Table 1:** Pottery samples from the archaeological site near Mošnje

**Tabela 1:** Vzorci lončenine z arheološkega najdišča pri Mošnjah

Sample	Location	Type	Surface colour	Time frame	
	Grid square			Stratigraphic unit	Munsell colour chart
K1 (4254)	L10	187	coarse ware	7.5YR5/1 (gray)	1.–3. (?) Century
K3 (3264)	L10	137	fine ware	7.5YR6/8 (reddish yellow)	1.–3. Century
K6 (1722A)	N7, O7	162	coarse ware	7.5YR6/4 (light brown)	1.–1. half of 2 <sup>nd</sup> Century
K7 (1909)	L9	196	fine ware	10YR4/1 (dark gray)	1.–2. Century
K8 (6366)	L13	529	coarse ware	10YR3/1 (very dark gray)	1.–2. Century
K10 (2447)	M9, N9	198	coarse ware	10YR4/1 (dark gray)	1 <sup>st</sup> half of 1. Century
K12 (1688)	N7, O7	162	fine ware	5YR7/6 (reddish yellow)	1.–1. half of 2 <sup>nd</sup> Century

### 3 RESULTS AND DISCUSSION

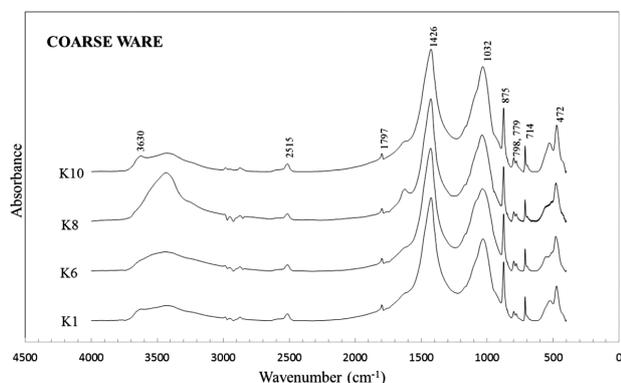
#### 3.1 FTIR analysis

On the basis of the FTIR spectra, all the analysed pottery sherds could be divided into two main groups according to the presence or absence of calcite. The obtained FTIR spectra are shown in **Figures 1** and **2**.

As can be seen in **Figure 1**, absorption bands at around (2515, 1797, 1426, 875 and 714)  $\text{cm}^{-1}$  that are characteristic of calcite were observed in the spectra of all the Group-1 samples (K1, K6, K8, and K10), which represent calcite-tempered coarse ware.<sup>16</sup> Another intense absorption band appears at around 1030  $\text{cm}^{-1}$ , indicative of clay minerals such as illite.<sup>9</sup> The small absorption band at 1164  $\text{cm}^{-1}$ , the shoulder at 1080  $\text{cm}^{-1}$ , the doublets at 798  $\text{cm}^{-1}$  and 779  $\text{cm}^{-1}$ , and the band at 694  $\text{cm}^{-1}$ , together indicate the presence of quartz in all the samples within the group.

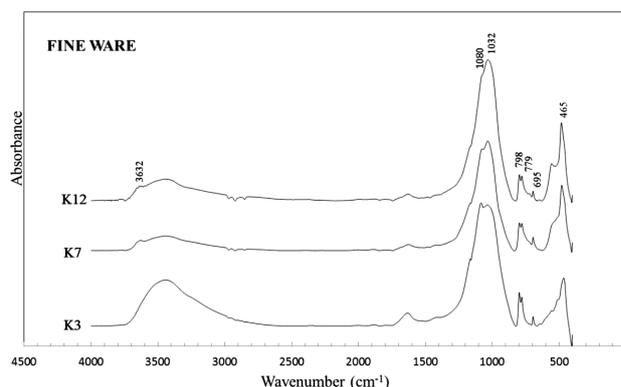
According to the literature<sup>21</sup>, the absorption band at around 3630  $\text{cm}^{-1}$  is due to hydroxyl groups that persist up to 800 °C. The small absorption band at around 3630  $\text{cm}^{-1}$ , and which is assigned to the illite/muscovite, is clearly observed in sample K10, and slightly preserved in sample K1. This indicates that these two samples might have been fired below 800 °C, as already presumed in a previous study.<sup>16</sup> In contrast, those samples not exhibiting the absorption band at around 3630  $\text{cm}^{-1}$  were likely fired to temperatures of 800 °C or above (samples K6 and K8).

