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# Development of a new procedure for the assessment of particulate matter (PM) carbonaceous fraction on stone materials exposed to atmospheric pollution

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**Abstract.** The present study deals with the set-up and development of a new methodology to quantify the carbonaceous fraction (i.e., OC, organic carbon and EC, elemental carbon) in black crusts samples present on marble stone surfaces of historical buildings and monuments exposed to outdoor pollution. It is worth noting that OC and EC represent one of the main fractions of atmospheric particulate matter and, mainly EC, is responsible for the black colour of the crusts. The same method has been applied to resuspend known quantities of atmospheric particulate matter on marble mock-up specimens suitably realized to study the crusts' formation process starting from known quantities of the precursors in the formation process, i.e., PM and SO<sub>2</sub>, and submitting them to an accelerated aging process.

## 1. Introduction

Atmospheric pollution represents a threat for human health but also for cultural heritage [1-4] and this issue has been widely considered. In particular, 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. Consequently, the study of the impact of atmospheric pollution on outdoor cultural heritage represents a topic of great interest. The most common phenomenon observable on stone buildings and monuments exposed to atmospheric pollution is the accumulation of pollutants on their surface causing the formation of dark coloured patinas known as "black crusts". These crusts are formed by gypsum inside which atmospheric particulate matter (PM) is embedded. The carbonaceous fraction, i.e., OC (organic carbon) and EC (elemental carbon), is one of PM's main constituents and in particular elemental carbon is responsible for the characteristic black colour. Gypsum is formed because of the reaction of the primary mineral (CaCO<sub>3</sub>) used in the constructions and building materials with SO<sub>2</sub>



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present in the urban polluted atmosphere. Starting from reference standards acting to simulate black crusts composition [5, and references therein], a new method based on a thermal protocol has been developed and applied to the quantification of OC and EC in black crusts samples taken from monuments exposed in highly polluted environments.

At present a further improvement in the analysis of OC and EC is represented by a method developed for the quantification of these two components in PM present in powder form (so not deposited on quartz fiber filters). This procedure can be also applied to quantify OC/EC on black crusts.

In order to study the deterioration phenomenon that occurs on marbles exposed to atmospheric pollution, a common and consolidated practice is represented by the employment of marble specimens exposed for known interval times to atmospheric pollutants in real atmospheric conditions [6,7].

Aiming to better understand the stone deterioration process and, hence, to interpret and prevent the weathering phenomenon even by mathematical modelling, a series of studies has been performed over the last two decades using accelerated aging chambers [8-13]. If on the one hand these studies have paved the way towards an effective method to reproduce urban pollution favoring stone sulfation, on the other hand none presents a comprehensive simulation including the main factors all together (i.e., SO<sub>2</sub>, humidity, temperature, metal catalysts, particulate matter, UV-light irradiation). In order to compensate this gap, we are setting up an experimental apparatus where a series of marble samples ('white Carrara') undergoes accelerated aging inside simulated atmosphere chambers under controlled parameters. A key point is the role played by particulate matter (PM) in the fixation of atmospheric sulfur dioxide as gypsum on marble stone surfaces in the presence of humidity.

Since particulate matter is essentially a mixture of carbonaceous matter (OC and EC) and metallic particles (namely, Fe, Cr, Ni, Cu, Mn, Pb, V), which varies depending on its source, a thorough extraction of PM from outdoor sampling supports and determination of its composition are requested prior to aging tests. Before starting the assays, some marble specimens are pretreated by depositing the PM extracts over their surface following a procedure optimized on the basis of reported protocols [8-12]. These marble specimens are compared to other ones bearing individual components of particular matter (EC and selected metals), deposited over their surface after sonication of the corresponding aqueous suspensions. Some metals commonly present in particulate matter, in fact, seem to be responsible for the catalytic activation of stone sulfation with the aid of the carbonaceous fraction itself, as reported in literature [12,14-16]. The as-pretreated samples will then undergo the same accelerated aging tests aiming to discriminate the role played by the individual components in black crusts formation.

The first fundamental step is the extraction of particulate matter from outdoor sampling supports, followed by quantification and speciation of the carbonaceous fraction using thermal-optical analysis, as reported in the experimental section. The aforementioned accelerated aging tests over properly treated marble specimens are on-going and will be reported in an upcoming paper.

## 2. Experimental

PM<sub>2.5</sub> samples in powder form were used for the development of a new procedure aimed at the quantification and speciation of the carbonaceous fraction using thermal-optical analysis. All analyses were performed on quartz fibre filters (Whatman, QMA grade, diameter 47 mm) using a thermo-optical analyser from Sunset Laboratory (OC-EC Lab Instrument, Model 5, Sunset Laboratory Inc.) and working in transmittance mode. The analytical protocol used for the quantification and speciation of the carbonaceous fraction is NIOSH-870, a variation of the wide-spread NIOSH protocol.

The powder was obtained following an extraction and filtration treatment specifically designed to remove particulate matter from the filters. In particular, the filters underwent an extraction phase exploiting multiple sonications in ultrapure water and a filtration phase in which most of the glass fibres were removed to obtain the final residue [17].

The powder was then resuspended in ultrapure water and homogeneously dispersed on a clean quartz fibre filter (punch area = 1.00 cm<sup>2</sup>) using a newly developed method that involved the fine-tuning of

several parameters in order to obtain reproducible results in terms of organic and elemental carbon. Specifically, the vials used contained around 2.30 mg of PM which was initially resuspended using 150  $\mu\text{L}$  of ultrapure water. The suspension was then sonicated for 30 minutes in a water bath and a portion was immediately transferred using a micropipette onto a clean quartz fibre filter. Tests have shown that the optimal amount of suspension to be transferred is equal to 30  $\mu\text{L}$ , carried out in two separate depositions of 15  $\mu\text{L}$ . In between one transfer and the other, the filter must be dried to completeness and before adding the second aliquot the suspension needs to be sonicated for 2 minutes to ensure homogeneity. At the end of this process the filter must be completely dried once again before submitting it for thermal-optical analysis. It is worth mentioning that a 2-minute sonication before the transfer of the aliquots on the filter is also necessary if one wishes to perform multiple tests on the same sample.

