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Thermochimica Acta 321 (1998) 215–222

thermochimica acta

Evaluation of atmospheric deposition on historic buildings by combined thermal analysis and combustion techniques

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Received 28 April 1997; accepted 10 April 1998

Abstract

Black crusts collected from monuments and historic buildings were analyzed. The analytical methodology adopted involved a preliminary characterization of the samples by means of X-ray diffraction (XRD), optical microscopy (OM) and scanning electron microscopy (SEM-EDAX). The anions present were quantified using ion chromatography (IC). Differential thermal analysis (DTA) and thermogravimetric analysis (TGA), combined with combustion techniques, allowed the quantification of the products of degradation and atmospheric deposition. In addition, the carbon of atmospheric origin was identified and quantified in its carbonate, non-carbonate, elemental and organic fractions. © 1998 Elsevier Science B.V.

Keywords: Black crust; Carbon compounds; Cultural heritage; Oxalates; Thermal analysis

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1. Introduction

Atmospheric deposition of gas and aerosols on building materials is one of the major causes of damage to stones and mortars of artistic interest [1,2]. The study of damage processes due to atmosphere/material interaction is of fundamental importance, for both a correct planning of conservation works on historic buildings and the maintenance of modern buildings.

The degradation of building materials has been extensively studied and the attention of researchers focused on the sulphation process occurring on carbonate rocks due to the deposition of atmospheric sulphur compounds [3].

Buildings and outdoor statues and monuments act as repositories of airborne organic and inorganic pollutants, which accumulate at the surfaces in zones frequently soaked by rainwater but not washed out. Dry- and wet- deposition processes, combined with gypsum crystal growth, result in dirty, grey-to-black crust formations where aerosols, spores, pollen, dust and every class of particulate matter are entrapped in the mineral matrix. Urban pollution changes the surface composition of building stones by causing the formation of gypsum crusts and the deposition of primary and secondary organic compounds [4] which play a determining role in the development of physico-chemical and biological degradation.

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PII: S0040-6031(98)00462-6

This paper aims at focusing on the role of thermal analysis combined with combustion techniques in evaluating the degradation of ancient buildings and identifying the different components due to the atmospheric deposition of environmental pollutants.

1.1. Sulphate, oxalate and carbon on black degradation patinas

Sulphate, the main product of the interaction between material surfaces and atmospheric pollutants, is encountered in degradation patinas in the form of gypsum ($CaSO_4 \cdot 2H_2O$). The black crust also embeds the organic substances of atmospheric deposition, including oxalate, which plays a primary role in the development of biological deterioration (i.e. oxalate patina formation) [5].

Anions can be quantified by means of ion chromatography (IC), while gypsum can be identified and quantified using differential and gravimetric thermal analyses (DTA-TGA) from water loss between 130–190°C. DTA-TGA also permits the quantification of carbonates from the loss of CO_2 between 650° and 900°C, while the reciprocal interference of combustion and/or decomposition peaks in the 200–600°C range render the technique difficult to use in the quantification of carbon in the alteration patinas.

After sulphur, carbon is the main element of anthropic origin present in damaged layers on monuments and buildings [6]. Carbon, present in the alteration patinas, may be of three different origins:

(a) calcium carbonate, deriving almost exclusively from the underlying materials (stones and mortars), since the contribution due to aerosol deposition is negligible [7];
(b) deposition and accumulation of atmospheric particles containing elemental and organic carbon compounds, originating from both primary and secondary processes [8]; and
(c) biological weathering due to the action of micro-organisms, such as fungi and lichens, at the surface, where calcium oxalate monohydrate and dihydrate, whewellite and weddellite, have been indicated as the main products [9,10].

In this way, the measurement of total carbon in damaged layers turns out to be insufficient for characterising the carbon of atmospheric origin. Total carbon (C_t) can be considered as being composed of two main fractions:

$$C_t = C_c + C_{nc}$$

where C_c is the carbonate carbon, and C_{nc} the non-carbonate carbon, and

$$C_{nc} = C_e + C_o$$

C_{nc} is, in turn, composed of elemental carbon (C_e) and organic carbon (C_o).

