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A new analytic methodology for the characterization of the carbonaceous fraction in black crusts present on stone surfaces

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Abstract **The aim of this research work is the development of a method to characterize and quantify the various components present in the black crusts that due to atmospheric pollution have developed on the surfaces of buildings and monuments. The carbonaceous fraction is the main cause of blackening of architectural surfaces and is involved in black crusts formation. A new methodology based on the use of TGA/DSC and CHN analysis has been set up in this work allowing easily to determine organic carbon (OC) and elemental carbon (EC). Four standard samples were prepared, with the aim to simulates black crusts composition, and analysed with the set-up methodology in order to validate it. The new method has been subsequently applied to the analysis of real crusts samples from monuments and buildings placed in cities heavily affected by atmospheric pollution.**

I. INTRODUCTION

The degradation processes of stone materials are strictly correlated to air pollution and the situation is even worse in urban centres characterized by high anthropogenic emissions. The most common phenomenon observable on buildings and monuments is the accumulation of pollutants on their surface causing the formation of dark colour patinas known as "black crusts" (hereafter named BCs). These crusts are formed by gypsum crystals inside which atmospheric particulate matter (PM) is embedded. Gypsum forms because of the reaction of calcium carbonate, i.e. the main stone constituent, with SO_2 present in polluted atmosphere. In the damaged layers carbonaceous particles (organic carbon, OC, and elemental carbon, EC) and heavy metals [1-12] are embedde. Elemental carbon causes darkening, while heavy metals represent the catalysts of heterogeneous oxidation of SO_2 [13-15]. It is worth noting that the carbonaceous species in BCs are, in order of abundance, the second most important anthropogenic species, after sulfur. Total carbon (TC) includes two main fractions: carbonate carbon (CC) and non-carbonate carbon (NCC) which includes both elemental carbon (EC) that organic one (OC).

Black carbon (also known as elemental carbon, EC, because of its structure quite similar to that of graphite) is emitted by combustion processes, such as traffic and biomass burning [16-18] and is the main responsible for soiling on monuments surfaces [19-21]. On the other hand, OC that includes hundreds of organic substances of different nature, is emitted by combustion processes as primary pollutant but is also of secondary origin and can form starting form gaseous organic precursors (i.e. volatile organic compounds, VOC) [22-27].

The aim of this research is the development of a new method for the characterization and quantification of the various components present in crusts samples collected from buildings and monuments of historical, artistic and cultural interest.

The quantification of OC and EC contributions to TC in BCs is important for the identification of fixed and mobile combustion sources. The analysis of these constituents in the crusts is challenging because of the analytical difficulty to separate the two contributions and also because of the presence of the substrate which, being a carbonatic stone, represents an interference.

Recently, an alternative simpler methodology with respect to what already present in the literature [28] has been applied bringing to satisfactory results [29]. This approach has been applied and further developed in the present work starting from the study of standards suitably created to simulate BCs composition.

The new method here proposed is based on the use of both elemental analysis CHN (Carbon Hydrogen Nitrogen analyses) and thermal analyses such as TGA/DSC (Thermogravimetric analysis and Differential Scanning Calorimetric analysis).

II. MATERIALS AND METHODS

The analytical protocol applied in this study is a thermal method based on the fact that OC and EC show a different thermal behaviour: while OC decomposes at lower temperature (about 350 °C), EC and CC are stable up to high temperatures.

A Carbon Hydrogen Nitrogen analyser CHNS/O Perkin Elmer 2400 Series II Elemental Analyser equipped with an accessory for the analysis of solids has been employed to quantify total carbon (TC). Thermogravimetric analyses (TG) were carried out by a Mettler Toledo TGA/DSC3+ instrument, which allows simultaneous TG and DSC analyses. The analyses were conducted in the range 30–800 °C, increasing the temperature with a rate of 20 °C/minute and using about 0.2mg of sample for each analysis. The samples were analysed both in inert and oxidizing atmosphere, the latter made it possible to calculate EC value.

