

Attribution Testing of Marble Statuary

Arminas ŠTUOPYS^{1*}, Algimantas ŠPOKAUSKAS²

¹Department of Building Materials, Kaunas University of Technology, Studentų 48, LT-51367 Kaunas, Lithuania

²Institute of Thermal Insulation, Vilnius Gediminas Technical University, Linkmenų 28, LT-08217 Vilnius, Lithuania

Received 10 September 2007; accepted 08 November 2007

During the archaeological research of some XVI – XVII century possessions' of Kaunas old-town there were found marble statuary fragments and architectural decorations' elements. The aim of the present research was to prepare assumptions for the study of art and historical research of the discovered statuary and architectural decoration elements. It was important to determine mineral composition of the historical statuary fragments, as well as to analyse and describe weathering processes of their rock and to determine the original location of statuary raw materials. The majority of identified statuary fragments were chiselled from marble and some, supposedly, architectural decoration elements, from dolomite of foreign origin. Because of the lack of comparable marble and dolomite rock samples the determination of the discovered statuary fragments' raw rock's original locations (quarries) was impossible. The research results confirmed the assumptions about presence of rock in the surface cultural soil layer for a long time. The results of analysis of soil found in the statuary fixing hole proved that the statuary laid in the soil of Kaunas city or its regions. The results of instrumental research have not answered to the main question – who is the author of the broken statuary and in which historical period they were chiselled. The search of these answers is a task for qualified experts of study of art and purposeful historical-archival approach of analysis.

Keywords: marble statuary, X-ray diffraction analysis, FTIR analysis, calcite, illite, chlorite, dolomite, lime mortar.

1. INTRODUCTION

Almost 25 years ago, in the eastern part of the 6th block of Kaunas old-town were provided archaeological diggings of some XVI–XVII century possessions' area which is almost not destroyed by town expansion. Providing the diggings there were excavated very interesting findings. Such findings, exploring Lithuanian old-towns, were found for the first time. In one of the stone house basements, swamped with garbage, scrap and soil, marble statuary fragments and architectural decorations' elements were found. Some of them are quite big and good enough persisted, some are especially small-sized, badly damaged and considered as unidentified purpose debris (see Fig. 1). Unfortunately, thus far statuary remains, held in the museum storage, were not researched neither on the aspect of materials science, nor on study of art. The following article is the consideration of the first before-mentioned research results.

The reports of archaeological and historical researches state, that judging from the remains of settlement pottery and formed aggregate layer stratigraphy, found in the original location, the statuary were brought here not later than in the third quarter of the XVII century [1]. However from the end of XVI century until the early XVII century this building belonged to people, whose social status raises doubts if they could decorate their home with such pieces of art. Therefore the question is who are the real owners and authors of those statues and when they were sculptured. Historians relate the destruction of statuary with Russian army that occupied Kaunas in the middle of XVII century. Some parts of the statuary are sooty. This fact proclaims fire traces, therefore it already may be impossible to identify statuary owners. Besides, the

question about the statuary attribution from viewpoint of authorship or at least historical period is not answered yet. In this instance there are two possibilities: to concede the statuary as original creations of Roman Empire period or (what is more presumable) to consider, that they have been sculptured in XVI–XVII century by Italian masters or counterfeiters of Antiquity art ware [2].



Fig. 1. Statuary fragments and architectural decoration's elements

The aim of the present research is to prepare assumptions for the study of art and historical research of the discovered statuary and architectural decoration elements. For the following purpose it is important to determine mineral composition of the researched fragments, as well as to analyse and describe weathering processes of their rock and, if possible, to determine the original location of statuary raw material (materials). With reference to the following and other discovered attributes it is also important to classify all the material supplied by the archaeologists. Another aim of the following research is a

*Corresponding author. Tel.: +370-686-08874; fax.: +370-37-300465.
E-mail address: arminas.stuopys@ktu.lt (A. Štuopys)

search and the initial evaluation of the specific features and signs of the historical events (destruction, statuary carriage or portage, conditions of stratification in the cultural stratum) of the attribution of the important pieces of art (sculpture technique, structural technology and, in case of success, historical period). Besides, providing the following research it was pursued to verify the assumptions about the specific techniques of marble protection used by the sculptors or statuary owners. It seemed likely, that they processed (impregnated) the surface of the artwork with wax, oil or other natural materials.

