INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
I.C.T.P., P.O. BOX 586, 34100 TRIESTE, ITALY, CABLE: CENTRATOM TRIESTE

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
INTERNATIONAL CENTRE FOR SCIENCE AND HIGH TECHNOLOGY
c/o INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS 34100 TRIESTE (ITALY) VIA GRIGNANO, 9 (ADRIATICO PALACE) P.O. BOX 586 TELEPHONE 040-224572 TELEFAX 040-224575 TELEX 460449 APH I

SMR/760-11

"College on Atmospheric Boundary Layer and Air Pollution Modelling"
16 May - 3 June 1994

"Characterization of Atmospheric Particles on Monuments by Scanning Electron Microscopy/Energy Dispersive X-ray Analyses"

T. TIRABASSI
Institute FISBAT/CNR
via Gobetti 101
Bologna, Italy

Please note: These notes are intended for internal distribution only.

MAIN BUILDING Strada Costiera, 11 Tel 22401 Telefax 224163 / 224559 Telex 460392 ADRIATICO GUEST HOUSE Via Grignano, 9 Tel 224241 Telefax 224531 Telex 460449
MICROPROCESSOR LAB. Via Beirut, 31 Tel 224471 Telefax 224600 GALILEO GUEST HOUSE Via Beirut, 7 Tel 22401

Characterization of atmospheric particles on monuments by scanning electron microscopy/energy dispersive X-ray analyses

Sabbioni C

ISTITUTO FISBAT - CNR, Via Castagnoli 1, 40126 Bologna, Italy

ABSTRACT

Atmospheric particles produced by various anthropogenic sources have been identified both on monuments and in the indoor enivironment by means of scanning electron microscopy/energy dispersive X-ray analyses.

INTRODUCTION

The deterioration of the cultural heritage is an important issue of current concern (1). Studies on artistic objects are today performed using highly sophisticated instrumentation, among which electron microscopy has made a valuable contribution (2-5).
So far, the study of damage caused by atmospheric pollutants to stone monuments of archeological interest has attempted to evidence both the role of gases, mainly sulphur dioxide, nitrogen oxides and ozone, as well as that of atmospheric aerosols.
Atmospheric aerosols, of natural or anthropogenic origin, vary in size from 0.005 to over 50 microns. Among the anthropogenic components, the aerosol emitted by combustion sources, i.e. industrial plants, heating units, automobile traffic, accounts for a considerable part. Once deposited on the surface, such particles lead to a number of different effects.
The experimental work carried out by our research team aims to reveal the presence of atmospheric particles, both in the alteration patinas of stone monuments outdoors and in the indoor environments which are host to works of artistic interest (museums, church interiors etc.).

EXPERIMENTAL WORK

Outdoor Monuments

Surface crusts, generally black in colour, are frequently observed on monuments in urban environments. These crusts are the product of interaction between stone, rain-water and atmospheric pollutants (6).
The main constituents of the crusts, analysed by means of X-ray diffraction (XRD), differential thermal analyses (DTA), thermal gravimetric analyses (TGA), combustion and infrared technique (LECO Apparatus Carbon Sulphur Determinator), are gypsum (i.e. calcium sulphate dihydrate), calcite (i.e. calcium carbonate) and noncarbonate carbon.
The noncarbonate carbon (Cnc) is defined by the following relation:

$$Cnc = Ct - Cc$$

where Ct is the total carbon content of the black crust and Cc is the carbonate carbon, that is, the

carbon present in the crust as calcite.
The noncarbonate carbon has been assumed as a quantitative index of the carbonaceous particles embedded within the framework of gypsum crystals, giving rise to their characteristic colour. Our experimental results indicate the carbonaceous particles to be the main component of the anthropogenic aerosols found in the black crusts (7,8).
Alongside bulk analyses, a study has been performed in order to evidence the different typologies of the carbonaceous particles present on damaged monuments in Italy.
The sampling was performed at eight sites in Northern and Central Italy: Milan, Venice, Rome, Bologna, Ravenna, Verona, Trento and La Spezia. The choice of sites was made in order to cover different typologies of urban areas: large (Milan and Rome), medium (Bologna and Venice), small (Verona and Trento), industrialized (Milan and Ravenna) and maritime (Venice, Ravenna and La Spezia). At each site, black crusts were collected from monuments situated in different areas and conditions, for example, town centres, suburbs and streets with varying levels of traffic, so as to ensure that the sampling was representative of the whole site rather than of a single monument.
The black crust samples were studied with a Scanning Electron Microscope fitted with a microanalysis system by selection of X-ray energy. Analyses were carried out on both bulk samples and on samples dissolved in chloridric acid N 10 and then filtered on Millipore filters. The fragments of black crusts and the insoluble particles obtained were mounted on double-adhesive tape affixed to aluminium stubs. They were then evaporatively coated with carbon to help reduce charging effects.

