Instrumental Analytical Techniques Applied to Old Gate Tower from Corvins’ Castle

R M Ion¹,², S Tincu³, I Minca¹, I D Dulama⁴, I A Bucurica⁴, M L Ion⁵ and A I Gheboianu⁴

¹ National R&D Institute for Chemistry and Petrochemistry – ICECHIM, Research Group „Evaluation and Conservation of Cultural Heritage“, Bucharest, Romania.
² Valahia University of Târgoviște, Doctoral School of Materials Engineering, Târgoviște, Romania;
³ Corvin’s Castle, Hunedoara, Romania.
⁴ “Atelierul de Creatie” NGO, Bucharest, Romania.
⁵ Multidisciplinary Science and Technology Research Institute of Valahia University of Târgoviște - ICSTM-UVT, Târgoviște, Romania.

*E-mail: rodica_ion2000@yahoo.co.uk

Abstract. Nowadays, a better understanding of the factors (including environmental) that influence the degradation of materials from different buildings and monuments, is absolutely necessary. In this paper some analytical techniques, as Fourier Transformed IR Spectroscopy (FTIR), X-ray diffraction (XRD), X-ray fluorescence (XRF), optical microscopy (OM) and SEM-EDS, have been used for evaluating the structure and chemical composition and the characterization of the degradation products, causes and mechanisms of disintegration / degradation of materials and aging processes. Few samples from the Old Gate Tower of the Corvins’ Castle, Hunedoara, have been collected and subjected to be analysed and fruitful conclusions have been obtained referring to the raw materials provenance and weathering / deterioration processes which they supported. Similar minerals with those identified at the other towers from Corvins’ Castle have been evidenced: quartz, calcite and dolomite, being majority, and additional apatite minerals. Also, ion chromatography could be used to identify the presence of different ions, responsible for the accelerated process of the monument’s walls.

1. Introduction

Known as one of 10 most beautiful castles in Europe, the Corvins’ Castle was built in 1446, over the site of an older fortification, the orders of John Hunyadi (in Hungarian: Hunyadi János, in Romanian: Iancu or Ioan de Hunedoara). Built in a Renaissance-Gothic style Corvin Castle, the castle is recognized as an imposing structure with eight towers, colourful roofs and many balconies adorned with sculptures and embroidery in stone [1]. The castle is flanked by 4 rectangular towers and 3 circular towers, which is considered an innovation for the military architecture of the 15th century Transylvania [2-4]. The castle has two bridges, two platforms, 42 chambers and is built on an area of 7000 square meters. The main entrance into the castle contains a wooden bridge, sustained by 4 massive piers built of dolomite limestone blocks, with crenels at the top. Also, the external yard was added during the 17th century used for administration and storage [5]. The castle contains 8 towers: 2
of rectangular shape and 6 with circular shape. The rectangular towers (the old gate tower, the new gate tower), are placed in the northwest and southeast areas of the castle.

The Old Gate Tower is located in the south-eastern part and was built during the time of Ioan de Hunedoara. With a rectangular form, with two levels of defense that superimpose the access corridor, it had the last floor provided but battlements and its exterior was covered by a painting with geometric motifs, of German origin. The entrance to the tower was blocked by the construction of the White Tower in the days of Prince Gabriel Bethlen.

The castle in the XVIth century was one of the few civil constructions, built from this part of Europe. Now, the Old Gate Tower has brick and brick vaults with missing bricks, dislocated and the stone floor is damaged.

Consideration is given to sanitation, cleaning, filling, roasting, undoing of cement plaster and repairing them with breathable plaster and paint based on lime, painting restorations, carpentry repairs, wood ceiling restoration works, and overhaul.

Whereas the New gate tower has been partially characterized in our previous studies [6], the Old Gate tower has never been characterized and evaluated from compositional, structural or morphological point of view. From this period there are few civil constructions, identified in the old tower area of the gate on the occasion of the last restoration works. Consideration is given to sanitation, cleaning, filling, roasting, undoing of cement plaster and repairing them with breathable plaster and paint based on lime, painting restorations, carpentry repairs, wood ceiling restoration works, and overhaul. total installations, renouncing gas heating and switching to electric heating.

The purpose of this work is to study some samples taken from the Poarta Veche Tower, Figure 1, in order to identify the origin of the raw materials, possibly from the exploitation of natural resources in this area and to highlight the processes and mechanisms of alteration / deterioration of this tower. For this purpose, sensitive analytical techniques were used such as: FTIR, WDXRF, XRD, OM SEM-EDS and, ion chromatography, and their results will be discussed in detail.

