BIODETERIORATION-INDUCED CHANGES IN THE OPTICAL CHARACTERISTICS OF MARBLE

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ABSTRACT

Various technogenic and microbiological factors affecting the sculptural and architectural monuments produce changes not only in their appearance, but also in the properties, and the optical ones in particular, of their material. This may influence our perception of art objects and even lead to their loss in case of strong or weak but long-lasting effects that can rupture the material. So it is of paramount importance to have timely and comprehensive information on the monument's condition, that will make it possible to take effective measures against harmful influences and prevent its destruction.

The visual examination of the object being protected to evaluate its condition is prone to subjective errors. Therefore application of additional instrumental tools for non-destructive testing and diagnostics of the object's state can minimise probable crude errors and enhance the sensitivity of observations, thus allowing one to take certain protective measures at the early stages of deterioration.

As an instrumental tool for non-destructive testing of the marble surface, we chose reflected light spectrophotometry in the visible light spectral region, that made possible comparison of the measurement results with those of direct visual examination.

The purpose of the work was to study and analyse: spectral dependence's of reflection indicatrix spatial distribution for marble of various origin and biodeterioration-induced changes in marble reflectance.

Materials and Methods

Experimental studies of the reflection indicatrix spatial distribution were carried out on the marble samples from the deposits Pentelic, Thasos and

Carrara. Marble biodeterioration was studied on the samples from deposits in Greece (Pentelic, Attica, Dionysos, Kavala, Thasos, Joannina, Micaena and Epidavros) belonging to the collection of the Oldenburg University. The samples were infected with strain Ch56 fungus cells isolated from the deteriorated monuments of the Chersonessus of the Taurida at an initial surface concentration of $(10^8 - 10^9)$ m^{-2}. The samples were held in a damp atmosphere at 25^0 C.

Experimental Set-Up and Results

The marble reflectance was measured on an experimental unit assembled around a multichannel optical spectrometer for measurements in the visible spectral range from 380 to 700 nm.

The tested sample was positioned on a three co-ordinate translation stage. The probing radiation was delivered to the sample via an optical fiber, whose exit end was placed over the tested portion of the marble surface, so that the incident light flux was normal to the surface and formed a light spot $3*10^{-3}$ m in diameter. Via another optical fiber, the reflected flux was transmitted to the optical spectrometer for spectrum recording. The entrance end of that optical fiber was located close to the tested surface area, its optical axis making an acute angle with the normal to surface, variable in the range from 30^0 to 60^0 with a precision device. The reflection properties of marble samples from different deposits were measured with reference to a diffusely reflecting standard sample. The changes in reflectance of the infected area ($4*10^{-3}$ m in diameter) with respect to that of the non-infected one were observed for 3 months. The reflected light was detected at 45^0 to the sample surface normal.

Figs. 1-3 present spectral dependence's of reflection indicatrix spatial distribution for the marble from Pentelic, Carrara and Thasos. The results are derived from the data obtained on five samples from each deposit.

The reflectance of the infected sample area was measured on 4-th, 18-th, 45-th and 93-d days of the sample infection with fungus cells. The most typical dependence's obtained on the Thasos (Fig. 4) and Joannina (Fig. 5) samples are given and discussed in this work.

Discussion

The incident probing radiation penetrates a certain depth into the tested sample and the light flux is absorbed, reflected and scattered by the grains, microinclusion particles, and binders constituting the marble structure. Fungus spore infection of the marble surface causes additional light scattering and absorption on micromycetes and their activity products. The published data show that the spatial intensity distribution of the light flux reflected from the sample depends not only on the surface microroughness, but also on the size, shape, density of the grains and inclusion particles, optical properties of their material (Toporets [1], Ivanov and Loiko [2]).

The reflection properties of objects have recently come into use for their identification (Guangyou Xu, Hai Hong and Shiqiang Yang [3]).

It may be supposed that the marble from a certain deposit has its individual combination of grains and microinclusions of specific size and shape with perhaps a distinct quantitative relationship between microinclusion particles. So the marble samples from different deposits must have different spectral dependence's of reflection indicatrix distribution. Our earlier data (Evstrapov, Kurochkin and Panina [4]) on the reflectance of the marble from Italy (Carrara), Greece (Pentelic, Thasos), Russia (the Urals) and the Crimea (Proconnessus) prove the presence of individual features in spectral dependence's of samples.

The spatial distribution of reflection indicatrices is a more informative complex estimation of optical properties. Measurements on three marble samples of various origin have shown substantial differences in the spatial distribution of reflectance.

The Pentelic sample (Fig. 1) exhibits high reflectance, the absence of appreciable absorption bands in the visible spectral region at detection angles chosen. In fact, this sample is pure white in color and fine-grained in structure.