Performing the research, statuary attribution task was aggravated because of the lack of comparable marble rock examples from different quarries (stone plants). The first step in performing similar researches and in building restoration practice is the determination of rock origin [3]. The lack of comparable marble rock examples allowed to reduce the amount of necessary research and to narrow down the methodology by choosing X-ray diffraction (XRD), Fourier transform infrared (FTIR) and atomic emission spectroscopy techniques, which are traditional and reliable in archaeological and preservation work [4–6].

2. EXPERIMENTAL

2.1. The object of the research

Among the archaeologists' findings there were remains of relatively well persisted but split male bust (see Fig. 2), underneath fragments of pedestal, badly damaged statuary fragments of two male heads, the remains of lion head relief (see Fig. 3), tiny, unidentified details and, possible, fragments of architectural interior or exterior decoration elements (Fig. 4).

It is baffling, that shaping technique of sculptural men heads and their artistic benefit are different. For instance, the physiognomies and features of relatively well persisted bust and lesser man's head fragment are very realistic, but the details of the third man's head are more similar to stylized or roughcast ones. If to acknowledge the Roman origin of the discovered statuary, aforementioned attributes would show that these statuaries were chiselled not in the same period. Hair forms, the representation of eye-socket details, the roughness of stone surface treatment and other similar details are important features of Roman statuary's. On the other hand, these features may be the eclectic stylistics attestations of the XVI century masters'.

The fixation of relatively well persisted bust details (the forms and decoration elements of armour pieces, as well as fibulas), especially realistic hairstyles and beard characteristics could be a researches' object of study of art. The compositional principle and shaping of extant lion's head fragments gives the presumption, that these fragments were a part of a bigger sculptural group (for instance, of separate pan or big relief, or perhaps of statuary pedestal).

2.2. The methods of the research

A list of statuary marble XRD analysis samples contains 13 positions (see Table 1) – the samples of various statuary parts, architectural details and fragments of unknown purpose (apparently, formerly they were artefacts), mortar remains, which were adhered to statuary

bearing parts, and soil (dirt). The total amount of the performed XRD patterns was several times bigger, because XRD patterns of some samples were made 2 or 3 times. Besides, several samples were taken from the majority of XRD analysis objects.



Fig. 2. Three-pieces remains of the split male bust

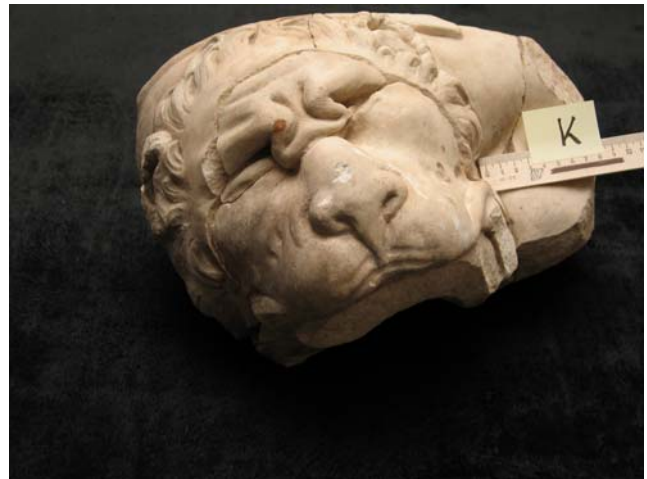


Fig. 3. Remains of the lion head relief [7, 8]



Fig. 4. Pieces of the decoration elements

XRD analysis of powdered samples were performed with a diffractometer DRON-5 (Cu anode, Ni filter, $U = 30$ kV, $I_a = 8$ mA – 10 mA). The rotation speed of the samples was (1–2) $^\circ$ /min. It was expected to identify the mineral

composition of the statuary, all discovered fragments and scurf. Chemical methods were used as auxiliary methods of XRD analysis, id est, rock samples were melted in the solution of the hydrochloric acid of 1 N concentration. Thus scurf and filtrate components were extracted and then processed with the solution of ammonia.

Some pieces of lesser statuary debris were analysed by methods of qualitative optical emission and Fourier transformed infrared (FTIR) spectroscopy.

The aforementioned debris were researched with a spectrometer Spektrum GX FTIR System and spectrograph ISP-28 using standard sample preparation techniques. The analysis was performed in order to find the evidence of usage of impregnants of organic origin on the surface of statuary fragments. For that reason IR molecular absorption spectral analysis for the surface and inner statuary fragments was performed.