2. Experimental part
2.1. Materials
The samples received from archaeologists are only stone samples, they are degraded, as shown in Figure 3. These samples are samples detached from the tower, without heritage value, they can no longer be reused.

2.2. Equipments
For X-ray diffraction (XRD) analysis, a X-ray diffractometer Rigaku Ultima IV (Cu anode (2 kW) as X-ray tube, detector of NaI) has been used. A PDXL 2.2. (processing) software has been used for data processing.

For X-ray Fluorescence Spectrometry (WDXRF) has been used a Supermini200 - Rigaku as a Benchtop sequential spectrometer, wavelength dispersive with a PC-controlled system and equipped with solid and liquid sample accessories.

For Fourier-transformed infrared spectroscopy (ATR-FTIR) a Vertex 80 spectrometer (Bruker Optik GMBH, Germania) has been used, with DRIFT technique. All the measurements have been recorded over the range 4000-200 cm⁻¹.

For microscopic analysis, the optical microscopy (Primo Star ZEISS, with transmitted light and magnification 4X - 100X) and Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) (SU-70 (Hitachi, Japan), have been used.

These microscopic techniques allowed both a clear and sensitive image of the samples, and an elementary analysis of them was allowed.

Ion chromatography was performed using a Dionex ICS-1000 ion chromatograph, with an Ion Pac AS14A Dionex anion column, equipped with a Dionex ASRS-ULTRA suppressor. The analyses were performed on a solid sample in water solution.
3. Results and discussion

The Hunedoara region is located in the Southern Carpathian area, and from a geological point of view, it is composed of sediment-volcanic units and sedimentary formations such as: limestone, marl, clay shale, conglomerate, sandstone, magmatite (basalt), chert, andesite and pyroclasts [7,8]. From a mineralogical point of view, it contains mostly quartz and dolomite, with K-feldspar, plagioclase, biotite, muscovite, garnet and various opaque minerals. Apart from these, the presence of the apatite is noted, which could be an explanation for the sustainability of this monument as a whole. The apatites are present in this area as minerals that accompany gold deposits and are recognized as good stabilizers and antimicrobial agents [9-11].

The stone from the Old Gate Tower, is differently coloured with aspect that varies from different shades of grey to reddish, due to the deposits of ferrous minerals; also, are visible the alteration changes caused by the weather or possible restoration processes carried out over time and about which not much details are known.
The whole composition of the stone present in this tower, should be evaluated by using different analytical techniques, in order to offer to the restorers, the solution of the new compatible that should be used.

In order to determine the main chemical components from the investigated samples, FTIR analysis have been recorded (Figure 2), and led to the following composition, Table 1.

**Table 1.** The FTIR bands and assignments for the Old Gate Tower samples.

| FTIR band, cm\(^{-1}\) | Assignment                        |
|-------------------------|-----------------------------------|
| 1088-1092               | quartz                            |
| 796                     | Si-O (stretching mode)            |
| 777-783                 | Si-O (symmetrical stretching)     |
| 692-694                 | Si-O (bending modes)              |
| 752-758                 | Feldspars                         |
| 646                     |                                   |
| 465-471                 |                                   |
| 1400                    | calcite                           |
| 900–1000                | SO\(_4\)\(^2-\) (most probably from gypsum, that could overlap each other in the region) |
| 560 - 600               | PO\(_4\)\(^3-\) (apatite [12])    |
| 1000–1100               |                                   |
| 630                     |                                   |
| 868                     |                                   |
| 397                     | CO\(_3\)\(^2-\) (apatite [12])    |
| 1799                    |                                   |

![Figure 2. The FTIR spectra of Old Gater Tower samples.](image)

XRD indicates mostly the presence of dolomite, calcite and quartz, with small amount of illite, muscovite, paragonite, montmorillonite, wonesite, feldspars, chlorite and some clayey raw material:
whitmoreite, kornelite, micas and other heavy minerals. Also, hydroxyapatite was identified, too and recognized by the used analytical techniques (Figure 3).

Figure 3. XRD diagram for the stone collected from the Old Gate Tower.

Except the above-mentioned minerals, mica, zircon and titanite could be identified by the XRD analysis, but in very low concentration, such result being in agreement with those expected to Gneiss stones mentioned by the literature [13], known as a common and widely distributed type of metamorphic rock. Gneiss is formed by high temperature and high-pressure metamorphic processes acting on formations composed of igneous or sedimentary rocks. Gneiss nearly always shows a banded texture characterized by alternating darker and lighter colored bands and without a distinct foliation.