Absorption in the blue spectral region in the whole range of detection angles is typical of the Carrara sample (Fig. 2) with medium reflectance. The sample structure is characterized by small and middle size grains. The sample color is greyish as compared to the previous sample. The Thasos sample (Fig. 3) demonstrates rather low reflectance and evident absorption bands in the blue spectral region at large detection angles (50^0-55^0). The marble from this deposit is inhomogeneous a coarse-grained in structure and yellowish in color.

Of course, to make definite conclusions, more detailed studies on samples from many different deposits and more statistical data on the results of investigations are required, but already now it is clear that the spectral dependence's of reflection indicatrix spatial distribution can be used as additional characteristics for marble identification.

The analysis of marble reflectance variation upon infection with fungus spores reveals three kinds of dependence. In more detail, they are discussed elsewhere. Here it may be reasonable to give the most typical ones. The dependence of the first kind obtained for the Thasos sample (Fig. 4) is characterized by an initial (on the 4-th day of infection) decrease in reflectance followed by an increase (on the 18-th day). 45 days later, the reflectance substantially decreases and then slightly increases on the 93-d day. This type of behavior has been observed for the Attica, Pentelic Kokinakos and Micaena samples. Another kind of dependence obtained for the Joannina sample (Fig. 5) is characterized by the tendency of gradual decrease in reflectance in the course of fungus growth. The increase in reflectance (for the first kind of dependence) is an evidence of changes in the tested area of marble: forming of new intermedium boundaries and modification of the old ones, creation of laminated or quasi-film structures, new inclusions and complexes. The fungus development is accompanied by the biomass growth and, hence, by the increase in light absorption of the measured area. Meanwhile, creation of layered and quasi-film structures leads to an increase in reflectance of the tested surface area. Thus, at this stage of infection the resulting reflectance will be defined by the above two effects of one phenomenon of fungus development. A further change in reflectance will be defined mainly by the growth of the melanin-containing fungus biomass, and a considerable contribution to the resulting dependence will be made by the spectral dependence of light absorption typical of melanin. The maximum biodeterioration-induced change in marble reflectance can be observed in the 400 to 500 nm region, that allows persistent detection of the fungus development process on the sample surface. The data obtained 93 days after infection show an ever increasing effect of melanin absorption on the shape spectral dependence. For some samples, the reflectance slightly increases due to some thickening of the quasi-film zone as a result of fungus growth inside the sample. The latter phenomenon is confirmed by visual examination of the infected surface with an optical microscope. Thus, the spectral dependence of marble reflectance is subject to substantial changes (1-1.5) month after infection with fungus spores. The visual examination of the surface is not always adequate because major changes in reflectance occur in the short-wave spectral region where the human eye's sensitivity is low.

To prove the measurement correctness, we performed model experiments demonstrating the existence of the reflectance dependence on the fungus biomass in the measured range. The microamounts of the black yeast model solution were applied on a nitrocellulose membrane with pore diameters of $3*10^{-7}$ m. Upon drying-out, the reflectance of the spots formed on the membrane was measured. In the 400 to 500 nm rang, the obtained dependence of the spot reflectance estimates on the number of particles on the membrane was linear. So the employed reflected light measurement technique ensures correct evaluation of the number of light absorbing particles on the tested area.

This measurement technique furnished with self-powered reflected light spectrophotometric detectors can be used in field applications, that might make much easier the supervision and monitoring of architectural and sculptural monuments and allow diagnostics of biodeterioration of samples at the early stages of infection.

Conclusion

The spectral dependence's of reflection indicatrix spatial distribution that characterize the optical properties, shape and size of structural grains and microinclusions of the sample material may serve as additional parameters for marble identification.

Reflected light spectrophotometric measurements of marble samples make possible the high-sensitivity nondestructive diagnostics of marble biodeterioration at the early stages of infection.

Acknowledgements

This work was supported in part by INTAS, Grant INTAS 93-1659. The authors wish to thank CADIX-(R) Ltd. for assistance at the final stage.

References

1. Toporets A.S. The optics of Rough Surfaces. Leningrad, Mashinostroenie. 1988. P.191.
2. Ivanov A.P., Loiko V.A. The Optics of Photographic Layers. Minsk, Nauka i Teknika. 1983. P.303.
3. Guangyou Xu, Hai Hong, Shiqiang Yang "Detecting and analyzing the body reflection characteristics of objects". Optical Engineering, Vol. 33, No. 1, 3082-3086. (1994).
4. Evstrapov A.A., Kurochkin V.E., Panina L.K. "Spectrophotometric investigation of marble". In: Abstr. International Conference on the Application of Natural Science Methods in Archaelogy. 27-30 November, 1994. St. Petersburg. Vol. 2, 128. (1994).