As shown in **Figure 2**, the spectra of the Group-2 samples that represent fine ware with predominant silicate grains (K3, K7, and K12) are, besides the absence of absorption bands, characteristic of calcite, characterised by a most intense band at about 1035  $\text{cm}^{-1}$ , which is attributed to the Si-O vibrations of silicate (clay) minerals. Sample K3 does not exhibit an absorption band at around 3630  $\text{cm}^{-1}$ , indicating a firing temperature higher than 800 °C. This band is slightly preserved in samples K7 and K12, indicating a lower firing temperature for these samples. The absorption



**Figure 1:** FTIR spectra of the calcite-tempered pottery sherds (coarse ware)

**Slika 1:** Spektri FTIR odlomkov lončenine z dodatkom kalcitnih zrn (groba keramika)



**Figure 2:** FTIR spectra of the pottery sherds with a predominantly fine silicate fabric (fine ware)

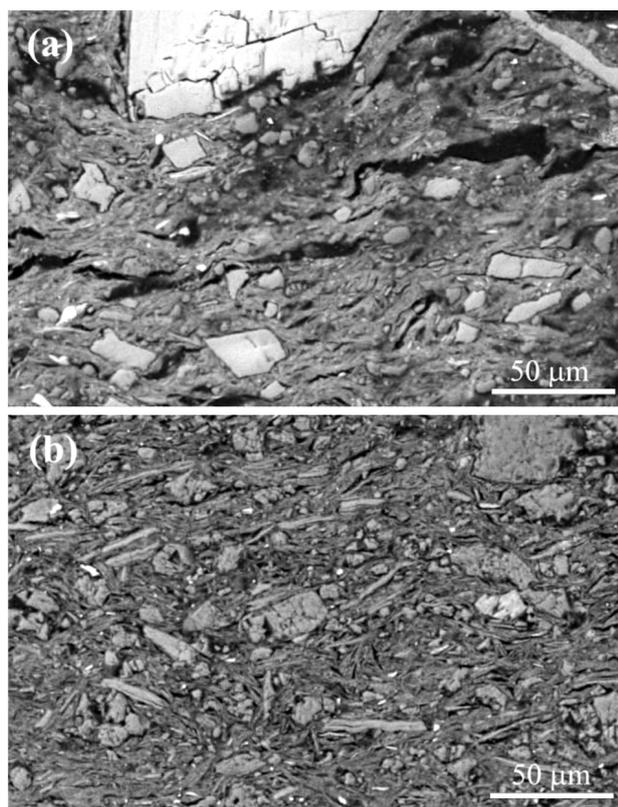
**Slika 2:** Spektri FTIR odlomkov lončenine, ki vsebujejo pretežno drobna silikatna zrna (fina keramika)

band at 1161  $\text{cm}^{-1}$ , the shoulder at 1080  $\text{cm}^{-1}$ , the doublets at 797  $\text{cm}^{-1}$  and 779  $\text{cm}^{-1}$ , and the band at 694  $\text{cm}^{-1}$ , are evidence of quartz in all the samples, with levels being especially high in sample K3. Sample K3 also has an additional shoulder at 1013  $\text{cm}^{-1}$ , suggesting the use of a different clay than that in samples K7 and K12. Together with those at around 720  $\text{cm}^{-1}$  and 646  $\text{cm}^{-1}$ , this band has been ascribed to feldspars previously identified in larger amounts in the same sample.<sup>16</sup>

#### 3.2 SEM

The examination of the fresh fracture surfaces and the polished sections provided some insight into the microstructure of the pottery sherds. As can be seen in the SEM microphotographs in **Figure 3**, the differences among the coarse and fine ware were observed in terms of their pore morphology and pore volume in the matrix. Information regarding the pottery's internal morphology, which developed during the original firing in antiquity, as well as the extent of vitrification, was revealed by the analysis of freshly fractured samples, as shown in **Figure 4**.

