THE USE OF FT-IR SPECTROSCOPY FOR SURFACE ANALYSIS OF ATMOSPHERIC POLLUTED ANCIENT MARBLES

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ABSTRACT

Fourier Transform Infrared (FT-IR) spectroscopy is a widely used technique for structural and compositional analysis of inorganic, organic and polymer samples. In this preliminary work we used FT-IR spectroscopy to investigate the effects of air pollutants on the surface of ancient marbles. From vibrational spectral analysis it was clear the presence of sulfur compounds on the surface of marbles. The bands at 518, 1038, 1420 and 2515 cm^{-1}, are due to the absorbance of the groups S-S stretching, S=O and/or carbonate stretching, sulfoxide bond, sulfuric ester and free thiol, correspondingly, while the band at 608 cm^{-1} is assigned to scissoring mode of $-SO_2-$ group. From the strong band at 1630 cm^{-1} it was also indicated the effect of nitrate or amide pollutants on marbles. Furthermore, the strong band at 1316 cm^{-1} is attributed to the presence of carboxylic groups and arises from C-O coupled with an O in-plane deformation vibration. This is an important finding since it seems that this carboxylic compound was included in the materials, which were used from ancient Greeks for treatment of marbles. From the above data it is well established that the compounds that were found on the surface of the marbles come from pollutants emitted from cars, petroleum refineries, such as SO_2, NO_x, hydrocarbons, etc.

INTRODUCTION

A great deal of knowledge has accumulated on pollution of marbles of ancient monuments. Several techniques have been used until today in order to study the surface deterioration of ancient monuments[1]. The atmospheric gasses and air contained particles interact with the surface of the marbles, and thus contaminate them. It is well known that the greatest danger for the historical monuments is weathering and air pollution. Weathering effects on the marbles of monuments could change their physicochemical and mechanical properties. These properties are related to the chemical and structural changes which in turn correspond to spectroscopic changes that could be followed by monitoring their spectra.

In this work we report preliminary experiments obtained by Fourier Transform Infrared spectroscopy (FT-IR) on white marbles as well as polluted marbles taken from ancient monuments. The majority of Greek monuments were constructed from natural white marbles, in particular the pentelic marbles. We endeavor to investigate the phenomenon of weathering and environmental pollution on the white marbles and in particular to measure the impact of the pollution of the air on the aging of the buildings, starting with Acropolis, humanity's patrimony.

EXPERIMENTAL

Materials

The materials were obtained from ancient marbles (Acropolis, Eleusis, etc.). The white marble from Penteli, as a reference, was obtained from a dealer in Athens. The samples have been powderized in an agate mortar and used as such. The DRIFT method or the method of pressed pellets with KBr or KCl have been used in order to have transparent discs and to record their spectra.

Infrared spectroscopy with Fourier Transform

The infrared spectra were recorded with a BOMEM MB100 and BOMEM MB150 Fourier Transform Infrared spectrophotometer. 100 scans were used for each spectrum and the resolution was 2 or 4 cm^{-1}. The spectra were not treated except for a small correction of the base line. There has not been performed on the spectra any smoothing nor deconvolution. They are, as we call them, "raw spectra".

RESULTS AND DISCUSSION

The FT-IR spectra of Acropolis columns have been recorded in the region 400-4000 cm^{-1} (Fig. 1). From the totality of the spectra we observed several bands are attributed to sulfur groups, such as S-S, S=O and RSO_2R, carbon groups, such as C=O, C-O and C-H. These bands are compatibles with the presence of oxalates in the samples obtained from the surface of marbles. In addition, there is evidence of the presence of carbonates, which is normal

($CaCO_3$), while no one characteristic band of $CaSO_4$ was observed. Furthermore, the band at 875 cm^{-1} is assigned to silicates (Table I).

The weak band at 514 cm^{-1} is assigned to S-S stretching[2-5]. The band at 710 cm^{-1} is assigned to a secondary amide group (-NH), however it could also be a C-S group. Bellamy[2] gives the absorption of a C-S group in the region 715-620 cm^{-1} and Theophanides[3] in the region 700-590 cm^{-1}.