XRD indicates mostly the presence of dolomite (25%), calcite (23.6%) and quartz (42.8%), with minor amount of other minerals (ankerite, illite, orthoclase, halloysite, celestine, anglesite, cerussite, zircon, rutile, ilmenite) and some clayey raw material (whitmoreite, kornelite, micas). Furthermore, this sample also contained feldspars - orthoclase visible by XRD. The presence of apatite is visible and marked in the area 2 theta = 28-30 degree), Figure 3.

The XRF of this sample (Table 2) coincides with the FTIR analysis, showing high amounts of CaO and SiO2, present in many of the minerals presented above.

Table 2. XRF analysis of the sample from Old Gate Tower.

| Component | Result (mass%) |
|-----------|---------------|
| MgO       | 13.995        |
| Al2O3     | 7.0008        |
| SiO2      | 37.7993       |
| P2O5      | 0.4317        |
| SO3       | 1.9603        |
| Cl        | 0.0688        |
| K2O       | 1.1202        |
The WDXRF results put into evidence the existence of P2O5 and Cl− SO3 and K2O most probably related to the hanksite and gypsum (as basanite, which is generated during the transformation of anhydrite into gypsum, possibly due to poor baking and the climatic factors that occurred in time). Also, a high amount of calcite is obtained, followed by halloysite and celestine and sand, due to its use in some restoration works.

Also, some information regarding not only the internal morphology that developed in antiquity, but also the extent of the vitrification (the glassy phase) has been obtained by optical microscopy. The presence of porous structure is visible by OM and SEM-EDS (Figure 4) [14, 15].

![Figure 4. OM and SEM images of the samples collected from Old Gate Tower.](image)

In the obtained images, it is visible a whitish structure, with a roughly round shape, with multiple openings, porous that seems detached from the basic structure. These can be attributed to
hydroxyapatite, also identified by the disordered structure as agglomeration of particles of different sizes and morphologies, visible in SEM images.

Also, the gypsum is visible in images, as an advanced state of deterioration, by the dark areas, and also the calcite, through the hexagonal structures present near the gypsum areas.

From all these analytical techniques, different minerals present in the samples taken from this tower could be identified, and even though each technique partially identifies different minerals, depending on its performance and sensitivity, it is important that all these data be corroborated in order to provide solutions for an optimum and viable conservation procedure.

Thus, the EDS technique (Figure 5) revealed high iron concentrations, which leads to the conclusion that there are ferrous mineral reserves in this area (a fact well known and reported in the literature [7]), and these can be corroborated with the reddish aspect observed by the OM technique. The stone samples from Old Gate Tower are in open areas and are vulnerable to physical, chemical, mechanical and biological weathering, irreversibly affecting their structural properties and aesthetic aspects. Atmospheric conditions and atmospheric pollutants have led to a complex process of aging of the stone. Different forms of stone degradation, such as black crusts, efflorescence and discoloration could be identified by the presence of salts in the form of sodium sulphate, which is recognized as one of the most destructive agents in porous stones [16]. The gypsum and halite crystals generated inside the porous stones of the building lead to the destruction of the basic structure of the stone, on the one hand due to the internal pressure induced by the newly formed compounds, and because of the shrinking of the pore space it is [17]. The qualitative and quantitative identification of the different anions responsible for the alteration and degradation of the stone was obtained by ion chromatography, Table 3.
Figure 5. EDS analysis for the Old Gate Tower.

Table 3. The anions concentration of the investigated soil (in mg/l).

| Anion     | Concentration (mg/l) |
|-----------|---------------------|
| F         | 0.014               |
| Cl        | 0.137               |
| NO₃⁻      | 0.134               |
| PO₄³⁻     | 0.08                |
| SO₄²⁻     | 0.847               |

The white spots found on some samples indicated efflorescence, an alteration caused by NaCl (high concentration of chlorine anion), identified by the ion chromatography technique, in agreement with the literature [18]. Also, the highest concentration of sulphate anions, is a good indicator for gypsum present here, also responsible for degradation processes occurred at this monument.

4. Conclusions

In this paper, an archaeometry study of some samples from the Old Gate Tower, Corvins' Castle was analyzed. Through the used analytical techniques were identified: the origin of the raw materials, of the natural resources and highlighted the processes of alteration and deterioration of these samples, as well as their causative factors. Sensitive and performant analytical techniques, such as FTIR, WDXRF, XRD, microscopic techniques such as OM and SEM-EDS, in conjunction with ion chromatography data, have led to the elucidation of mineralogical composition, structure, but also degradation forms, which affect stability and durability of the monument. All these data will optimize the restoration and preservation of the monuments, preserving our cultural heritage.

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