Elemental carbon is predominantly a product of combustion processes and is, therefore, a good tracer for the combustion-generated aerosol deposited on monument surfaces and embedded in damaged layers. The organic carbon, of anthropic and biological origin, in all systems can be due to the following layers:

(a) the deposition of primary pollutants, due to the incomplete combustion of fossil fuel [11], and secondary pollutants, formed by the photochemical oxidation of olefine compounds [8];
(b) biological weathering due to lichens, which produce oxalic acid that reacts with the underlying materials, leading to the formation of calcium oxalate monohydrate and its dihydrate, i.e. whewellite and weddelite [12]; and
(c) the transformation of organic materials (oils, waxes, etc.) used in the past as protective and/or enhancing treatments [13].

Thus, the measurement of non-carbonate carbon, the discrimination of elemental and organic carbon and the characterisation of the organic fraction are all essential for a complete identification of the principal components constituting the damaged layers on historic buildings.

2. Experimental

Extensive sampling was performed on damaged layers found on historic buildings and monuments located in Bologna, as an example of a polluted urban area.

Samples of black crusts were collected from the Bologna Medieval Wall, particularly from the gate, such as the Zamboni Town Gate, which were built in the 14th century. The sampling was performed on joint mortars of the ancient masonry at a height of ca. 1.5 m.

Samples of damaged surface layers were collected, both as bulk fragments and where the degradation patina was of sufficient thickness; the material was scraped away in order to measure the atmospheric deposition on surfaces and its effects on building materials.

Once collected, the specimens were dried, ground for bulk analysis and preserved at a temperature of 20°C in an inert environment (N_2) up to the time of the analyses, carried out using a combination of physicochemical analytical techniques.

Firstly, a preliminary characterisation was performed on the samples by means of X-ray diffraction (XRD) with a Philips PW1730 diffractometer, equipped with a proportion counter, employing $\mathrm{Cu}K_\alpha$ radiation filtered by nickel at the following operative conditions: 40 KV/30 mA, 2° min velocity, TC=4 and R=2000.

The structural properties of the samples were observed in thin section, using a transmitted light optical microscope (OM) for mineralogy (Zeiss Pol. III) and a Philips XL20 scanning electron microscope equipped with a dispersive energy microanalyser (SEM-EDAX).

Anion concentrations, with particular attention focused on the values of sulphate and oxalate, were measured by ion chromatography (IC) using a Dionex 4500i, following a methodology described previously [14].

Gypsum and carbonates were determined by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). DTA and TGA were simultaneously performed with a Netzsch Simultane Thermoanalyse STM 429 apparatus, under air flow at a heating rate of 10°C min^{-1}.

In order to observe the thermal behaviour of calcium oxalate, a combined DTA-TGA analysis of a standard sample of whewellite ($CaC_2O_4{\cdot}H_2O$) was also performed.

The C_{nc} and C_o contents of our samples were determined, according to a methodology developed and described in previous works [15,16] through combustion using a Carlo Erba CHNSO analyser, after elimination of C_c and C_o, respectively.

3. Results and discussion

XRD analyses (Fig. 1) clearly revealed significant concentrations of crystalline phases, showing gypsum as the most abundant species, followed by quartz, calcite and plagioclase.

Optical microscopy observations (Fig. 2), performed on thin transversal sections, show a thin surface layer embedding a large number of spherical black particles from the atmospheric deposition of combustion aerosol emissions and the mineralogical transformation of the carbonate matrix with the disaggregation of the inert component (sand).

SEM-EDAX analyses confirmed the formation of gypsum crystals with laminar structures and the presence of carbonaceous particles deposited on the surface of the damaged layers (Fig. 3).

The ion-chromatography data of all the analysed samples show (Table 1) the presence of the following anions in variable concentrations: SO_4^{2-}, NO_3^-, NO_2^-, PO_4^{3-}, Cl^-, F^-, $C_2O_4^{2-}$ and CHO_2^-.