The coarse ware matrix is characterised by the occurrence of elongated pores or fissures and cracks around the calcite grains (**Figure 3a**). Samples K1 and especially K6 contain larger amounts of non-plastic inclusions (quartz, illite/muscovite) than do samples K8 and K10. The laminar habits of the phyllosilicates (illite/muscovite) in samples K1 and K6 are still preserved, which is also in accordance with the FTIR results, as the latter spectra included an absorption band associated with the hydroxyl group. Cultrone et al.<sup>22</sup> previously reported that samples fired at 700 °C and 800 °C still preserve the laminar habit of phyllosilicates, although muscovite crystals clearly exfoliate along basal planes, as also observed in sample K1. In this temperature range no clear evidence of sintering or partial melting should be detected, as vitrification occurs above 900 °C. In addition, according to Maniatis and Tite<sup>11</sup>, low refractory non-calcareous clays fired in oxidising conditions with no



**Figure 3:** SEM photomicrographs of polished thin sections of pottery: a) elongated pores in sample K8, b) illite micromass in sample K7

**Slika 3:** SEM-mikrofotografija poliranih zbruskov lončenine: a) podolgovate pore v vzorcu K8, b) ilitna mikromasa v vzorcu K7

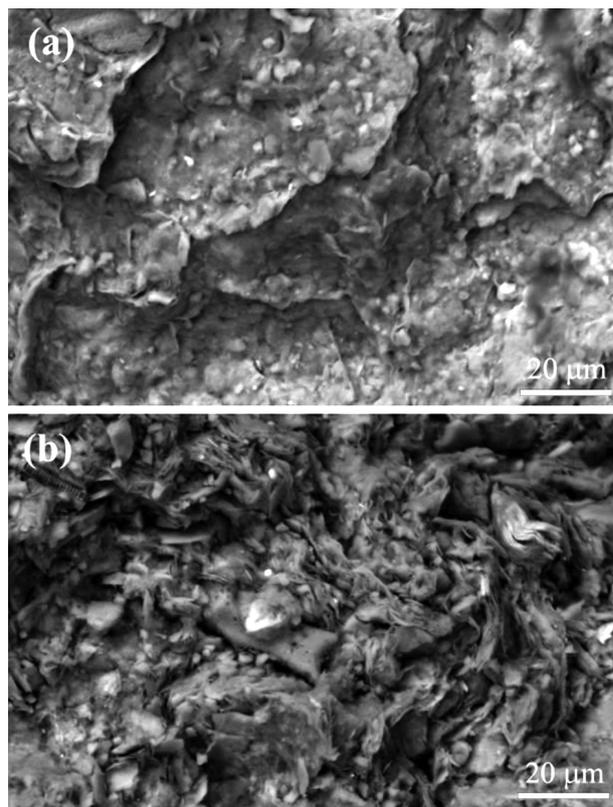
vitriification stage were fired below 800 °C. Thus, samples K1 and K10 belong to the first group (NV), which contains pottery exhibiting no vitriification. Samples K6 and K8 could belong to the initial vitriification stage (IV) that is developed typically at firing temperatures in the range of 800–850 °C. This is suggested by the appearance of smooth-surfaced areas and the rounded edges of the clay plates (**Figure 4a**).

The matrix of the fine ware samples is relatively homogenous, with an illite micromass observed in samples K7 and K12 (**Figure 3b**). Among the fine ware samples, the preserved laminar habits of phyllosilicates presented in samples K7 and K12 (**Figure 4b**) indicate that these sherds were not subject to vitriification (NV). In contrast, the rounded particle edges in sample K3 are suggestive of the initial vitriification stage (IV).

### 3.3 Mercury-intrusion porosimetry

**Table 2** presents the sample parameters determined via mercury-intrusion porosimetry (total porosity, average pore diameter, bulk density and apparent density).

