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Thermal analysis in cultural heritage safeguard: an application

Nadia Ghedini [a,b,*], Cristina Sabbioni [a], Marta Pantani [a]

[a] *Istituto ISAC–CNR, Via Gobetti 101, 40129 Bologna, Italy*
[b] *Dipartimento di Scienze Farmaceutiche, Università di Bologna, Via Belmeloro 6, 40126 Bologna, Italy*

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Abstract

Damage layer formation on buildings is due to the deposition of atmospheric pollutants and their interaction with the underlying materials. The composition of black crusts is therefore closely related to the characteristics and levels of pollution in the surrounding environment. Thus, the study of its constituents is of fundamental importance in planning strategies for the protection and conservation of monuments and historic buildings. Damage layers have been shown to be primarily composed of carbonaceous particles embedded in gypsum, pointing to the overwhelming role of combustion-derived air pollution in their formation. The identification and evaluation of elemental carbon and other carbon species constituting the non-carbonate fraction of total carbon is required in investigating the damage on historic buildings in urban areas. The removal of organic carbon is a critical step in the analytical methodologies used for the measurement of elemental carbon. The paper describes a study performed on black crust samples from historic buildings of two Italian towns, on which the carbon compound discrimination was achieved by applying an analytical methodology based on thermal analysis.

Keywords: Combustion analysis; Carbon speciation; Elemental carbon; Material damage; Cultural heritage

1. Introduction

It is well known that atmospheric pollution is the main agent responsible for the damage encountered on calcareous buildings located in urban areas [1]. On sheltered surfaces, the weathering of stones and mortars leads to the formation of damage layers which commonly present a characteristic dark colour [2]. This phenomenon causes serious stone decay processes, especially on carbonate matrices, and appears to have accelerated over the past 50 years, as can be easily inferred from the continual blackening and repeated restoration of historic buildings and monuments currently occurring in European cities.

Black crusts have been found to be primarily composed of carbonaceous particles embedded in gypsum [3], and since they originate from combustion processes, their presence testifies to the overwhelming role of combustion-derived air pollution in the formation of the damage layers [4].

Over recent decades the degradation of stones and other structural components used in ancient and modern masonry has been extensively studied, with particular attention focused on the sulphation process occurring on carbonate materials. However, only a few recent works report measurements on the atmospheric content of carbonaceous particles, addressing the issue of their possible role in gypsum formation [5–7].

* Corresponding author. Tel.: +39-051-6399577; fax: +39-051-6399649.
E-mail address: n.ghedini@isao.bo.cnr.it (N. Ghedini).

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In the atmosphere, carbonaceous particles primarily derived from various combustion processes, and over the last century their concentration in urban areas has undergone a drastic, quasi-exponential increase. All combustion processes produce abundant amounts of carbonaceous species that contain organic and elemental carbon [8]. While the atmospheric concentrations of sulphur dioxide (the first pollutant responsible for sulphation) have been drastically reduced in recent years, the air contents of carbonaceous particles has continued to rise.

Because combustion is a ubiquitous pollution source, carbonaceous particles are observed in damage layers in all environments. The few existing data on the speciation and measurement of carbon material show that non-carbonate carbon is, after sulphur, the main element originating from atmospheric deposition [9].

The carbon found in black crusts may have different origins, such as (a) calcium carbonate, basically due to the underlying material [10]; (b) deposition of atmospheric particles from multipollutant sources [11–13]; (c) biological weathering due to organisms that produce, among their metabolic secretions, formic, acetic and oxalic acids [14–17]; (d) treatments with organic materials used in the past to preserve monuments and buildings [18].

The total carbon (TC) present in damage layers on stones and mortars is composed of three main fractions:

$$\mathrm{TC} = \mathrm{CC} + \mathrm{OC} + \mathrm{EC}$$

where CC is carbonate carbon, nearly all of which originates from the stone or mortar constituting the monument or building; OC is the organic carbon of both biological and anthropic origin, linked to the action of micro-organisms on surfaces and to the deposition of primary and secondary pollutants; and EC is elemental carbon, mainly due to the aerosol emitted by combustion processes and, therefore, a quantitative index of the carbonaceous particles embedded in the black crusts [19]. Together; OC and EC constitute the non-carbonate fraction of total carbon (NCC).

Since EC and many of the components of OC are tracers of specific anthropic sources typical of urban areas, such as vehicle exhaust, road dust, industrial combustion and domestic heating systems [20,21], the measurement of non-carbonate carbon, the discrimination of EC and OC and the characterisation of the organic fraction, are all essential for a complete identification of the main components of the damage layers on monuments, and for the characterisation of sources.

The availability of a correct, accurate and reproducible analytical method for a complete carbon balance in black crusts is of major importance in studying the effects of the interaction between atmospheric pollutants and the environment, including those on human health and the conservation of cultural heritage [22].

The literature contains a wide variety of carbon speciations in complex carbon compound materials on atmospheric samples, performed by means of several different techniques. However, the analytical procedures adopted in such studies make their results unsuitable for comparison. In fact, the critical step in common to all the procedures is the removal of organic carbon.

Furthermore, information regarding the carbonaceous components in black crusts on buildings and the carbonaceous particles in damage layers is generally limited to the identification of the different types of embedded particles, on the basis of their morphology and elemental composition by optical microscopy and scanning electron microscopy [23,24]. Finally, data on elemental and organic carbon in black crusts are extremely rare [25].

Since buildings and outdoor statues and monuments act as repositories of airborne pollutants, the chemical composition of black crusts directly reflects the surrounding atmospheric environment [26]. The characterisation and evaluation of carbon compounds in damage layers on monuments are necessary for a correct partitioning of pollutant sources and identification of the threshold levels required for a sustainable protection and conservation of cultural heritage.

We present below a study carried out on the carbonaceous material in damage layers on monuments of two Italian cities, where carbon speciations were obtained by applying a methodology based on thermal analysis preceded by specific chemical treatments.

2. Experimental

Samples were collected from the black damage layer (Fig. 1) on monuments and buildings located in