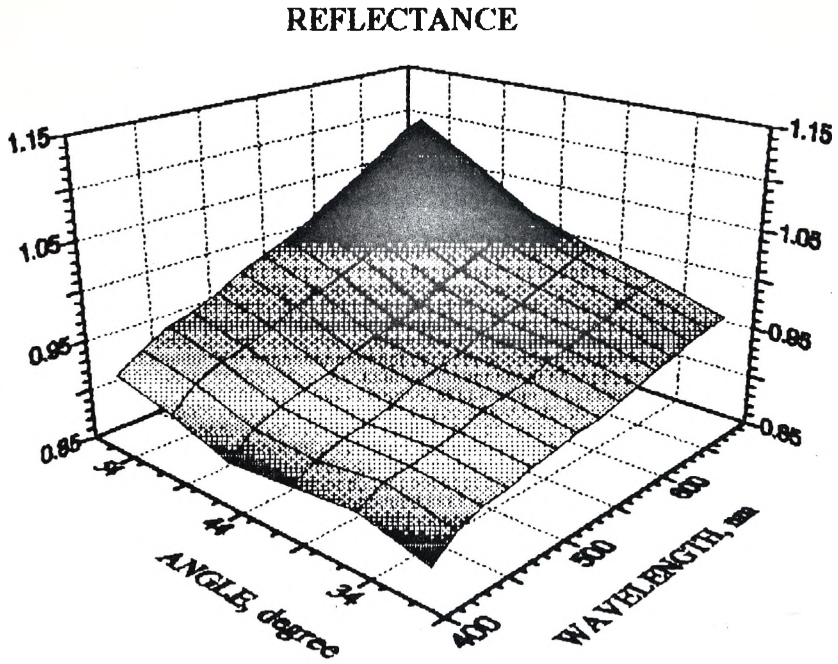

Figure 1
Spectral dependencies of Pentelic marble reflectance spatial distribution