A final parameter that has been optimised is the placement of the filter inside the oven: indeed, it is crucial that the laser beam points directly into the centre of the deposition. To ensure that this is the case, one needs to position the spoon so that its placement corresponds to a minimum reading of the initial transmittance value. Only in this case it can be assured that the beam is in fact directed towards the spot and not partially hitting parts of the nude filter around it.

### 3. Analytical results

OC and EC represent one of the main fractions of atmospheric particulate matter. The difficulty linked to the quantification of OC and EC in these kinds of samples is due to the fact that the methodology available for the determination of the same components in the atmospheric aerosol requires PM to be homogeneously dispersed on quartz fiber filters. The procedure here proposed has been validated starting from filters where PM was collected and resuspended in MQ water. Subsequently it has been deposited on quartz filters and analysed by the TOT (thermal optical transmittance) technique, i.e., the reference method applied for OC/EC analysis in PM samples.

The results obtained demonstrated a good reproducibility with regards to all the parameters analysed, hence TC, OC and EC, as shown by the tables below (table 1, table 2).

The quantification of organic matter was made using 1.6 as the mean molecular to carbon ratio, which is a value typically used for urban aerosol [18]. Hence, the PM<sub>2.5</sub> sample analysed has an organic matter content of 22.5 ( $\pm 0.8$ ) % and the carbonaceous fraction contributes to 23 ( $\pm 1$ ) % of the total mass of the powder. Whilst the amount of organic matter is in line with values found in European urban areas, the percentage of elemental carbon is below the ones commonly reported in literature [19,20]. As already hypothesised by Rovelli et.al., (2021), despite an average recovery rate of the extraction and filtration procedure equal to 75%, it is possible that the various components of the powder are recovered with different efficiencies. Particularly, in view of the high hydrophobicity of elemental carbon, the extraction efficiency associated with this component is probably scarce, which would explain the low percentages obtained. Differently, water-soluble organic compounds (WSOC) can make up more than 50% of all organic carbon, suggesting an easier extraction and therefore greater efficiencies.

**Table 1.** Mean mass percentage values of TC, OC and EC in the analysed aliquots of PM<sub>2.5</sub> in powder form.

	Mean / %	$\sigma$ / %	CV / %
<b>OC</b>	14.1	0.5	3.54
<b>EC</b>	0.53	0.05	9.43
<b>TC</b>	15	1	6.67

**Table 2.** Mass percentage of TC, OC and EC in analysed aliquots of PM2.5 in powder form.

	OC / %	EC / %	TC / %
<b>C-11</b>	14.90	0.55	15.45
<b>C-11</b>	15.65	0.67	16.32
<b>C-11</b>	15.33	0.63	15.96
<b>C-10</b>	12.34	0.47	12.81
<b>C-10</b>	13.63	0.42	14.05
<b>C-10</b>	13.03	0.42	13.45
<b>C-10</b>	13.22	0.50	13.24
<b>C-10</b>	13.38	0.50	13.88
<b>C-10</b>	12.85	0.52	13.37
<b>C-10</b>	13.62	0.51	14.13
<b>C-10</b>	12.94	0.53	13.47
<b>C-10</b>	13.32	0.53	13.85
<b>C-7</b>	16.94	0.68	17.63
<b>C-7</b>	15.35	0.64	15.99
<b>C-7</b>	16.26	0.72	16.99
<b>C-8</b>	14.97	0.69	15.66
<b>C-8</b>	13.89	0.65	14.54
<b>C-8</b>	14.05	0.56	14.60
<b>C-5</b>	13.07	0.38	14.32
<b>C-5</b>	13.53	0.40	14.83
<b>C-5</b>	13.50	0.40	14.79
<b>C-5</b>	13.54	0.37	14.82

This procedure can be also applied to quantify OC/EC on black crusts after having powdered the crust. The powder obtained is resuspended in MQ water and then aliquots of known volume analysed using the TOT method, repeating the measurement to assess reproducibility and sample homogeneity.

The same approach has been then applied to recover PM collected from high volume quartz filters in order to deposit it on marble specimens that will be submitted to accelerated aging carried out in climatic chambers in presence of controlled SO<sub>2</sub>, humidity, temperature, UV-light and metal catalysts.

#### 4. Conclusions

This study focused on the development of a new methodology to quantify the carbonaceous components of particulate matter (PM<sub>2.5</sub>) in powder form using thermal-optical analysis. Samples were obtained through an extraction and filtration process which enabled to remove the particulate matter from the filters. After testing several aliquots in order to optimize all parameters, the final methodology was developed.

The results obtained are associated with variation coefficients below 10%, indicating a good reproducibility of the method. The percentage of organic matter found in the PM<sub>2.5</sub> sample analyzed is in line with literature values for European urban areas, whereas the amounts of elemental carbon are below the relative values. However, this is probably due to the limited capability of the extraction and filtration method to completely remove this hydrophobic component from the filters.

The development of the aforementioned methodology allows to extend the applicability of the thermal-optical analysis to black crusts samples on marble stone surfaces of historical buildings. Moreover, the carbonaceous fraction of particulate matter placed on marble mock-up specimens submitted to an accelerated aging process can be correctly characterized using this method, providing a tool to better understand the crusts' formation process.

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