Chemical Analysis of Mortars of Archaeological Samples From Mediana Locality, Serbia

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Abstract:
Mineralogical and chemical composition of mortar from the floor, ceiling and wall of Stibadium B, from the archaeological site of Mediana (Serbia) have been analysed using ICP-OES, FTIR and XRD-spectroscopy and chemical analysis. The results show that hydraulic lime mortar was used with crushed bricks as artificial puzzolanic aggregate. Large contribution of silicon- and aluminum-oxides, indicate the presence of quartz and phyllosilicate minerals derived from the aggregate, river sand and crushed bricks. Also, high content of Pb and Cu was observed in investigated samples.

Keywords: Chemical analysis; Archaeological samples; Mediana.

1. Introduction

Mediana is one of the most important sites of late antiquity in South-Eastern Europe. The ancient town of Naissus and Mediana was located in a large valley, which is surrounded by high mountains and traversed by the rivers South Morava and Nišava [1] occupying the central position in the Roman province Dardania [2]. It was formed at the end of the 3rd and the beginning of the 4th century, and in the ancient period it was the largest settlement in the vicinity of Naissus [3]. It is located 3 km from the center of city of Niš, and covers an area of about 40 ha (Fig. 1).

Archaeological excavations of ancient Naissus began Felix Kanitz 1856, and the first serious and organized research began in 1932 under the control of Earl Adam Oršić-Slavetić. In 1961, the excavation works determined the size of the settlements and investigated fewer thermal spas, while systematic excavations during the 1970s and 1980s examined many buildings, such as villa with peristyle, the octagon house, villa rustica, Horeum, castellum aquae. During the period 1994-1996, two complexes of military barracks, economic buildings and necropolis were excavated, and excavations in the period 2000-2007 have revealed two

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early Christian churches, the monumental entrance to the complex of villas with a peristyle and well-preserved bronze railings with Herms of Asclepius and the Luna [4].

Until now no much studies have focused on the characterization of the mortar used in Roman settlement Mediana [5]. The subject of this work was the mineralogical and chemical analyses of collected samples of mortar from Stibadium B located at archaeological site of Mediana in order to provide information on crystalline phase presented and chemical composition (content of principal components, content of trace metals, their distribution between binder phase and aggregates).

2. Materials and Experimental Procedures

2.1. Samples

![Fig. 1. Geographical location of Mediana.](image)

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![Fig. 2. a) Place of sampling, mosaic with geometric and floral motifs in stibadium B, b) A schematic representation of a villa with a peristyle with a marked position of stibadium B.](image)

Fig. 2. a) Place of sampling, mosaic with geometric and floral motifs in stibadium B, b) A schematic representation of a villa with a peristyle with a marked position of stibadium B.
Samples were collected from Stibadium B (Fig. 2) located on the northwest side of the villa with peristyle. It occupies an area of about 50 m², and its research was started in 2010. Stibadium B with Stibadium A with some rooms and the thermae heighten the privacy and representativeness of the imperial villa, were added during the second phase of construction, between 330 AD and 378 AD [6]. Central room has almost circular shape, circa 7 m in diameter and with floor covered with high quality mosaic [7]. Mosaic with geometric and floral motifs in stibadium B is fully unveiled in 2011 when preventive protection was done. Numerous glass mosaic cubes indicate decorating of the vaults, and perhaps the walls of stibadium [8]. After collection, all samples were dried at 40 °C for at least 12 hours, with exception of the samples for chemical analysis, which were dried at 105 °C. In Fig. 2 is a schematic representation of a villa with peristyle, and stibadium B is designated as 2b. Mortar samples are shown in Fig. 3.

![Mortar samples](image)

**Fig. 3.** a) sample 1 – mortar from the floor, b) sample 2 – mortar from the ceiling, c) sample 3 – mortar from the wall of Stibadium B

### 2.2. Fractination procedure

Chemical analysis of the mortars was performed following the procedure defined by Alvarez et al. (1999) to separate binder phase from aggregates [9]. Despite the described method, hot hydrofluoric acid (HF:HCl, 3:1 w/w, hot-plate open beaker digestion procedure with Teflon beakers) was used to dissolve siliceous aggregate phase. After digestion, diluted fractions were analyzed by atomic emission spectroscopy with inductively coupled plasma.