The porosity values range from 21.34 % to 44.03 %. In general, the total porosity of pottery sherds with coarse inclusions is lower (21.34–30.33 %) than that of the fine ware pottery sherds, in which the porosity ranges



**Figure 4:** SEM photomicrographs demonstrating the degree of vitriification in the studied coarse ware and fine ware: a) smooth-surfaced areas could indicate initial vitriification in sample K8, b) preserved laminar habit of phyllosilicates indicates no vitriification in sample K12

**Slika 4:** SEM-mikrofotografija prikazuje stopnjo vitriifikacije pri grobi in fini keramiki: a) zaobljena površina lahko nakazuje začetno stopnjo vitriifikacije v vzorcu K8, b) ohranjena laminarna struktura filossilikatov nakazuje, da do vitriifikacije še ni prišlo, vzorec K12

from 36.49 % to 44.03 %. Furthermore, the average pore size diameter of the fine ware sherds is lower than that of the sherds with coarse inclusions. The sample bulk densities vary from 1.32 g/mL to 1.99 g/mL, whereas the apparent densities range from 2.52 g/mL to 2.68 g/mL.

**Table 2:** Porosity, average pore diameter, bulk density and apparent density of the investigated pottery samples

**Tabela 2:** Poroznost, povprečen premer por, volumenska in navidezna gostota preiskanih vzorcev lončenine

Sample	Porosity (%)	Average pore diameter (µm)	Bulk density (g/mL)	Apparent density (g/mL)
<b>Coarse ware</b>				
<b>K1</b>	21.43	5.54	1.98	2.52
<b>K6</b>	30.33	0.22	1.82	2.61
<b>K8</b>	21.34	4.60	1.99	2.54
<b>K10</b>	29.15	58.94	1.90	2.68
<b>Fine ware</b>				
<b>K3</b>	44.03	0.66	1.32	2.36
<b>K7</b>	36.49	0.38	1.60	2.52
<b>K12</b>	37.11	0.37	1.60	2.54

All the samples with coarse inclusions exhibit a distinctive bimodal pore distribution, which is reflected

in a higher average pore diameter. These samples are also characterised by the presence of elongated pores in the matrix and sizeable cracks around the large calcite inclusions, as seen in SEM observations; these features thus contribute to the shift towards larger pores. Nevertheless, the main peak, with a higher intrusion, is observed at around 7.5  $\mu\text{m}$  to 10  $\mu\text{m}$  in all coarse ware samples with the exception of K10, where the distribution curve is shifted significantly to the right (85  $\mu\text{m}$ ). The minor intrusion peak occurs at around 0.07  $\mu\text{m}$  to 0.15  $\mu\text{m}$  in samples K8 and K10, while in samples K1 and K6 this peak is shifted slightly to the right at around 0.5  $\mu\text{m}$ . Samples K6 and K10, respectively, exhibit the lowest and highest average pore size diameters. Whereas the intrusion peaks at higher pore diameters are most probably related to the presence of fissures and pores in the matrix, the peaks at smaller pore diameters are associated with the composing clay minerals. The latter peaks occur at lower values in the group of pottery sherds containing calcite temper than in the non-tempered pottery, thus indicating the use of different types of raw clay in their manufacture. In samples K8 and K10 the minor peak is shifted to even smaller values, since these sherds were found to contain very little illite/muscovite.<sup>16</sup> Most porosity observed before 800 °C depends on the type of clay, as well as on the size and concentration of the inclusions.<sup>23</sup>

The porosities of the pottery sherds containing fine particles are unimodally distributed, with the largest intrusions being around 0.60  $\mu\text{m}$  (K7, K12) or 0.85  $\mu\text{m}$  (K3). While samples K7 and K12 have similar total porosities and average pore size diameters, sample K3 exhibits the highest porosity among all the samples, as well as an average pore size diameter larger than that of the other two samples. The latter were also found to have a higher percentage of phyllosilicates, as observed via SEM-EDS<sup>16</sup>, together with a different type of matrix to that seen in sample K3. The total specific surface is related to the grain size, with the smallest values found in sample K3.

