The assessment of the carbonaceous component in black crusts damaging the stone surfaces of historical monuments

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The issue of conservation of the monumental heritage is mainly related to atmospheric pollution that causes the degradation of stone surfaces. Black crusts can be formed as a result of different chemical and physical reactions between the stone surface and environmental factors (such as gaseous pollutants and aerosol particulate matter, PM). These black layers present on the stone monuments reflect the composition of the aerosol particulate matter to which the surfaces are exposed. In particular elemental carbon (EC, also known as black carbon, typically emitted by combustion processes) is the PM component responsible for the characteristic black color of the crusts where it is embedded together with calcium sulphate due to the conversion of calcium carbonate, the main constituent of the stone. Organic carbon (OC) represents the other carbonaceous component of PM and it is present in the black crusts, too. It is of both primary or secondary origin and is linked to numerous sources (traffic, heating plants, biomass burning, etc.).
A deep knowledge of the crust composition in terms of OC and EC optical properties is mandatory in order to get information on the sources responsible for the surface darkening.
OC/EC in PM samples are generally quantified by a reference method (TOT, Thermal Optical Transmittance) not suitable for the analysis of these components in the crusts.
A new approach for OC/EC quantification (1,2) based on a thermal protocol and including CHN and TGA analyses, has been here proposed. The method validation has been performed analyzing suitable reference standard samples prepared by mixing different chemical species in order to simulate the composition of the black crusts present on the monument surfaces.
In addition the characterization of OC optical properties with UV-visible spectrometry has been performed, to understand the role of light absorbing carbon (i.e. brown carbon) on surface stone darkening. The chemical composition of OC was further investigated with Fourier Transform infrared spectrometry (FT-IR) to identify the contribution of the different organic functional groups to the ageing/browning of stone surfaces.
This research aims to get a new simple method for the evaluation of the carbonaceous component of the black crusts which are formed on carbonate stone surfaces. The protocol has been applied to some real samples of black crusts of different provenance.

References:
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