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Determination of the carbonization temperature of wood in the study of archaeological artifacts by Raman spectroscopy

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A study of the pyrolysis temperature of organic materials at the carbonization stage was performed by Raman spectroscopy. The analysis was carried out on the basis of the ratio of the amplitudes of the characteristic D and G bands for amorphous carbon. The research was carried out to check applicability of this method for an objective analysis of archaeological material. The obtained values of the carbonization temperature for organic inclusions in ancient ceramic fragments made it possible to determine the bonfire firing regime which is distinctive for the technology of hand-made medieval pottery manufacturing. The study of coal from the remains of wooden ancient Russian fortifications revealed the temperature of their carbonization, which corresponds to the smoldering regime. This indicates that they were completely covered with soil at the time of the fire.

Keywords: Raman spectroscopy, amorphous carbon, coal, carbonization temperature.

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Introduction

Raman scattering spectroscopy (RS) of light is currently an effective and sought-after tool for scientific research. Reflecting the structural features of the material, associated with its nature and physical properties and sensitive to external influences, it finds almost unlimited application in various fields of science and technology [1]. RS is also actively used in the study of carbon-based materials [2–4].

When it comes to spectral analysis of archaeological artifacts and works of art, the results of studies of ancient metal products, in most cases made of copper and bronze, are usually considered (see, for example, [5,6]). RS has significantly expanded the possibilities of studying objects made of clay, glass and various minerals [7–12]. However, wooden heritage assets have been practically not studied. At best, it is referred to art works [13].

In this aspect, it is the study of carbonaceous components, the forms of distribution of which in nature are diverse, that is of the greatest interest, since carbon compounds and their transformation in both organic and inorganic compounds make it possible to conclude the various processes occurring with assets due to natural causes, and due to artificial ones, for example, during heat treatment, combustion and charring.

As application to the study of archeological heritage objects, it should be noted that amorphous carbon is certainly present in the cultural layer, being a natural result of the use of fire, the mastery of which became one of the fundamental moments of human development. Consequentially, the study of anthropogenic coal provides important information both for dating archaeological remains and for studying the manufacturing products or the conditions of their transformation. In application to the study of fired clay pottery manufacturing technology, information about the structural composition of carbon inclusions in the molding mass can be used to determine the burning-point temperature [14,15]. These inclusions are formed as a result of carbonization of organic substances that are present in the clay initial products [16], and can also be added during the production process.

Calcination of medieval-era fired clay pottery was made at temperatures ranging from 500 to 1200°C. This range corresponds to the first stage of pyrolysis of solid hard-bodied materials, i.e. carbonization, in which the reactions of destruction of non-aromatic molecules, the appearance of aromatic molecules with side chains, and the formation of polycyclic aromatic systems [17], sequentially occur. In this case, crystallites appear, consisting of flat carbon layers. Occurring changes in the structure of the material can be traced based on RS. As the carbonization temperature increases, the band centered around $1350\,cm^{-1}$ (D the band), reflecting the disorder of the structure, undergoes significant changes. In this case, the so-called graphite band (G, the band) with a center around $1580\,cm^{-1}$ is preserved and enhanced. Thus, the ratio of the amplitudes of the indicated bands H_D/H_G becomes an indicator of the processing temperature of carbonaceous raw materials. Suggested approach was successfully tested by its authors on European archaeological remains [14]. In domestic practice, there is an example of its use in the analysis of Karelian medieval-era ceramics [18]. This work presents the results of using RS to determine the temperature regime of carbonization of organic matter for the analysis of archaeological materials from excavations in the city of Vladimir.

1. Equipment and materials

RS from the studied samples were obtained using the Probe Nano Laboratory INTEGRA spectra (ZNL INTEGRA Spectra, NT-MDT, Zelenograd, Russia). Linearly polarized radiation from an LM473 solid-state laser with a wavelength of 473 nm was used as a probing beam. Laser radiation with a power of 2 mW was focused on the surface of the samples using a Mitutoyo M Plan Apo 100 objective with a numerical aperture of 0.7 into a spot with a diameter of 0.4 μm. Studies of the structure of coal samples to confirm the species of the original wood were carried out using a Quanta 200 3*D* scanning-electron microscope at accelerating voltage of 30 kV.