The other task of spectrographic research, supplementing XRD analysis, is to ascertain if the discovered raw rock of small fragments is identical to the one of lesser damaged fragments and to search for specific features of the rock (the traces of heavy and rare metals). Answers to these questions would let to subsume tiny and unidentified purpose fragments to the same sculptural composition. It was expected that they would let approximately define the raw origin of the statuary (the original location of the rock).

Different tasks of the research were determined by different size of XRD analysis objects, their sampling circumstances and condition. These samples may be distributed into several groups according to the size and condition of the represented artefact fragment. Samples, which were sampled from big sculptural fragments, id est, rifted or relatively unbroken men's heads or bust fragments, are the most simple to describe.

Special group of specimens consisted of the following mortar and soil samples: white powder, scratched off of the bearing parts of pedestals, and soil, scratched from the statues' cavities and their fixing holes. The aforementioned samples were sampled from bigger statuary fragments. It was expected that the analysis of specimens will allow to ascertain the method of statuary fixing and their purpose more precisely, because the purpose is not absolutely clear from the inspection of fragments (parts of bas-relief, sculptural compositions fixed in hovels). It was considered that the analysis of one statuary hole contents' will answer to the questions about possibly different stratification places and conditions of these works of art (their fragments).

One more part of the analysed objects' included pretty smaller but obvious artefacts of unknown purpose, id est, the fragments of statuary and architectural details. In this case a mineral composition also had to be determined and, in accordance with the results, the assumptions about fragments' relation with one or another sculpture or architectural detail had to be made.

3. RESULTS AND DISCUSSION

3.1. Results

Performing XRD analysis of statuary fragments' from chemical and mineralogical viewpoint, marble with quartz

and other admixtures (see Table 1, Fig. 5) was identified as statuary raw rock and the decay process of statuary surface was estimated. All identified marble samples have the following characteristics: they contain well crystallized calcite (CaCO_3) and consist of the admixtures of quartz (SiO_2), mica hydration and decay product illite ($\text{KAl}_2[(\text{Al}, \text{Si})_4\text{O}_{10}](\text{OH})_2 \cdot n\text{H}_2\text{O}$) and dolomite $\text{CaMg}(\text{CO}_3)_2$. However, the amount of this rock's deposits insoluble in the hydrochloric acid is small – from 0.7 % to 1.0 % of mass. Quartz and feldspars ($\text{M}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, $\text{MO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$,) (Fig. 6) dominate in the deposits.

Table 1. Mineral compositions of statuary and architectural fragments (in accordance to XRD analysis)

Sample marking	Sample place	Identified minerals
1.	Rifted man's head	Calcite, quartz
2.	The bottom of pedestal fragment	Calcite, quartz
3.	The bottom of another pedestal fragment	Calcite, quartz
4.	The fragment of unknown purpose (artefact)	Calcite, quartz, illite
5.	The fragment of broken bust (presumptive)	Calcite, quartz
6.	Another fragment of the broken bust	Calcite, quartz, dolomite
7.	The fragment of unknown purpose (artefact)	Calcite, quartz, illite
8H	Tiny artefact	Calcite, quartz
9i	Light grey ball of unknown purpose	Dolomite, calcite, quartz
10J	Dark greenish ball of unknown purpose	Dolomite, quartz
11.	Soil scratched from the hole in the bust	Illite, quartz, feldspars, calcite, dolomite, amphiboles
12.	Lime paste traces on the bearing planes of pedestals	Calcite, quartz
F	Small-sized artefact	Calcite, quartz

As it was supposed, white powder, scratched off of the pedestals, were the remains of slaked lime mortar (paste of slaked lime). Clay minerals (illite and chlorites ($\text{X}_m\text{Y}_4\text{O}_{10}(\text{OH})_8$, wherein X is a cation, Y – Al^{3+} , Si^{4+} , $m = 4 \dots 6$) are found in the sample deposits affected by the solution of hydrochloric acid.

Quartz, feldspars, clay minerals, illite and amphiboles ($\text{A}_{0-1}\text{B}_2\text{Y}_5\text{Z}_8\text{O}_{22}(\text{OH}, \text{F}, \text{Cl})_2$, wherein A – Ca, Na, K; B – Ca, Fe^{2+} , Li, Mg, Mn^{2+} , Na; Y – Al, Cr, Fe^{2+} , Fe^{3+} , Mg, Mn^{2+} , Ti; Z – Al, Be, Si, Ti) (Fig. 7) are dominant.