The methodology involves several steps, each of which was carried out on a different portion of the same standard sample:

1. TC was quantified using CHN;
2. NCC was determined by an acid treatment in accordance with the literature (Ghedini et al., 2006); CC was calculated as the difference between TC and NCC;
3. TGA analysis was performed to determine CC, OC and EC also thank to the comparison between the standards behaviour in the two atmospheres.

Standard samples were prepared in the laboratory with the aim to simulate the composition of BCs present on the surfaces of buildings and monuments exposed to air pollution. The composition of the standard was chosen in accordance to what reported in Gedini et al., [16].

Since real crusts contain a wide variety of organic compounds and to simplify the standards composition and the subsequent interpretation of results, benzoic acid, as representative of substances that decomposes at lower temperatures, and sodium oxalate, which degrades at higher temperatures, have been chosen as surrogate for OC. Graphite was used to simulate EC. Calcium sulphate dehydrate (gypsum), silica and calcium carbonate have also been added to the mixtures.

For the standards preparation the powders have been weighed and ground in an agate mortar in order to achieve a great uniformity and reproducibility for the subsequent analyses. Four different standards mixtures have been prepared starting from the single components. Their composition is reported in table 1 as w%.

Table 1. Composition and percentages values of the mixtures standard samples.

	%			
	STD.1	**STD.2***	**STD.3**	**STD.4***
Calcium carbonate	36.0	34.7	11.4	11.3
Silica	49	47.0	15.5	15.3
Graphitic carbon	5.5	5.3	1.8	1.7
Benzoic acid	9.5	9.2	3.0	3.0
Sodium oxalate	-	3.7	-	1.2
Gypsum	-	-	68.3	67.5

III. RESULTS AND DISCUSSION

First of all, thermograms were acquired both in oxidant and in inert atmosphere for all the substances used for the correct weight losses and to highlight the corresponding temperature ranges. In the specific case of calcium carbonate and graphite, mixtures with silica were prepared to verify the correct quantification of these two compounds since both of them decompose at high temperature.

Benzoic acid, used as representative of organic compounds that decomposes at low temperatures, sublimates between 100 and 200° C both in oxidizing and inert atmosphere. In both atmospheres it is possible to see from DSC analysis an endothermic event in the temperature range 100- 200° C.

Sodium oxalate decomposes in two steps. The first step occurs at 500-600° while the second one occurs at higher temperatures, more than 850° C, and in both atmospheres only the beginning of the process can be observed.

Calcium sulphate dehydrate (gypsum) shows the loss of water of hydration between 100 and 200° C; the subsequent decomposition reaction of calcium sulphate to calcium oxide at higher temperatures has not been observed. As regards graphitic carbon and carbonate carbon they have been mixed whit silica in order to prepare a standard whit the suitable concentration with respects to BCs.

As an example of analysis on a mixed standard, in Fig.1 the thermogram acquired for a mixture of silica and graphitic carbon is reported. In this case the mixture contained 90% of SiO_2 and 10% of graphitic carbon. In inert atmosphere no weight losses were observed while in contrast a weight loss was observed in oxidizing atmosphere in the temperature range 400-600 ° C (Fig.1); the loss can be attributed to graphitic carbon that decomposes because it interacts with oxygen to form carbon dioxide.

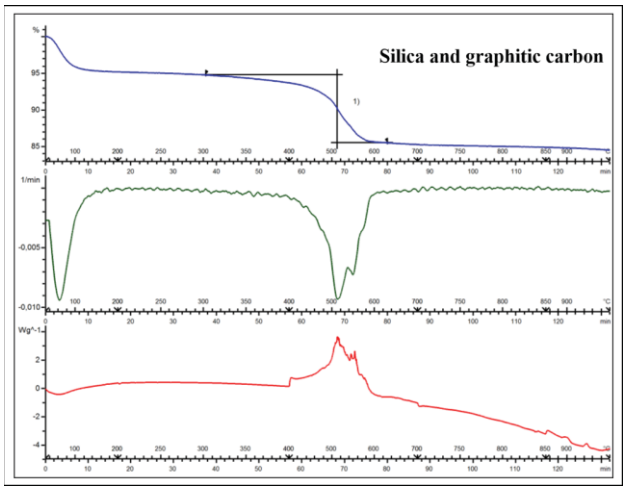

Fig. 1 Thermogram of silica and graphitic carbon (blue curve), its first derivative (green curve) and DSC analysis in oxidant atmosphere.