The degree of carbonization of organic materials was studied in two directions. Firstly, the RS of the molding composition of fragments of earthenware from the collection from the archaeological heritage site „Settlement Poganoe (Paganets) I", dating back to (XI–XII). were obtained and analyzed. The historical scientific artifacts is located in the forested area of the city of Vladimir on the right bank of the Klyazma river. This territory has been practically unexplored in the aspect of archaeological. The archaeological remains discovered during the study of the archaeological site is represented exclusively by fragments of ceramic dishes made from red-burning clay. The rough execution of the dishes allowed, on the basis of expert assessment, to classify them as molded ones and make an assumption that they to the local indigenous Finno-Ugric population belonged are [19]. However, to confirm the typification and periodization of ceramic material, an important factor is objective data on the firing technology. It is believed that the molded earthenware in XI–XII centuries, was subjected to heat treatment using the fire method, which ensures a temperature of 700–800°C [20]. The purpose of the spectroscopic experiments was to determine the thermal processing conditions of the ceramic fragments under study in order to objectively confirm or correct their expert assessment.

The second direction of research is related to the analysis of the degree for carbonization of coals from the remains of burnt Old Russian wooden structures discovered during archaeological excavations of the defensive earthworks of the city of Vladimir on the territory of the house № 32 on modern Ilyich Street. At the time of archaeological work, these remains were located in the sub-surface of the earthworks. Determining the carbonization temperature of wood will allow it to conclude whether the logs of the log structures were completely surrounded by soil during the fire, or whether they rose above its free surface.

2. Results and discussion

2.1. Clay products

The molding mass of medieval-era pottery contains numerous fairly large crystalline inclusions: grains of quartz, calcite, mica, etc. When a spot of probing laser radiation hits the spot, all of them can introduce pronounced peaks into the RS that do not carry information useful for the research being carried out. Therefore, when analyzing ceramic fragments, areas with a guaranteed absence of them were selected. All the obtained spectra contain fairly wide bands characteristic of amorphous carbon with centers around 1350 and 1580 cm^{-1}. Typical Raman spectra obtained using ZNL (Probe Nano Laboratory) INTEGRA Spectra are presented in Fig. 1. They show the results of the analysis of two layers in the structure of the studied pieces of broken crockery: light and dark. The first corresponds to the oxidative firing regime. It is adjacent to the outer surface of the vessel and occupies from 50 to 80% of the thickness of its wall. The second one was formed under conditions of a reducing atmosphere. Obviously, the ceramics were fired without providing forced aeration. As a result, an area with a low oxygen content was created inside the vessels, which led to the appearance of iron oxide FeO in the molding mass, the black color of which caused the dark shade of the specified layer. The RS of the dark (Fig. 1, curve *1*) and light (Fig. 1, curve *2*) layers in the range of 800–2000 cm^{-1} are qualitatively the same.

The heights of$H_D$and H_G were determined for the maxima in the *D*- and *G*E bands, respectively. In a series of measurements carried out on samples of medieval-era

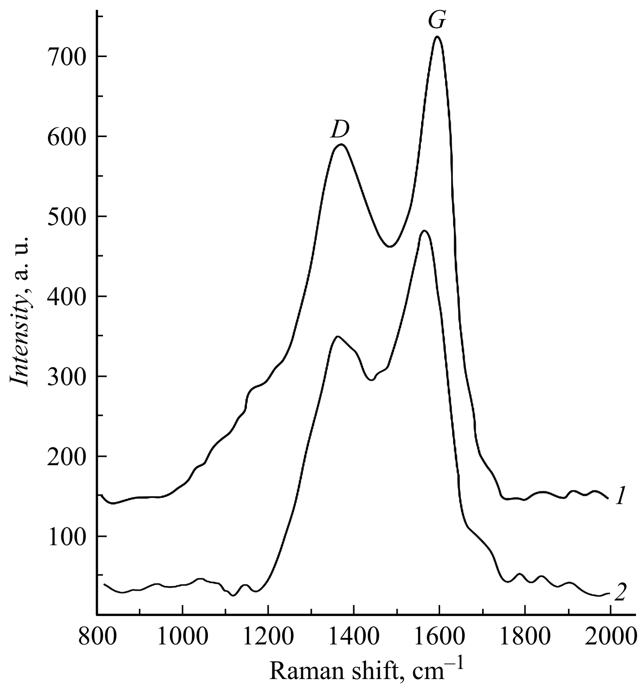

Figure 1. Characteristic RSs of ceramic test: *1* — dark layer, *2* — light layer.

