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A NEW APPROACH FOR THE CHARACTERIZATION OF THE CARBONACEOUS FRACTION IN BLACK CRUSTS SAMPLES PRESENT ON A GRANITE SUBSTRATE

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Abstract – This research deals with the characterization of black crusts collected from an historical building in the city of Vigo. 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). The black crust can be considered as a passive sampler of pollutants. For this reason, in order to fully characterize those samples, several techniques were used such as: XRD, SEM-EDS, CHN, TGA, FT-IR/ATR and IC. This integrated approach allowed us to gain information about the mineralogical phases and the elements within the crusts giving the possibility to identify the pollution sources causing the stone decay within the buildings, as well as the variability in composition depending on the exposure of the analyzed surfaces.

Key Words – CHN, TGA, OC, EC

I. INTRODUCTION

Air pollution is one of the most important causes of surface decay in urban environment. Among the degradation processes due to airborne pollutants, the formation of black crusts is one of the most dangerous one. Currently, emissions from mobile combustion sources are the main agents responsible for pollution, although a significant decrease is expected in Europe within the next decade. During the crust formation, particulate matter can be embedded into the gypsum, providing the characteristic black colour. EC (elemental carbon) and OC (organic carbon, including hundreds of organic substances of different natures) are the two main constituents of particulate matter (PM) carbonaceous fraction. Several authors [1-7] showed how the characterization of the carbon into the black crust, as well as the analysis of trace metals, can provide information on the influence of pollution sources in the degradation products formation processes; moreover black crusts can act as passive samplers of air pollution. This research deals with the characterization of the black crusts collected from the Antiguo Monasterio de los Ancianos Desamparados, an ancient building located in the historic city of Vigo (Spain). This city suffers pollution from the industrial area, as well as from vehicular and maritime traffic. In particular, the monument was selected because it showed the formation of degradation surfaces on different substrates than the usual carbonate (marble, calcarenite). In fact samples were taken from a granite stone substrate, the material used in building the Monasterio.

II. MATERIALS AND METHODS

Vigo is a city in the North-West of Spain and it is located in the autonomous community of Galicia (Fig. 1), in the province of Pontevedra; with around 300,000 inhabitants is the largest city in the region. The city is located in a large bay (ría) at the Atlantic coast, and it is surrounded by parks and forests. The city's economy is based on the automobile industry, the presence of large shipyards, engineering and food industries. Especially the most important sectors are those related to port activities, as well as the processing and preserving of fish.

The black crust samples (VIGO A and VIGO B) (Fig.1) examined were taken from an ashlar extracted from the Antiguo Monasterio de los Ancianos Desamparado, located in Vigo city. The building is constructed with a fine grained granite, composed of quartz, potassium feldspar, sodium plagioclase, muscovite and biotite as main minerals.

Figure 1. A: Vigo location in Spain map. B: A view of the Antiguo Monasterio de los Ancianos Desamparados. C: Photograph during the ashlar extraction.

For a complete characterization of black crusts, the following analytical techniques were employed. In order to quantify the carbonaceous components (OC and EC) present in the black crusts CHN analyses were performed by a CHN analyser (CHNS/O Perkin Elmer 2400 Series II Elemental Analyzer using an accessory for the analysis of solids). TG analyses were carried out by a Mettler Toledo TGA/DSC 3+ instrument which allows simultaneous TG and DSC analyses. The analyses were conducted in the range 30°- 800° C,

Table 14 Cation and Anions concentrations (µg/g) determined for the two sample of black crusts.

	VIGO A	VIGO B
Na^+	1554	1717
NH_4^+	n.a	n.a
K^+	818	497
Mg^{2+}	n.a	n.a
Ca^{2+}	103962	103159
Acetate	284	369
Propionate	2136	124
Formiate	10138	n.a
MSA	n.a	n.a
Cl^-	259	205
NO_2^-	149	72
NO_3^-	174	90
SO_4^{2-}	308520	303260
Oxalate	816	546

increasing the temperature with a rate of 20° C/minute. Ion Chromatography has been employed for the quantification of the main ions. by using an ICS-1000 HPLC system equipped with a conductivity system detector. Anions analysis was carried out with an Ion Pac AS14A column using 8 mM Na_2CO_3/1 mM $NaHCO_3$, flow rate = 1 mL/min with for the detection a conductivity system detector working with an anion self-regenerating suppressor (ASRS-ULTRA). Cations determination was performed using a CS12A (Dionex) column and 20 mM methanesulfonic acid (MSA) as eluent at a flow rate = 1 mL/min and for the detection a conductivity system equipped with a cation self-regenerating suppressor (CSRS-ULTRA). Furthermore X-ray diffraction was performed to identify the mineralogical phases, SEM-EDS to investigate the elemental composition and ATR-FTIR analyses were carried out to identify mineralogical phases and possible organic compounds.

III. RESULTS AND DISCUSSION

XRD analyses have shown that gypsum in the crusts was about 10% and it was present together with granite forming minerals, namely, quartz, micas and potassium feldspar (coming from substrate). By SEM-EDS was performed on two black crust samples revealed the crust to have a thickness of 80–100 µm and the calcium sulphate layer to be clearly distinguishable from the substrate by its acicular habit (Fig.2). The crust–substrate boundary was clean in the case of the granite-developed crusts. FTIR spectrometry analyses confirmed the presence of gypsum in the crusts, with characteristic absorbance bands occurring at around 596 cm^{-1}, 667 cm^{-1}, 1619 cm^{-1}, 1682 cm^{-1}, 3492 cm^{-1} and 3525 cm^{-1}.

By IC analyses (Table 1) large amounts of calcium sulphate has been evidenced confirming the presence of gypsum, highlighted by the weight losses in TGA and FTIR analysis. It is quite interesting the presence of high concentrations of propionate

Among anions the presence of oxalates could derive from previous conservation treatments, microbiological activity or deposition of pollutants. Table 2 illustrates the different carbonaneous fractions determined with CHN analysis and TGA analysis. Vigo crusts have a much lower content of TC with respect to crusts present on marbles [6]. Low values of OC/EC could indicate the presence of primary emission sources such as vehicular traffic and combustion processes.

Table 2 Carbonaceous fraction composition for the two examined samples from Vigo (TC= total carbon; OC= organic carbon; EC= elemental carbon; CC= carbonatic carbon).

	VIGO A	VIGO B
TC_{CHN}%	0,57	0,35
$(EC + CC)_{CHN}$%	0,28	0,27
OC_{CHN}%	0,29	0,08
OC_{CHN}/EC	2,1	3,1
EC%	0,14	0,02
EC/TC	0,24	0,06

IV. CONCLUSION

Black crusts, which are formed on stone materials, have been collected from an historical building in the city of Vigo and analyzed by several analytical techniques. This city suffers pollution from the industrial area, as well as from the vehicular and maritime traffic. The black crusts are mainly composed of gypsum, with some traces of oxalate and other short chain organic acids.

As regards the carbonaceous species, traffic is one of the main source of pollution and represents a real risk for the monuments.

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