The study of the individual components has allowed us to identify the single components within the standards, which subsequently have been used as references in the analysis of real samples.
Precisely, T intervals considered are:
- 100-200 ° C corresponding to gypsum dehydration in both atmospheres
-150-600 °C corresponding to decomposition of organic substances
- 500-600 °C corresponding to decomposition of graphitic carbon that simulates the elementary component of carbon EC is observed only in oxidant atmosphere;
-600-750 °C corresponding to decomposition of calcium carbonate that simulates the stone substrate.
In table 2 the analysed single substances used for the standard preparation and two mixtures (silica +graphitic carbon and silica + carbonate carbon) are reported together with the corresponding decomposition temperature interval.

Table 2. Decomposition temperatures for the two atmospheres (inert and oxidant) for the different compound used in the preparation of the standards.

Compound	Atmosphere	Decomposition T °C
Benzoic acid	**Inert**	100-200
	Oxidant	
Sodium oxalate	**Inert**	500-600
	Oxidant	
Calcium sulphate dehydrate (gypsum)	**Inert**	100-200
	Oxidant	
Silica and calcium carbonate	**Inert**	600-750
	Oxidant	
Silica and graphitic carbon	**Inert**	-
	Oxidant	400-600

An example of the thermogram obtained analysing STD1 (composition: calcium carbonate 36.04%; silica 48.96%; graphitic carbon 5.46% benzoic acid 9.54%) in oxidizing atmosphere is shown in figure 2.

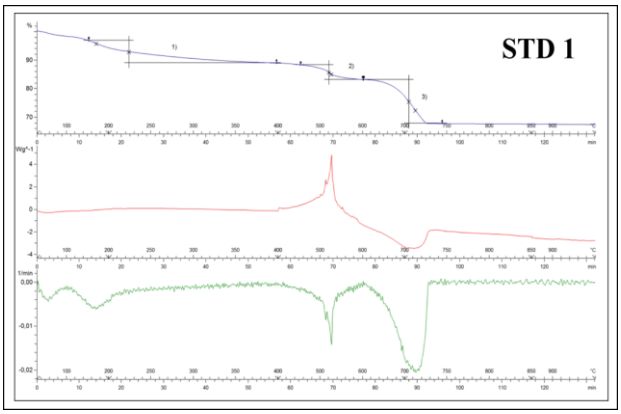

Fig. 2 Thermogram of STD.1 (blue curve), its first derivative (green curve) and DSC analysis (red curve) in oxidant atmosphere.

CHN analyses have been used to calculate TC in the standard mixtures allowing to reconstruct the standards composition.
It is important to underline that black crusts have a more complex composition than the standards because of their high morphological and chemical variability. Nevertheless, the set-up method resulted to be a reliable procedure for OC/EC quantification in BCs.
The method set-up by means of the analyses acquired on standard mixtures simulating real samples, has been than successfully applied to the analysis of BCs coming from different sites [8-9,12,30-31] affected by atmospheric pollution.

IV. CONCLUSIONS

The aim of this research was the development of a new method to characterize and quantify the various carbonaceous components present in the black crusts that due to atmospheric pollution have developed on the surfaces of buildings and monuments.

The research has allowed us to develop a simple method based mainly on the thermal analysis of standard samples realized to simulate real BCs composition. Reference temperature ranges, within which the decomposition of the main constituents of black crusts occurs, were identified thanks to the comparison with reference standards mixtures.

The definition of these temperature intervals has allowed to correctly quantify OC and EC within real black crusts coming from different sites, often placed in highly polluted urban centers.

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