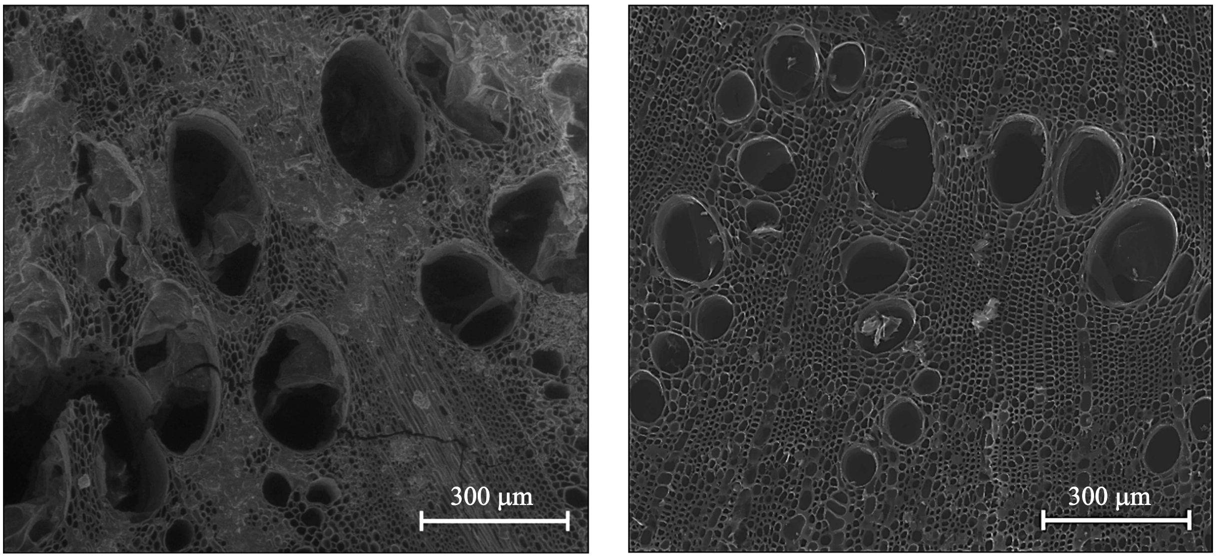

Figure 2. Coal structure: *a* — archaeological specimen, *b* — control specimen.

ceramics, the average values of the H_D/H_G ratio were 0.62 for the dark layer and 0.65 for the light layer. The obtained ratios of the amplitudes of the D and G bands were used to estimate the firing temperature of the studied ceramics. At the same time, a significant discrepancy was revealed in the calculation results based on the general equation proposed in the work [14] and the determination based on the calibration graph given there. Moreover, the latter correspond to the accepted firing temperatures for molded medieval-era ceramics. Probably, in the work [14] there is some inaccuracy in the description of the analytical model of the paleothermometer (the author's name of the method). As a result, the data presented in it (calibration graph) were approximated by the least squares method using the capabilities of the MATLAB software package and the following general equation I$T = f\ (H_D/H_G)$ was obtained:

$$T = 7679x^4 + 390x^3 - 22926x^2 + 21619x - 5092, \quad (1)$$

where $x = H_D/H_G$.

The carbonization temperatures determined on the basis of (1) were $730 \pm 20°C$ and $750 \pm 20°C$ for the dark and light layers, respectively. The expectedly found values have similar values with a slight decrease inside the heat-treated vessel. Certain temperatures correspond to the practice of fire firing used in the XI−XII centuries,both Old Russian and Finno-Ugric settlers in the manufacture of molded pottery.