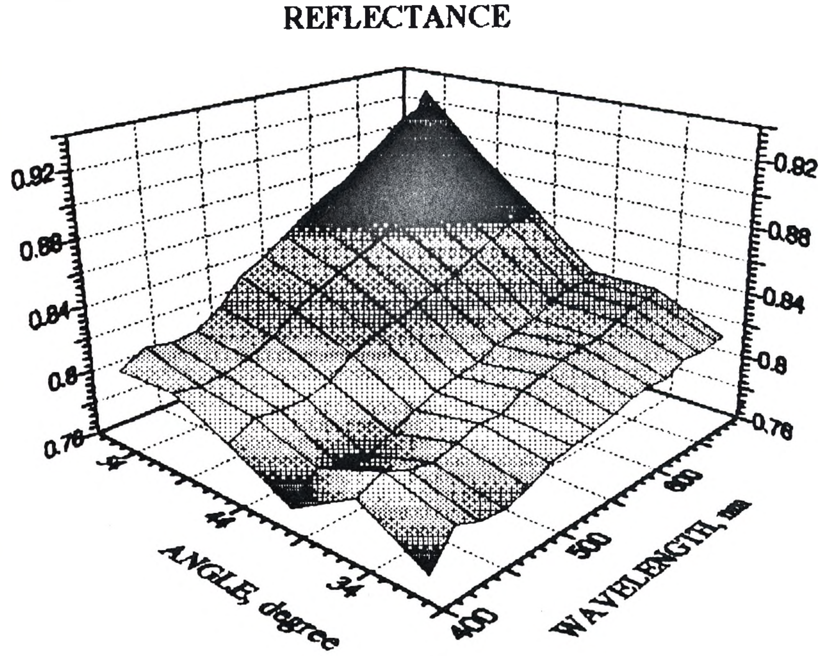

Figure 2

Spectral dependencies of Carrara marble reflectance spatial distribution

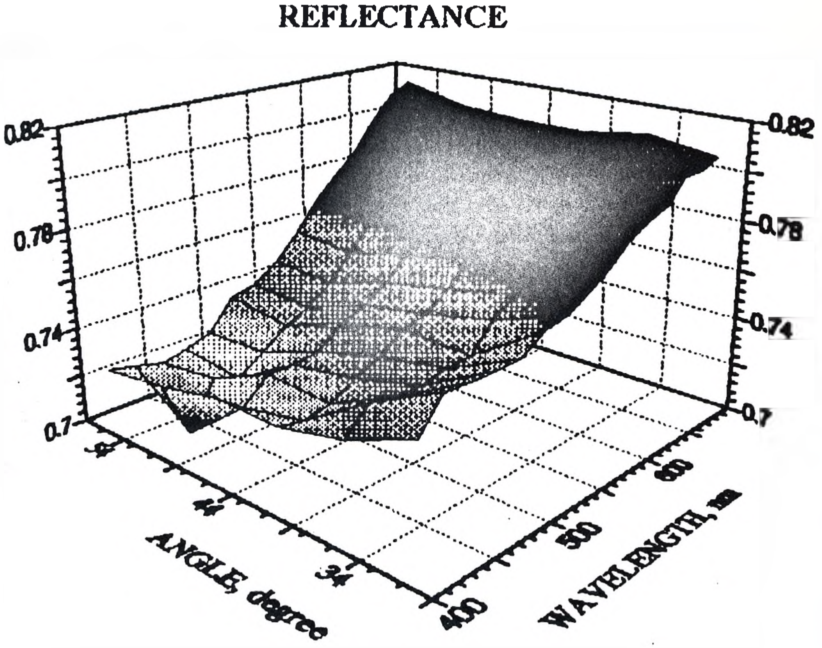

Figure 3

Spectral dependencies of Thasos marble reflectance spatial distribution

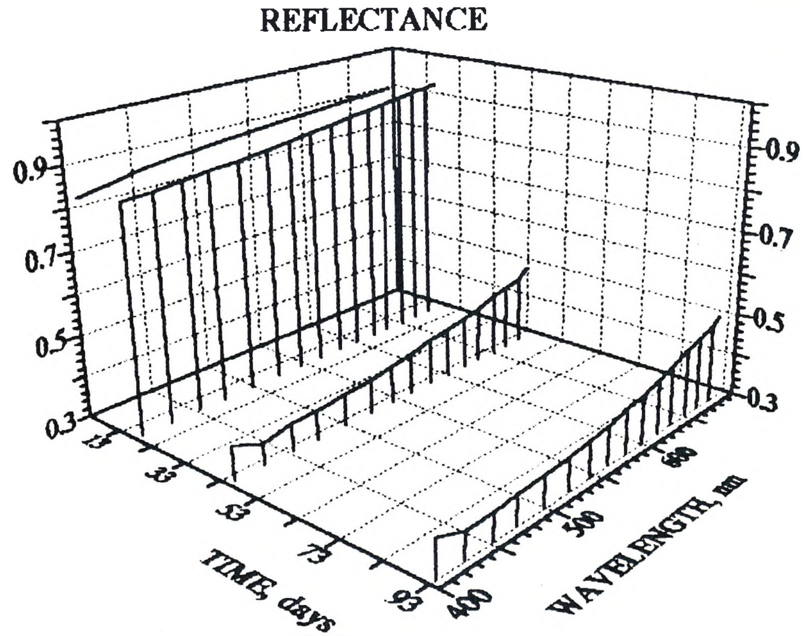

Figure 4
Reflectance spectrum variation dynamics for the Thasos marble area infected with strain Ch 56 fungus cells

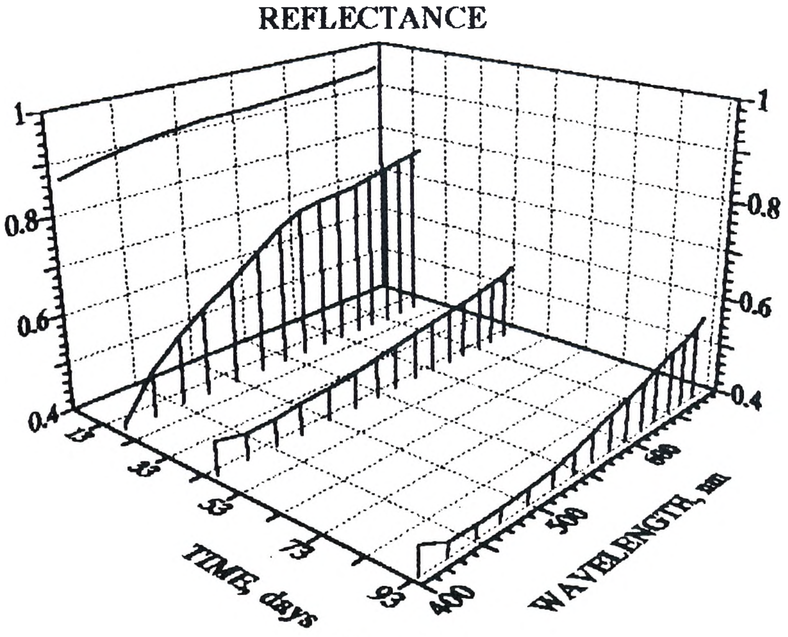

Figure 5
Reflectance spectrum variation dynamics for Joannina marble area infected with strain Ch 56 fungus cells