Table 1
Anion concentrations (ppm) measured by ion chromatography (IC) in the black crusts sampled on ancient masonry in Bologna

Sample	F^-	Cl^-	NO_2^-	NO_3^-	PO_4^{3-}	CHO_2^-	$C_2O_4^{2-}$	SO_4^{2-}
1	25. 7	212.1	79.6	508.7	30.9	23.5	697.7	697.7
2	13.8	98.5	6.8	421.2	5.8	201.9	276.3	276.3
3	11.4	162.6	76.3	443	34.9	11.7	903.5	903.5
4	16	161	106.4	606.9	57.7	6	1149.5	1149.5
5	16	141.3	6.3	672	1.1	13.3	309.5	309.2
6	14.2	150.2	1.2	1217.4	1.6	64.5	241.8	241.8
7	13.4	225.6	37.4	532.9	49.5	22.4	1095.9	1095.9
8	26.6	216.5	36.2	494.6	51.1	26.9	869.3	869.3
9	21.4	258.4	68	500.3	51.1	31.9	896.7	896.7
10	12.8	202.5	35.2	417.5	36.7	12.6	886.1	886.1
11	25.8	257.6	59.3	331	1400.4	29.6	1162.1	1162.1
12	15	171.9	85.2	360.2	51	28.3	946.7	946.7