Some analysed examples may be considered as architectural details, fragments of decoration elements of unknown purpose or, simply, artefacts. There are of is more or less finished form, but a determined mineral composition (dolomite with quartz admixtures) shows that if there is any relation to the statuary fragments discovered by archaeologists, they are not related by raw material. A specific feature of the dolomite rock is a small amount of deposits insoluble in the hydrochloric acid. It contains the following admixtures: quartz, feldspars, illite, and chlorites. It was found that the structure of this rock contains comparatively big amount of bivalent iron (Fe). If a solution treated with hydrochloric acid, is affected by

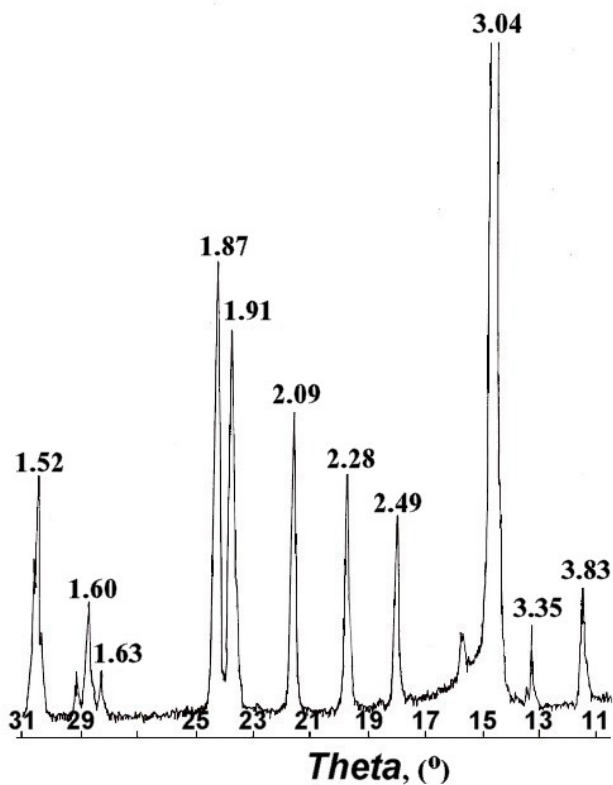


Fig. 5. XRD pattern of marble (calcite + quartz). The interplanar distances are given in angstroms, the intensity of peaks is relative

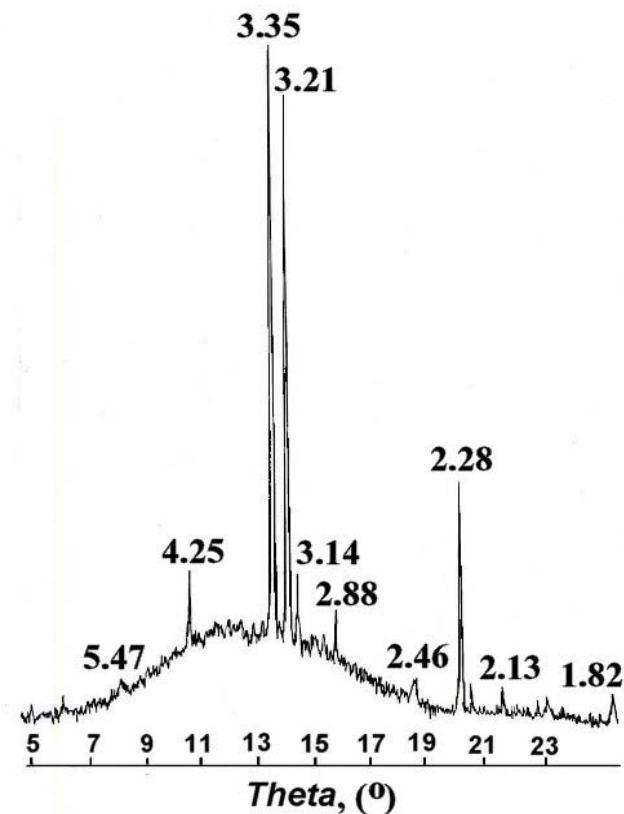


Fig. 6. XRD pattern of the insoluble deposits – peaks of quartz ($d = 3.35; 4.25; 2.28; 2.46; 1.82 \text{ \AA}$) and feldspars prevails in it