2.2. Wooden structures

RS analysis of the conditions of carbonization for wood of ancient Russian structures, the remains of which were discovered as part of the defensive earthworks, was carried out taking into account the use of oak logs in their construction [21]. This concept is confirmed by a microscopic examination of coals selected from archaeological material, performed using a Quanta 200 3*D* scanning electron microscope (Fig. 2). Each year ring of oak timber contains characteristic wide cellular tubes that abruptly turn into narrow ones. This structure is clearly visible in a transversal section, is preserved in coal and was identified both in archaeological specimens (Fig 2, *a*) and in coals obtained as a result of control burning-off from pedunculate oak wood (Quercus pedunculata), growing on the right bank of the Klyazma river within the city of Vladimir (Fig. 2, *b*).

As a rule, 900°C [22] is used as a reference value for the maximum flaming combustion temperature of oak wood. The temperature in furnaces, and even more so in crucibles, is much higher due to radiation effects and forced oxygen supply. But for conditions of natural (open) combustion, it should be focused on the specified value.

The characteristic RS of the studied coals from the remains of Old Russian structures is presented in Fig. 3, where a significant difference in the amplitudes of the D and G bands is clearly visible. The average value of the H_D/H_G ratio for this series of specimens studied was 0.5. This corresponds to the carbonization temperature $510 \pm 20°C$. The temperature determined for the studied coals is significantly lower than that accepted as a reference temperature for open burning of oak wood. Thus, they were obviously formed as a result of active smouldering combustion of logs. This situation is possible for wooden structures surrounded by soil on the surface of which there has been a strong fire. In addition, the RS contains a noticeable peak centered around $1740\,cm^{-1}$, indicating a significant content of substances with carbonyl groups (ketones, aldehydes, etc.) in coal. Such compounds should

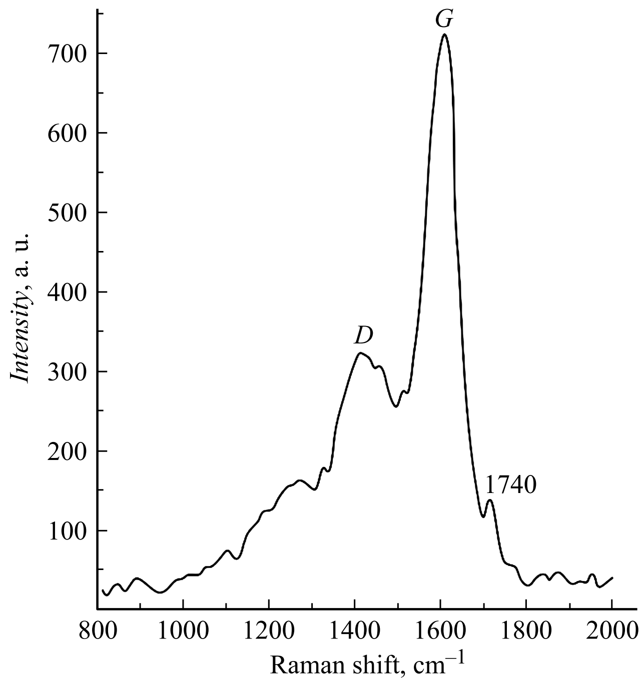

Figure 3. RS of oak coal, from the remains of wooden structures.

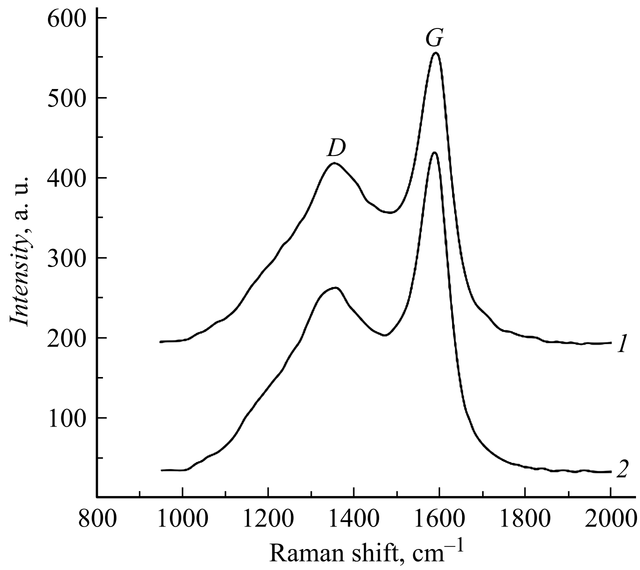

Figure 4. Raman spectra of control specimens: *1* — oak coal, *2* — birch coal.

have volatilized at the high temperature of open combustion, but may be partially preserved during gradual smouldering combustion.