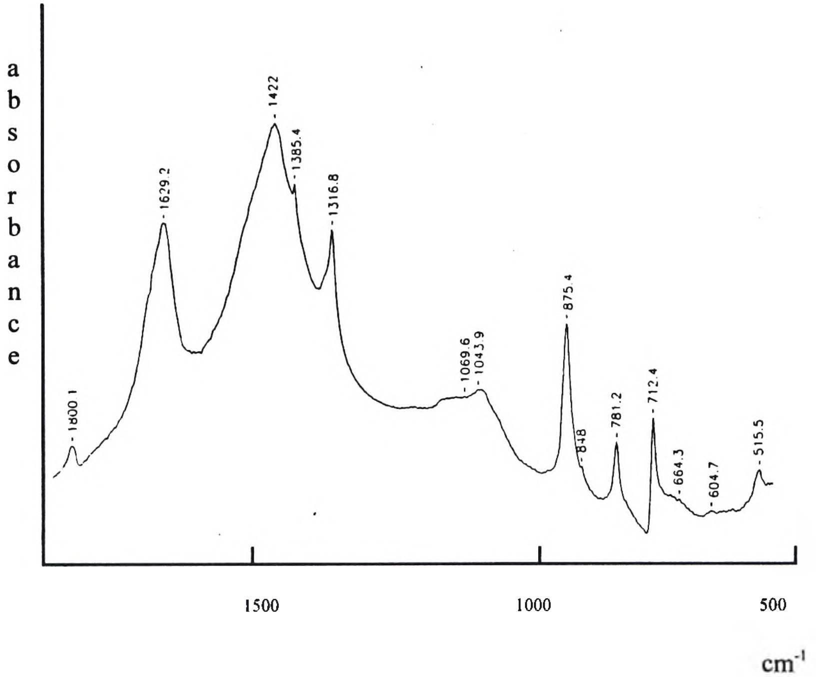

Fig. 1. FT-IR spectra of Acropolis' marble in the region 500-1900 cm^{-1}.

The absorption bands in the region 1070-1035 cm^{-1} may be due to the presence of sulfoxides, i.e. to the presence of groups C-SO-C, or O-SO-O. The formation of these products, which contain the above groups may be the result of photochemical interactions of atmospheric pollutants SO_2 with organic substances to form sulfuric esters.

Table I. Assignment of bands of FT-IR spectra of samples coming from Acropolis*

band cm^{-1}	chemical form	assignment
514 vw	disulfide	νS-S stretching
710 m	secondary amide	δN-H def. out of plane
780 w	amines	δNH_2 bending out of plane
875 vs	SiOH	δSi-OH bending
1044 br	acetal sulfoxide	νC-O or νS=O stretching
1316 m	carboxylic agroup (-COO^-)	νC-O stretching
1420 s	sulfuric ester $[(RO)_2SO_2]$ & inorganic carbonate CO_3^{2-}	νS=O stretching νC-O of CO_3^{2-}
1628 s	nitrate or amide I	$\nu O\text{-}NO_2^-$ stretching
1800 w	-O-(C=O)-O- or carbonyl (inclusion)	νC=O stretching
2515 w	free thiol	νS-H stretching

*Taken from the references 2-6. w=weak, vw=very weak, m=medium, s=strong, vs=very strong, br=broad.

It is well known that SO_2 through photochemical reaction is transfered as free radical according to the reactions[6]:

$$SO_2 \xrightarrow{hv} SO_2^{\cdot} \quad [1]$$

The $SO_2^{\cdot}$ radicals can easily interact with organic molecules from the atmosphere leading to the production of organic radicals:

$$SO_2^{\cdot} + RH \longrightarrow SO_2 + H^{\cdot} + R^{\cdot} \quad [2]$$

$$SO_2^{\cdot} + R^{\cdot} \longrightarrow RSO_2^{\cdot} \quad [3]$$

The $RSO_2^{\cdot}$ radical can react with O_2 to produce peroxyl radicals

$$RSO_2^{\cdot} + O_2 \longrightarrow RSO_2OO^{\cdot} \quad [4]$$

The peroxyl radicals are not stable and react with an organic radical $R^{\cdot}$' which was produced according to the reaction [2] to form sulfuric esters RSO_2OOR':

$$R\,SO_2OO^{\cdot} + R'^{\cdot} \longrightarrow R\,SO_2\,OOR' \quad [5]$$

It is well known that in polluted cities the concentration of peroxyacetyl nitrate, CH_3COONO_2 (PAN) and peroxypropionyl nitrate, $CH_3CH_2COONO_2$, (PPN) is about 50 and 60 ppb, respectively[7], depending on the weather. These very strong oxidants are produced by oxidation of CH_4 or CH_3CH_3 the most common and widely dispersed atmospheric hydrocarbons according to the reactions[6]:

$$CH_4 + O \longrightarrow H_3C^{\cdot} + OH \qquad [6]$$

The methyl radical reacts rapidly with O_2 to form peroxyl radicals:

$$H_3C^{\cdot} + O_2 \longrightarrow H_3COO^{\cdot} \qquad [7]$$

The $H_3COO^{\cdot}$ radicals interact further with NO_2 to form PAN:

$$CH_3COO^{\cdot} + NO_2 \longrightarrow CH_3COONO_2 \qquad [8]$$

The above reactions [1]-[8] can explain the presence in the FT-IR spectra of the groups C-SO-C, O-SO-O or N-CO-, etc.

By observing the spectra and making a spectral analysis, it is quite evident that in the surface of the marbles from Acropolis upon weathering and pollution we find on the surface sulfur bound to form disulfides, or bound to hydrocarbons and esters to form sulfoxides, thiols, amines, silyl derivatives, methyl acetals and other dimethyl or trimethyl groups. These groups remind us the presence refineries of hydrocarbons or pollutants of combustion engines (cars). The refineries maybe those in Eleusis or Pireus that produced these products upon aging of the marbles of Acropolis.

References

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