Velraj et al.<sup>21</sup> have previously reported that samples containing coarse particles exhibit higher porosity, the reverse of the pattern observed here. Although a high firing temperature will lead to low porosity,<sup>7,24</sup> the fact that in the present study the porosity of the coarse ware is lower than that of the fine ware is most likely due to the type of clay used, with the former made of plastic montmorillonite-illite clays and the latter characterised by the predominance of illite, potentially mixed with other clay minerals.<sup>16</sup>

### 3.4 Gas sorption

The sample BET-specific surface area varies from 2.90  $\text{m}^2/\text{g}$  to 91.55  $\text{m}^2/\text{g}$ , with the fine ware sherds characterised by significantly higher values (36.25–91.55  $\text{m}^2/\text{g}$ ) than those of the coarse ware (2.90–7.97  $\text{m}^2/\text{g}$ ) (Table 3). On the other hand, the coarse ware samples

exhibit a larger average pore diameter. Two samples, K7 and K10, present a pore size distribution with weak maxima of approximately 4 nm and 20 nm, respectively, whereas those of the other samples are either unclear or smaller than the detection limit. The volume of pores accessible to gas is larger in the case of the fine ware sherds. Similar to the previous results, the lower BET surface area of the coarse ware is the result of the presence of a coarse calcite temper. In contrast, the various fine fabrics characterising the fine ware sherds contribute to their higher BET surface areas, with sample K7 composed of a medium sand fraction<sup>16</sup> having the lowest BET surface area, and K12 composed of a very fine sand fraction having the highest BET surface area.

All of the samples studied present a type-II physiosorption isotherm characteristic of non-porous and macroporous materials.<sup>25</sup>

**Table 3:** Results of  $\text{N}_2$ -adsorption measurements for the investigated pottery samples

**Tabela 3:** Rezultati  $\text{N}_2$ -adsorpcijskih meritev preiskanih vzorcev lončenine

Sample	BET surface area	Total pore volume	Average pore diameter	Micropore volume
pha	$\text{m}^2/\text{g}$	$\text{cm}^3/\text{g}$	nm	$\text{cm}^3/\text{g}$
Coarse ware				
K1	2.90	0.0090	12.41	0.000052
K6	4.35	0.0113	10.36	0.000290
K8	7.97	0.0090	12.41	0.000572
K10	3.78	0.0165	17.41	0.000050
Fine ware				
K3	86.37	0.0976	4.52	0.009380
K7	36.25	0.0022	4.98	0.002232
K12	91.55	0.0836	3.65	0.012577

## 4 CONCLUSIONS

Samples of coarse ware and fine ware from an archaeological site near Mošnje (Slovenia), which according to previous analysis have been recognised as local or perhaps regional products, were investigated in order to characterise their porosity and estimate their firing temperature.

Based on FTIR spectra, the pottery sherds can be divided into two main groups, reflecting either the presence or absence of calcite. The firing temperature was estimated according to the presence of an absorption band at around 3630  $\text{cm}^{-1}$ , which is associated with hydroxyl groups persistent up to 800 °C. This band was observed in two coarse ware samples and two fine ware samples, indicating that these sherds might have been fired below 800 °C. In contrast, samples not exhibiting this absorption band would likely have been fired at temperatures of at least 800 °C or above.

Differences were observed among the coarse and fine ware samples in terms of their pore morphology and pore volume in the matrix, as well as the extent of the vitri-

fication. Two vitrification stages were recognised in the studied pottery samples: no vitrification and an initial vitrification stage. These results are consistent with the obtained FTIR data, as the absence of a vitrification stage is characteristic of pottery fired below 800 °C, whereas an initial vitrification stage is developed typically at firing temperatures in the range of 800–850 °C.

In general, the total porosity of the pottery sherds containing coarse inclusions was lower than that of the fine pottery shards, most probably due to the plastic clay used in the former. The fine ware samples had a significantly larger BET surface area than the coarse ware samples, which is mainly related to the fabric or temper grain size.

### Acknowledgements

This study was financially supported by the ARRS Program Group P2-0273.

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