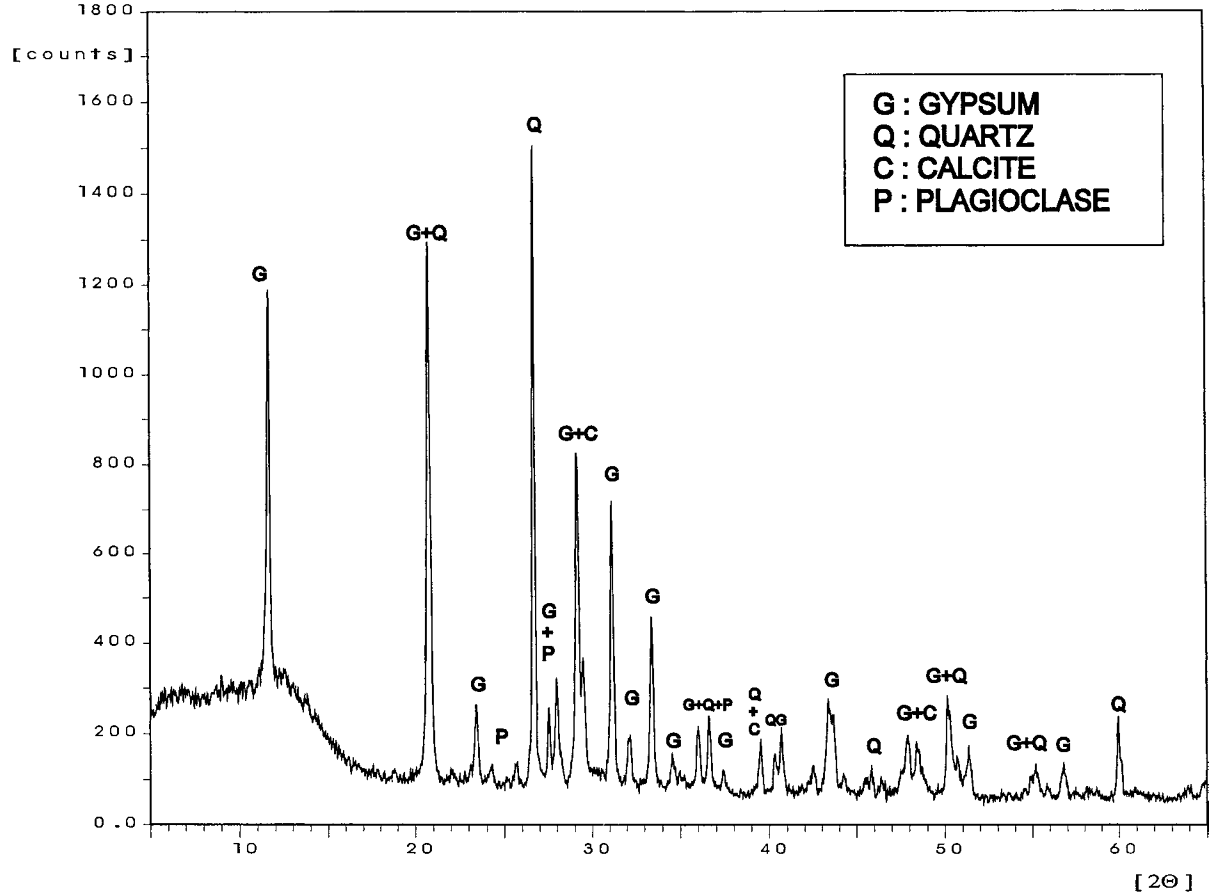

Fig. 1. X-ray diffractogram of a sample damaged layer.

Sulphate, the main anion found (mean value of 28.67%), is present in all the samples. Alongside nitrate (1.41%), nitrite (0.30%) and chloride (0.48%), a significant concentration of oxalate (0.79%) and small amounts of phosphate, fluoride and formate ions were observed.

Table 2 reports the concentrations of gypsum and carbonates measured by thermal analysis (Fig. 4) and gypsum evaluated from SO_4^{2-}, as measured by ion chromatography. Gypsum concentrations vary from a minimum of 40.60% up to a maximum of 60.00%, with a mean value of 48.00%, while carbonates (expressed as $CaCO_3$) present a mean concentration of 1.68%. The gypsum measured turns out to be slightly lower than that evaluated from the SO_4^{2-} values by ion chromatography, indicating that small amounts of other sulphates are present in the black crust alongside gypsum. Table 2 also shows the carbonate values measured by TA and those measured by TA corrected by oxalate concentration, as measured by IC.

In view of the considerable concentrations of oxalate, it was necessary to introduce a correction to the values for carbonates measured by thermal analyses.

In the alteration patinas on building materials, oxalate is present in the form of calcium oxalate [9]. In normal environmental conditions, this salt assumes a hydrated form: mono-, bi- and trihydrates. The monohydrate ($CaC_2O_4{\cdot}H_2O$), mineralogically referred to as whewellite, is the most stable form and is, therefore, the most widespread in nature. When

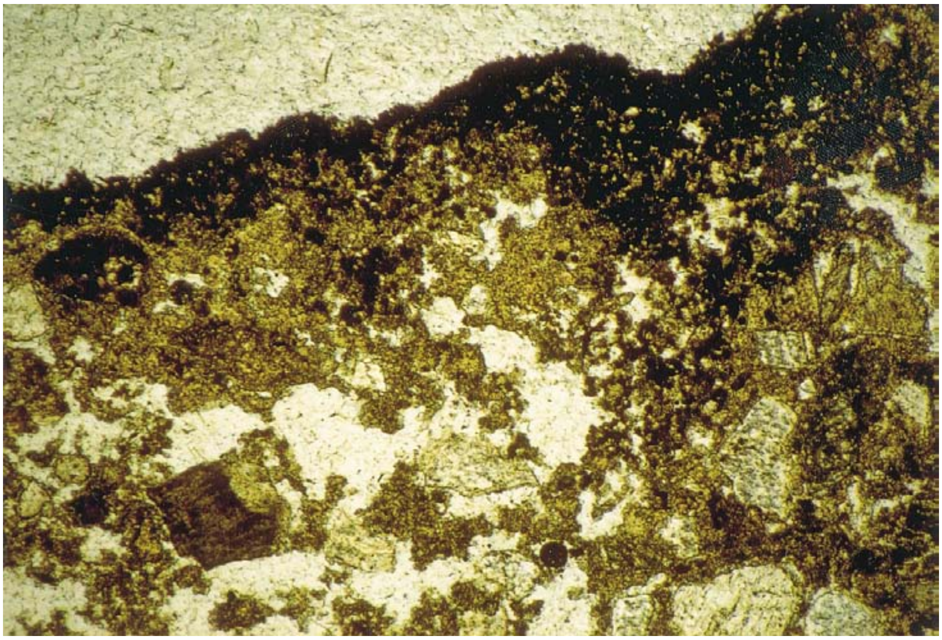

Fig. 2. Thin transversal section (nicols //) showing a thin surface layer with spherical black particles (soot) due to the atmospheric deposition of oil combustion emissions.