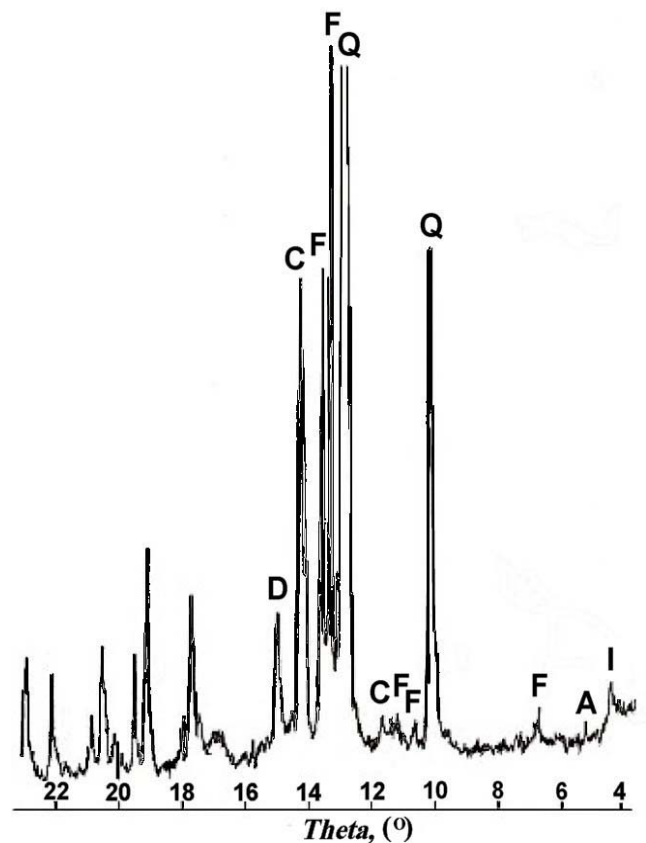


Fig. 7. XRD pattern of the soil (dirt) scratched from the hole in the bust (F – peaks of feldspars, D – peak of dolomite, A – peak of amphiboles, C – peaks of calcite)

ammonia, turquoise deposits of Fe hydroxide fall out. While being kept in air they eventually become brown because of the oxidation of iron (Fe) ions. According to our own experience and experience of some other authors [9; 254], dolomite, found in Lithuanian occurrences, tends to have a smaller amount of iron.

Comparing the IR spectra and spectra of atomic emission of powder of the rock, taken from the surface of debris and chiselled by sculptors, with analogous spectra samples, sampled from the deeper rock layers, qualitative differences were not noticed (Fig. 8). The IR spectra have intensive absorption bands in $1500 \text{ cm}^{-1} - 1300 \text{ cm}^{-1}$ and 875 cm^{-1} regions. With reference to literature data [10], these bands are referable to CO_3^{2-} vibrations. Inconsiderable differences of IR transmittance spectrum in the 3450 cm^{-1} band region are referable to, probably, bigger amount of absorbed water in the surface of the sculpture and changed structure of marble rock (polished by the sculptors hands and affected by the decay processes). Bands of vibrations, exclusively tended to the compounds of organic origin, such as beeswax and various oils (absorptional triglyceride compounds, C–H chains, ester groups' bonds C=O and C–O, bands in $300-2800, 1750-1730, 1300-900 \text{ cm}^{-1}$ regions [11, 12]) were not noticed in the IR spectra of marble fragments.

Analysis of statuary by method of qualitative optical emission showed, that calcium was the predominant one in all fragments of marble statuary. Lesser amounts of magnesium, iron and carbon, as well as traces of copper,