For a comparative assessment of the carbonization temperature of wood under open burning conditions, a control after-burning of coals was carried out using the fire method from oak and birch specimens. Oak was not only a material for important wooden structures of Old-Russian buildings, but also high-quality fire-wood. Birch as a source of fire-wood was also in wide demand due to its wide distribution in Central Russia and its fairly good caloric content. Characteristic RS obtained in the study of control oak and birch coals are presented in Fig. 4.

For control samples of oak coals (Fig. 4, curve *1*), the average value of the H_D/H_G ratio was 0.63 The carbonization temperature determined based on equation (1) was $740 \pm 20°$C. The resulting temperature is less than the specified value, but higher than the reference value. This discrepancy is apparently caused by the fact that in the latter case the maximum illuminance temperature was measured, determined by the glowing of the hottest part of the flame. However, it is obvious that the carbonization temperature of oak wood during open combustion is significantly higher than the value determined for charcoal samples from the remains of a structural timber work.

In addition, in the Raman spectra of control samples, the band of carbonyl compounds centered at about $1740\,\text{cm}^{-1}$ has very low intensity. It appears only in a weak bend at the edge of the contour of the G band. This confirms the concept about the almost complete volatilization of substances with carbonyl groups from the products of wood carbonization during open combustion.

For control samples of oak coals (Fig. 4, curve *2*), the average value of the H_D/H_G ratio was 0.59 This corresponds to the carbonization temperature $690 \pm 20°$C. Reference value of the maximum flame combustion temperature of birch wood is 816°C [22]. The temperature calculated on the basis of equation (1) is also lower than the reference temperature, as for oak coals, which is explained by similar reasons. Moreover, the ratios of temperatures determined using a paleothermometer to the maximum reference temperatures are comparable in both cases. In the Raman spectra of control samples of birch coal, the band of carbonyl compounds is practically not visible, which is explained by both their good volatility and the lower initial content in this wood species compared to oak.

Conclusion

The study of carbonated organics from archaeological materials using RS showed the potential of this approach to confirm or clarify the results of their interpretation. Analysis of the Raman spectra of organic inclusions in species of medieval-age majolica made it possible to estimate the temperature of their carbonization and, consequently, the conditions for firing vessels. The defined temperature is in the range $730-750 \pm 20°$C This corresponds to the crib fire regime for firing pottery. It should be noted that the carbonization temperature determined for control oak coal specimens obtained under open combustion conditions is equal to $740 \pm 20°$C, and also belongs to the above range. Thus, the objectively confirmed crib fire method for firing vessels, together with their obviously rough (molded) execution, indicates that the archaeological site „Stlmt Poganoe (Stlmt Paganets) I“, as the registered location of the studied ceramic fragments, belongs to the category of settlements of local indigenous Finno Ugric (most likely Meryan) population.

Analysis of the Raman spectrum of coals from the remains of wooden structures discovered during the archaeological study of the defensive earthworks revealed the carbonization temperature of wood at the level of $510 \pm 20^{\circ}C$. This excludes open burning of oak logs included in their composition and indicates carbonization in the smoldering mode. Such a process could only occur when wooden structures were surrounded by mineral soil at the time of their destruction by burning. The internal filling of log constructions with soil or stones was used in the construction of such elements of Old-Russian defensive structures as Gorodnya (i.e. fortification) [23]. Consequently, the conditions for the implementation of the smoldering regime were provided for the wall between neighboring Gorodnyas or the outer wall of their system, covered with an earthen embankment.

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Conflict of interest

The authors declare that they have no conflict of interest.

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