### 2.3. Inductive coupled plasma-atomic emission spectroscopy (ICP-OES)

The concentrations of metal ions from the solvent residue were determined by the ICP-Optical emission spectrometer series iCAP 6000, Thermo Scientific, Cambridge, United Kingdom. The content of the elements is verified in accordance with the ULTRA's ISO 9001 registered system by comparison with the standard for calibration independently prepared using the NIST SRM ("Certified Reference Material from the National Institute of Standards and Technology").

### 2.4. Fourier transform infrared (FITC) spectroscopy Transmission method

The FTIR sample analysis was performed using the BOMEM Michelson Hartman & Braun Series MB spectroscope in the range 4000-400 cm⁻¹ at a resolution of 2 cm⁻¹.
2.5. XRD analysis

The samples were grounded in the agate mortar before analysis. XRD method [10] was used for determination of mineral composition of investigated samples by apparatus GNR Explorer, with scintillating counter at a voltage of 40 kV and electric current of 30 mA. The intensities of diffracted CuKα radiation $\lambda=1.540598\,\text{Å}$ were measured at room temperatures in the steps interval of 0.02° 2θ within the range of 4-70° 2θ and with a 2 s measuring time per step. Only crystalline species can be detected by this method and the detection limit is 1-3% (w/w).

2.6. Stereomicroscopic analysis

The samples of mortar were thoroughly observed using Krüss stereo-zoom microscope with Nikon 4500 camera, and maximal magnification of 180 times.

3. Results and Discussion

3.1. Stereomicroscopic analysis

In Fig.s 4, obtained by stereomicroscopic analysis, it can be noticed that all three examined samples are heterogeneous. The binder is bright greyish and having carbonate composition. The structure of the mortar is porous and the limestone fragments are dominant. The fragments of aggregate differ in dimensions, color and roundness. Quartz fragments (river aggregates) are of good roundness. Reddish-to-brown fragments are parts of broken bricks which was common in Roman mortars due to enhancing their hydraulicity [11].

Fig. 4. Stereomicroscopic photographs of samples: (a) mortar 1, (b) mortar 2 and (c) mortar 3.
3.2. Mineralogical analysis

XRD diffractograms of analyzed mortar samples were presented in Fig. 5.

![XRD spectra of analyzed samples: (a) mortar 1, (b) mortar 2 and (c) mortar 3.](image)

**Fig. 5.** XRD spectra of analyzed samples: (a) mortar 1, (b) mortar 2 and (c) mortar 3.
Table I presents the mineralogical composition of the overall samples of mortars determined by X-ray diffraction analysis.

| Crystalline phase | Mortar 1 | Mortar 2 | Mortar 3 |
|-------------------|----------|----------|----------|
| Quartz            | +++      | +++      | +++      |
| Anorthite (feldspar) | +        | ++       | +++      |
| Calcite           | +++      | ++       | ++       |
| Calcite           | +++      | ++       | ++       |
| Biotite (mica)    | +        | +        | +        |
| Hornblende        | -        | +        | +        |
| Chlorite (amphibole) | +    | tr       | tr       |

+++ abundant, ++ moderate, + minor, tr traces, - undetected

The main binding material of the mortars is calcite and quartz is the dominant component of the aggregates. The presence of amphiboles could be related to river sediments [12], while feldspar could be related to the crushed bricks because anorthite forms in the process of burning clay [13]. Diffractogram of mortar 1 shows very weak (104) dolomite peak contrary to mortars 2 and 3 which show completely absence of this crystalline phase.

3.3. FTIR Spectroscopic analysis

The FTIR analysis provides additional information to XRD analysis. The spectra of mortars are shown in Fig. 6.