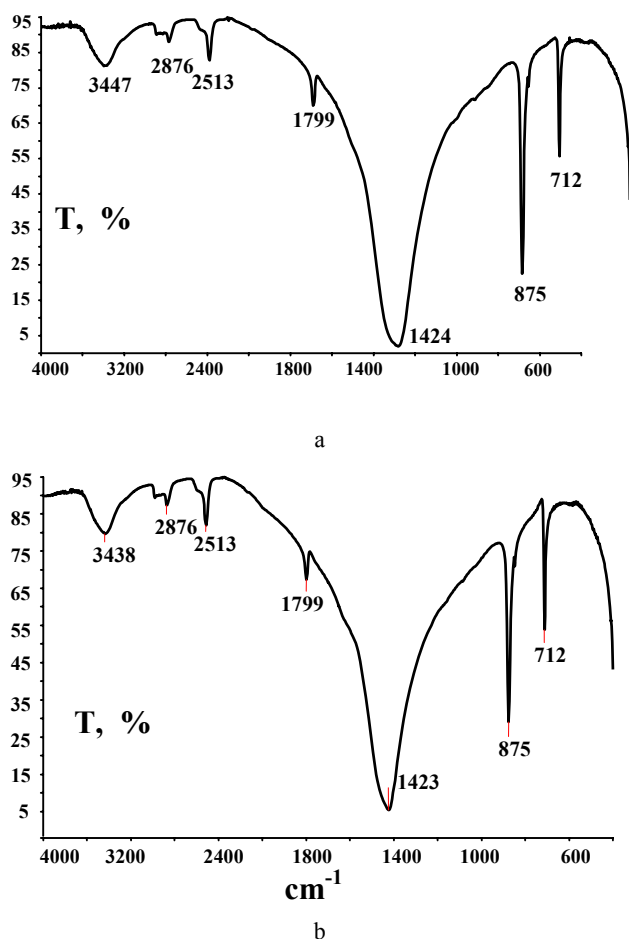


Fig. 8. The transmission IR spectra of the statuary rock: sample taken from the surface of debris (a) and spectrum sampled from the deeper rock layers (b)

aluminium and silicon were also found. Depending on these attributes fragments' rock was identical. Therefore it can be affirmed, that the raw rock of men's bust, shown in Figs. 1 and 2, and the raw rock of tiny fragmentary marble artefacts' of unknown purpose are identical (a sample, split off from the under part of big bust, was used for comparison of statuary raw rock). Probably they belonged to the same sculptural composition, but this proposition should be proved by means of the microanalytical (rare elements) analysis.

3.2. Discussion of the results

XRD and IR spectrometry analysis results show that some discovered fragments were made not from marble. Depending on chemical and mineral composition they can be described as sculptural or architectural (building decoration elements) fragments. Probably the dolomite rock, from which the aforementioned fragments are made, are dug out not in Lithuania.

All other analysed fragments are made from fine crystalline marble, especially appreciable by sculptors, and have quartz inserts (their chemical-mineral composition is defined as calcium carbonate – calcite CaCO_3 and crystalline quartz SiO_2) which are common in this rock composition. The surface of statuary fragments is defiled with clay minerals and other marble decay products. This shows that these fragments contacted with soil, groundwater and its

silt. Calcium carbonate, as basic salt, reacted with acid clay minerals and silicon dioxide melted in water. It confirms the archaeologists' assumption that the statuary laid unwiggled in the cultural city soil layer for a long time.

White powder, scratched from the underneath of statuary pedestal, is lime, which eventually became carbonized (lime calcium oxide reacted with CO_2 melted in water). The lime was quite pure (judging by XRD pattern of the sample) and without any impurities. Probably it was burned from relatively pure carbonates, for instance, the same marble. When lime is burned from carbonaceous rocks, currently mined in Lithuania, it is defiled with admixtures. Besides, mortar of thick slaked lime was used for statuary fixing: the pedestals were glued with paste of lime without sand aggregates.

The analysis of data (the composition of soil minerals) of bust fixing holes' content show, that these holes were defiled with a marl loam. It consists of a lesser amount of carbonates, which are common to composition of the Quaternary clay and clay loam in Kaunas city and its regions.

The XRD analysis of surface and deep layers of marble statuary fragments showed only different degree of decay. The method of qualitative optical emission analysis allowed to identify metal impurities in the marble of statuary. This may be useful in the future while comparing marble samples from different quarries.

The data of IR spectrometry confirmed that the basic substance of these fragments' is calcium carbonate (marble). Besides, it can be predicated that the traces of organic materials (impregnants, oil, beeswax and etc.) on the surface of statuary fragments were not found. The IR absorption patterns show that marble particles on the statuary surface are more shredded. It is caused by chiselling and polishing of statuary surface and by already mentioned processes of decay.

The results of the research did not answer to the main question – when and where the statuary was chiselled. Therefore we would suggest to construe it as a basis for future comparisons. With reference to similar researches' results, foremost material for comparative marble researches should be searched. Bigger and less valuable discovered statuary fragments should be used. According to [3] such research should include deeper mineralogical and spectrographic analysis of rock samples, chemical analysis of all elements, determination of stable isotopes and physical rock properties (water absorption, porosity, density and intensity).