Fig. 3. Scanning electron micrograph of a damaged layer showing gypsum with lamellar habit and carbonaceous particles.

it undergoes heating, whewellite loses the water of crystallisation at ca. 200°C, while on reaching 500°C it decomposes into $CaCO_3$, developing CO_2 (Fig. 5). The measurement of carbonates performed by means of thermal analysis, therefore, turns out to be overestimated when calcium oxalate is present.

Table 2
Concentrations (%) of gypsum and carbonates measured by thermal analysis and evaluated using the ion-chromatography data

Sample	Gypsum [a]	Gypsum [b]	Carbonates [a]	Carbonates [c]
1	45.72	48.08	3.81	3.01
2	53.70	59.82	1.95	1.63
3	54.04	57.08	2.13	1.11
4	59.29	62.15	1.40	0.09
5	59.20	62.70	0.39	0.04
6	60.00	65.28	1.61	1.34
7	42.43	45.95	1.43	0.18
8	40.60	43.38	1.38	0.39
9	37.98	38.77	1.79	0.77
10	39.66	43.77	1.70	0.69
11	42.76	45.24	1.41	0.09
12	40.56	44.05	1.14	0.06

[a] Measured by thermal analysis.

[b] Evaluated from SO_4^{2-} measured by ion chromatography.

[c] Evaluated by carbonates content measured by thermal analysis and corrected by oxalate concentration measured by ion chromatography.

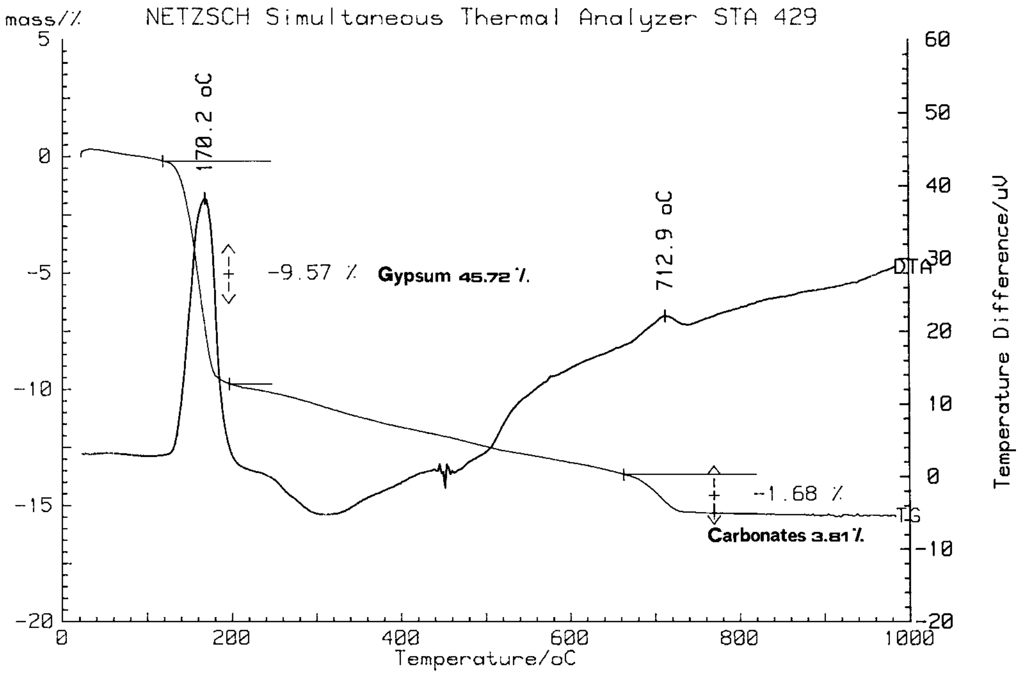

Fig. 4. Differential and thermogravimetric analyses (DTA-TGA) curves of a black crust showing the percentage concentrations of gypsum and carbonates.