![FTIR Spectra](image)

The resultant FT-IR spectra of the mortar 1 and 2 are very similar, which indicates that most probably usage of the same type of mortar. The presence of carbonates is characterized by the absorption peaks at 2872, 2920, 2513, 1796, 1440, 874 and 713 cm⁻¹. The band occurring around 1440 cm⁻¹ are from extinct ν₃ asymmetric CO₂⁻ vibrations. The weak band that appears at 1796 cm⁻¹ in all three samples originates from C=O vibration.

The medium intensity bands that appear in the spectra of samples around 1024 cm⁻¹ originate from extensively Si-O-Si vibrations of quartz presented. The bands that appear at
535, 533 and 526 cm\(^{-1}\) refer to Si-O-Al deformation vibrations, while the adsorption maxima occurring about 470 cm\(^{-1}\) refer to Si-O-Mg deformation vibrations. The silicates originate from aggregates, river pebbles, and part of clay minerals incorporated in bricks that are likely to be used to improve binding properties. A narrow band with a peak at 3400 cm\(^{-1}\) represents the O-H vibration of absorbed water \[14\]. These data are in accordance with the XRD results.

3.4. Chemical composition

The main elemental contents of the studied mortars were determined after complete dissolution of 1-g probe of each sample (Table II).

| Sample  | \(\text{Al}_2\text{O}_3\) | \(\text{CaO}\) | \(\text{K}_2\text{O}\) | \(\text{MgO}\) | \(\text{Fe}_2\text{O}_3\) | \(\text{Na}_2\text{O}\) | \(\text{P}_2\text{O}_5\) | \(\text{SiO}_2\) |
|---------|----------------|---------|---------|---------|---------|---------|---------|---------|
| Mortar 1| 8.53           | 38.70   | 2.55    | 3.47    | 0.66    | 2.39    | 0.46    | 43.24   |
| Mortar 2| 11.01          | 28.82   | 3.26    | 2.60    | 1.54    | 1.89    | 0.31    | 50.57   |
| Mortar 3| 9.41           | 50.95   | 2.91    | 0.89    | 0.73    | 2.21    | 0.43    | 32.47   |

A high CaO content indicates that it is lime mortar, with calcium carbonate binder. A low MgO probably originated from silicate minerals presented, suggests that calcite is prevailing carbonate. The largest content of MgO in mortar 1 could be related to presence of dolomite determined by XRD analysis (Fig. 5). \(\text{SiO}_2\) originates mainly from quartz and some silicate minerals which are constituents of river aggregates and minor from silicate minerals used for preparation of bricks. Content of \(\text{Al}_2\text{O}_3\) and \(\text{Fe}_2\text{O}_3\) can be linked to silicate minerals, while the latter is dominantly present in brick fragments. A high \(\text{SiO}_2\), \(\text{Al}_2\text{O}_3\), and \(\text{Fe}_2\text{O}_3\) content was observed in the mortar 2 with larger amount of crushed brick particles, indicating the significant hydraulic characteristics of this mortar. Results are comparable with results of SEM-EDX analyses \[15\] of mortars used for construction of floors of the nearby hypocaust systems.

The contents of selected trace metals in overall samples are presented in Table III compared to the average content of these metals in Earth's crust, limestone, clays and sandstones (material used for mortar construction \[16, 17\]).

| Sample  | Concentrations (ppm) |
|---------|----------------------|
|         | \(\text{V}\) | \(\text{Cr}\) | \(\text{Mn}\) | \(\text{Co}\) | \(\text{Ni}\) | \(\text{Cu}\) | \(\text{Zn}\) | \(\text{Cd}\) | \(\text{Pb}\) |
| Mortar 1| 13.76              | 25.38       | 107.71      | 5.71      | 31.46     | 23.64     | 35.78     | 0.43      | 59.80    |
| Mortar 2| 24.07              | 70.55       | 331.06      | 10.28     | 35.63     | 285.88    | 49.89     | 0.46      | 52.51    |
| Mortar 3| 18.27              | 28.13       | 153.27      | 3.39      | 15.80     | 178.00    | 36.97     | 0.29      | 51.88    |
| Crust*  | 53-60              | 126-185     | 716-1400    | 10-12     | 20        | 25-27     | 52-80     | 0.1-0.2   | 15       |
| Limestone*| 10-45           | 5-16        | 200-1000    | 0.1-3     | 5-20      | 5-10      | 10-25     | 0.04-0.1  | 3-10     |
| Clays* | 80-130            | 80-120      | 400-850     | 14-20     | 40-90     | 40-60     | 80-120    | 0.2-0.3   | 14-40    |
| Sandstone*| 10-60          | 20-40       | 100-500     | 0.3-10    | 5-20      | 5-30      | 15-30     | <0.04-0.05| 5-10     |