Otherwise, while searching for the dating evidence of the historical period, archaeological research material of original location should be revised one more time. It is necessary to perform thorough iconographical analysis of statuary fragments and the analysis of traces left by sculptor's tools (sculpture technique). Certainly, it would be useful to inquire well-known Antiquity – Renaissance art research centres, museums or universities.

CONCLUSIONS

1. The results of instrumental research have not answered to the main question – who is the author of the broken statuary and in which historical period they were

chiselled. The search of these answers is a task for qualified experts of art and purposeful historical – archival approach of analysis.

2. The results of physical and chemical analysis of the statuary fragments identified their mineral composition. The majority of identified statuary fragments are chiselled from marble and some, supposedly, architectural decoration elements, from dolomite of foreign origin. According to the mineral composition the discovered fragments of pieces of art were precisely classified. Because of the lack of comparable marble and dolomite rock samples the determination of the discovered statuary fragments' raw rock's original locations (quarries) was impossible.

3. Statuary and chiselled rocks of architectural purpose contain admixtures and minerals indicating decay processes. The aforementioned facts confirmed the assumptions about rock's presence in the surface cultural soil layer for a long time. The results of statuary hole soil analysis prove, that the statuary laid in the soil of Kaunas city or its regions.

4. The results of the research indicate that the pedestals were fixed to the base using paste of slaked lime. However the traces of marble statuary surface treatment with beeswax or oil were not found. Therefore the hypothesis of statuary surface treatment with wax (compounds of organic origin) is denied.

REFERENCES

1. **Vaškėlis, A., Juchnevičius, A.** Fragments of Marble Sculptures *Monuments of Architecture (Set of Scientific Papers)* 12 1989: pp. 29 – 32 (in Lithuanian).
2. **Kowalczyk, J.** Polish Portraits „all'antica“ of the Renaissance Plastic Art *Proceedings of the Selected Works on Art History (Materials of the Art Historians Session, Gdansk, December 1966)* Warsaw, Państwowe Wydawnictwo Naukowe 1969: pp. 121 – 136 (in Polish).
3. **Galán, E., Carretero, M. I., Mayoral, E.** A Methodology for Locating the Original Quarries Used for Constructing Historical Buildings: Application to Málaga Cathedral, Spain *Engineering Geology* 54 (3–4) 1999: pp. 287 – 298.
4. **Creagh, D. C.** The Characterisation of Artefacts of Cultural Heritage Significance Using Physical Techniques *Radiation Physics and Chemistry* 74 2005: pp. 426 – 442.
5. **Schreiner, M., Fruhmann, B., Jembrih-Simburger, D., Linke, R.** X-rays in Art and Archeology: an Overview *Powder Diffraction* 19 2004: pp. 3 – 11.
6. **Ajo, D., Casellato, U., Fiorin, E., Vigato, P. A.** Ciro Ferri's Frescoes: a Study of Painting Materials and Technique by SEM-EDS Microscopy, X-ray Diffraction, Micro FTIR and Photoluminescence Spectroscopy *Journal of Cultural Heritage* 5 2004: pp. 333 – 348.
7. **Sokolov, G. I.** About Technique of Roman Statuary Portraits *Art of East and Antiquity (Set of Scientific Papers)* Moscow, Nauka 1977: pp.72 – 83 (in Russian).
8. **Becatti, G.** The Art of the Ancient Greece and Rom. London, 1968.
9. **Grigelis, A., Kadūnas, V.** (eds.) Lithuania's Geology. Mokslas, Vilnius, 1994 (in Lithuanian).
10. **Price, B., Pretzel, B.** Infrared and Raman Users Group Spectral Database. The Infrared and Raman Users Group, Philadelphia, 2000.
11. **Rusak, D. A., Brown, L. M., Martin, S. D.** Classification of Vegetable Oils by Component Analysis of FTIR Spectra *Journal of Chemical Education* 80 2003: pp. 541 – 543.
12. **Stuart, B. H.** Analytical Techniques in Materials Conservation. John Wiley & Sons Ltd., Chichester, 2007: pp.118 – 120.

Presented at the National Conference "Materials Engineering'2007" (Kaunas, Lithuania, November 16, 2007)