Knowing the oxalate concentration, however, the values of carbonates can be corrected by subtracting from the value provided by thermal analysis the quantity of calcium carbonate forming from the decomposition of calcium oxalate. Table 2 gives both, the carbonate values provided by thermal analysis and the corrected values on the basis of the oxalate concentrations obtained by IC analysis.

The mean value for oxalate-corrected carbonate turns out to be 0.78%. This value, extremely low

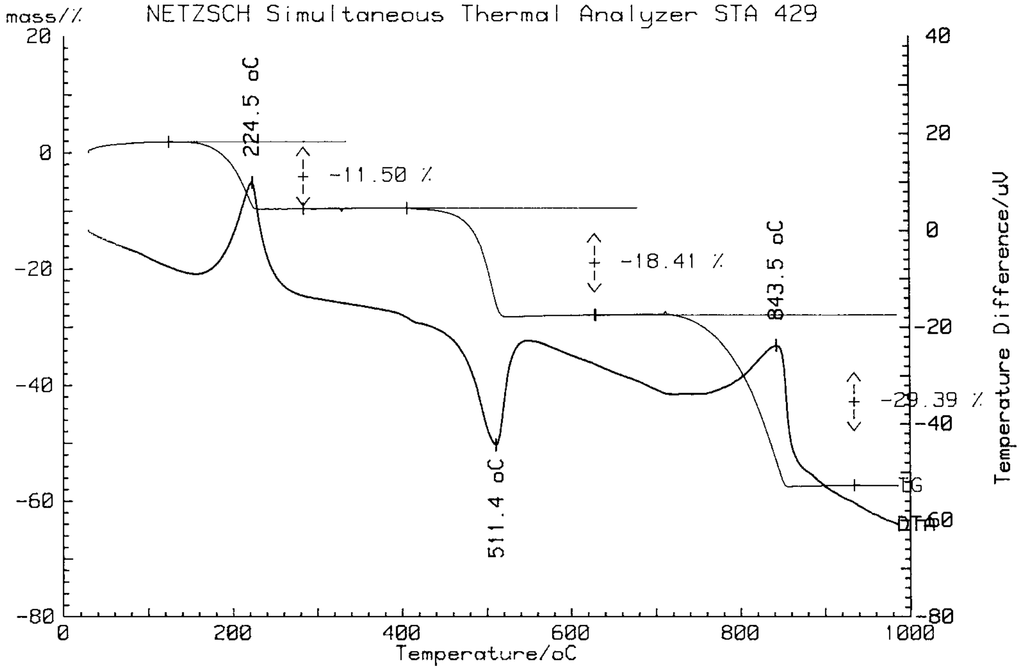

Fig. 5. Differential and thermogravimetric analysis (DTA-TGA) of standard monohydrate calcium oxalate.

compared to the carbonate matrix, indicates that the surface layer in contact with atmospheric deposits has been more or less totally transformed from carbonate into sulphate.

Taken together, the analytical data obtained by the adopted methodology allow a complete evaluation of the carbon content in black crusts (Table 3). Total carbon (C_t), calculated by summing carbonate

Table 3

Mean concentrations (ppm) of the total carbon (Ct), carbonates carbon (C_c), oxalate carbon (C_{ox}), non-carbonates carbon (C_{nc}), element carbon (C_e) and organic carbon (C_o) measured in the black crusts analysed

Sample	C_c [a]	C_{ox} [b]	C_{nc} [c]	C_e [c]	C_{org} [e]	C_t [d]
1	3612	1909	14 780	6481	8299	18 392
2	1956	763	22 360	9860	12 500	24 316
3	1332	2454	17 280	7749	9531	18 612
4	108	3136	20 190	7320	12 870	20 298
5	48	845	29 640	13 291	16 349	29 668
6	1608	654	20 060	9530	10 530	21 668
7	216	3000	12 830	6790	6040	13 046
8	468	2373	11 470	5050	6420	11 938
9	924	2454	9190	4780	4410	10 114
10	828	2454	12670	5180	7490	13 498
11	108	3164	10780	3920	6860	10 888
12	72	2591	11820	5900	5920	11 892

[a] Measured by thermal analysis and oxalate-corrected.