*Average content of selected metals \[14, 15\]

From results presented in Table III, it is obvious that the concentrations of almost all studied metals are the highest in mortar 2 which has the highest content of siliceous aggregates (brick fragments). Concentrations of Ni, Cd, Pb and Cu (for mortar 2 and 3) are higher than their average concentration in the compared referent values. The enhanced concentration of Pb could be related to leaching of the remains of a lead pipe which is located in channel discovered at the west of the Stibadium B. Also, enhanced concentrations of Cu, together with Pb, could be originated from leaching of bronze artifacts found in Stibadium B.
Concentrations of Cr, Mn, Co and Cu in mortar 2 are significantly higher than in mortar 1 (2.8; 3.1; 1.8 and 12.1 times, respectively) or mortar 3 (2.5; 2.2; 3.0 and 1.6 times, respectively). The differences could be related to the variety and heterogeneity of the aggregates, but this could not be the only explanation, especially for copper. As, Be, Hg, Mo, Se and Sn have not been detected in the samples.

Dissolution experiment in hot hydrochloric acid was carried out to obtain binder:aggregate ratio and to determine the distribution of trace metals among these two phases. Limestones, which often form a significant part of the aggregate fraction, are easily soluble in HCl. In other hand, while some authors [18, 19] reported that thermally decomposed clay minerals that form brick fragments are soluble in HCl, Alvarez et al. (1999) claimed that reaction time limited to half an hour would avoid the decomposition of clayey sands [9]. So, we can expect that binder phase contain dissolved limestone aggregates, while siliceous aggregate would stay unaffected. Ratio binder/aggregate for mortars 1, 2, and 3 is 65:35, 54:46 and 73:27, respectively.

The results show that most of the tested metals (except Ni, and Pb in mortars 1 and 2) are mainly in the binder phase which prevailed in all samples. Cd is the most likely incorporated into the crystal lattice of the CaCO₃ caused by isomorphous substitution of ions Ca²⁺ (100 pm) of Cd²⁺ ion (95 pm). On the other hand, Cu²⁺ (73 pm) and Zn²⁺ (74 pm) due to the large difference in ionic radii are not subject of isomorphic ion exchange, but are considered to be incorporated during crystallization that happens through decomposition reaction mechanism [20]. Manganese oxides are abundant in soils and soluble in HCl, so it is expected that phase dissolved in HCl mainly contains Mn. Lead, which probably originated from leaching of artifacts, would be rather adsorbed onto clayey materials than incorporated into calcite structure.

4. Conclusion

In mineralogical terms, the mortars are primarily composed of quartz, calcites and phyllosilicates. Minor components include feldspars, amphiboles. They are lime mortars supported with crushed bricks added as artificial puzzolanic materials to improve...
hydraulicity, which was characteristic for Roman mortars when the geological environment was lacking in this natural component. The enhanced concentration of Pb and Cu could be related to leaching of the remains of a lead pipe which located in channel discovered at the west of the Stibadium B and bronze artifacts found in Stibadium B, respectively.

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5. References

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Садржај: Анализирани су минералошки и хемијски састав малтера са пода, плафона и зидова Стибадијума Б, са археолошког налазишта Медијана (Србија) коришћењем ICP-OES, FTIR и XRD-спектроскопије и хемијских анализа. Резултати показују да је коришћени кречни малтер садржао ломљену опеку као вештачки пуцолански агрегат. Велики садржај оксида силицијума и алуминијума указују на присуство кварца и агломератних агрегата. Такође, у испитаним узорцима уочен је висок садржај олова (Pb) и бакра (Cu).

Кључне речи: хемијска аналзиза, археолошки узорци, медијана.