[b] Calculated by ion-chromatography analysis.

[c] Calculated by CHNSO.

[d] Calculated from C_c+C_{nc}.

[e] Calculated from $C_{nc}-C_e$.

carbon (C_c) and non-carbonate carbon (C_{nc}), varies from 10 114 to 29 668 ppm, with a mean value of 17 027 ppm. Of this, only 5.5% is in the form of C_c and 94.5% as C_{nc}.

The C_{nc} content must be considered as being entirely due to the deposition of atmospheric particles and to protective treatments. C_{nc} is made up of elemental carbon (C_e), 44.5%, and by organic carbon for the remaining 55.5% (Table 3).

Elemental carbon is predominantly a product of combustion processes and is a good tracer for combustion-generated aerosols. It constitutes a quantitative index of the carbonaceous particles embedded in black crusts [15].

The organic carbon present in black patinas can be due to the deposition of primary and secondary pollutants, biological weathering and the transformation of organic material [16]. The C_o/C_e ratio in our samples is 1.3, a value that is characteristic of the urban atmosphere, and is indicative of primary pollutant deposition [7].

4. Conclusions

An analytical methodology was developed for the complete analysis of the black degradation crusts found on ancient buildings.

The methodology is based essentially on the quantification of anions by IC and the application of DTA-TGA analyses combined with combustion techniques.

The procedure reported here permits the quantification of the main deterioration products found on building materials, the measurement of carbonates by DTA-TGA, also in the presence of oxalate, and the identification and quantification of the non-carbonate, elemental and organic carbon.

The data obtained consent a complete carbon balance in the damaged layers on monuments and historical buildings, which is of primary importance in the diagnosis of environmental damage and in planning correct conservation work.

Acknowledgements

The present work was supported by the National Research Council (CNR) within the Progetto Finalizzato Beni Culturali-Sottoprogetto 2.

References

[1] L. Leysen, E. Roekens, R. Van Grieken, Sci. Total Environ. 29 (1989) 263.

[2] N.S. Baer, C. Sabbioni, A.I. Sors, Science, Technology and European Cultural Heritage, Butterworth–Heinemann, Oxford, 1991.

[3] D. Camuffo, M. Del Monte, C. Sabbioni, Water, Air Soil Pollution 19 (1983) 351.

[4] B.J. Turpin, J.J. Huntzicker, Atmos. Environ. 29 (1995) 3527.

[5] M. Realini, L. Toniolo, Editeam s.a.s., Castello d'Argile (BO), The Oxalate Films in the Conservation of Works of Art, 1996.

[6] C. Sabbioni, G. Zappia, Sci. Total Environ. 126 (1992) 35.

[7] K. Pie, Aeolian Dust and Dust Deposits, Academic Press, London, 1987.

[8] B.J. Turpin, J.J. Huntzicker, S.M. Larson, Environ. Sci. Techn. 25 (1991) 1788.

[9] M. Del Monte, C. Sabbioni, G. Zappia, Sci. Total Environ. 67 (1992) 17.

[10] C. Saiz-Jimenez, Aerobiologia 11 (1995) 161.

[11] C. Saiz-Jimenez, Atmos. Environ. 27B (1993) 3527.

[12] C. Sabbioni, G. Zappia, Aerobiologia 7 (1991) 31.

[13] R. Rossi Manaresi, in Editeam s.a.s., Castello d'Argile (BO), The Oxalate Films in the Conservation of Works of Art, 1996, p. 111.

[14] G. Gobbi, G. Zappia, C. Sabbioni, Atmos. Environ. 29 (1995) 703.

[15] G. Zappia, C. Sabbioni, G. Gobbi, Atmos. Environ. 27A (1993) 1117.

[16] C. Sabbioni, G. Zappia, N. Ghedini, G. Gobbi, International Congress on Deterioration of Stone, Berlin, 1996, p. 333.