Indoor Environment

As well as the studies performed on outdoor monuments, experimental work was also performed indoors. By way of example, we outline here the work carried out in the Oratory of S. Maria delle Grazie in Milan, where Leonardo's Last Supper is housed.
Two sets of aerosol samples were collected during two campaigns, in Winter and mid-Summer, 1984. Samples were collected on Millipore filters on a continuous 24-hour basis and were divided into two parts: the first relative to the day-time hours when the public is admitted, the second relative to the night. The aim of this work was to identify the main particle typologies present in the sampled aerosol and advance some hypotheses as to the principle pollutant sources.

RESULTS

Outdoor Monuments

From SEM-EDAX observation various characteristic morphologies of atmospheric particles were found in the black crusts examined and the presence of common populations of particles was evidenced:
1 — the most numerous class is populated by spherical particles ranging from a few microns to 50 microns (Fig. 1 a), representative of particles emitted into the atmosphere from oil combustion by industrial plants, electricity generating units and big residential heating units (9, 10). Their abundance must be correlated to the fact that oil is the main fuel utilized in Italy for both electric energy production and domestic heating. The particles found show rounded pores and EDAX spectrum typical of soot particles where S and V are the principal elements;

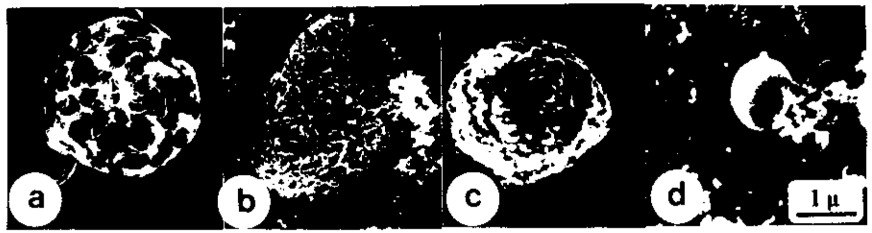

Fig 1 - Micrographs of atmospheric particles found in the damage layers of monuments: (a) carbonaceous particles emitted by oil combustion; (b) rounded particles and (c) spherical particles composed of submicron agglomerated particles typical of distilled oil combustion; (d) spherical aluminosilicate particles due to coal combustion.

2 — rounded and spherical particles with irregular and polygonal pores of submicron size (Fig. 1 b);
3 — spherical particles with a smooth surface and few circular pores;
4 — spherical particles composed of submicron agglomerated particles, as shown in Fig 1 c. Classes 2,3,4 were recognized to be typical of emissions from domestic heating units fueled by distilled oil (11). They all present a carbonaceous matrix with EDAX plot showing S and V as the main elements;
5 — more rarely, spherical particles with a smooth surface and a surface composition typical of aluminosilicate matrix were observed (Fig. 1 d). This morphology is typical of particles emitted by coal combustion (12);
6 — rare spherical smooth particles of 1 to 5 microns with Fe as principal element as shown by EDAX plot. Since these particles are emitted both by distilled oil and coal combustion (10,11), their source has not been identified.
In most cases, the distribution of particles in the crusts appear homogeneous, indicating that the black crusts have formed in recent times and therefore embed the atmospheric carbonaceous particles typical of present- day atmospheric pollution.

Indoor Environment

Analysed by SEM-EDAX, the particles sampled at the Oratory housing Leonardo's Last Supper yielded several results.
The winter samples revealed the following typologies:
— porous spherical particles with carbonaceous matrix of size ranging between 1 and 10 um. With regard to the elemental composition, S, Ca, Si and Al were found to be the main elements while V, Fe and Cu were secondary elements;
— irregular carbonaceous particles with EDAX plot similar to that of the previous class;
— smooth spherical particles ranging in size between 0.5 and 5 μm with metallic matrix.
These typologies are to be attributed to oil combustion for the purpose of both electricity production and domestic heating.
Conversely, the summer samples revealed the presence of submicron particles of size ranging

between 0.1 and 0.5 μm, with characteristics which can mainly be attributed to diesel-run engines, while the typologies re :aled by the winter samples, indicating domestic heating, are entirely absent. Thus, for conservation purposes, it appears necessary to limit the transport of particles from the surrounding areas into the interior of the Oratory, particularly from the 'piazza' infront of the Church of S. Maria delle Grazie, which constitutes an important source of particles emitted by diesel-run engines.

DISCUSSION

Carbonaceous particles represent a complex system, mainly composed of black carbon, primary and secondary organic compounds, sulphur and a small quantity of heavy metals, such as iron, vanadium and nichel. These particles play an important role in the damage of stone surfaces. They are responsible for the blackening observed on stone monuments and historical buildings in the urban environment and thus give rise to an undeniable aesthetic deterioration.
In addition to the visual impact, it has been suggested that the deposited particulate matter may also contribute to decay, particularly on stone materials, by contributing to the conversion of sulphur dioxide and nitrogen oxides to sulphuric acid and nitric acid respectively.
Furthermore, they participate in the structural damage arising from the sulphation of calcite into gypsum. Due to their sulphur content, carbonaceous particles contribute to the dry and wet deposition of sulphur on surfaces. The heavy metals present as oxides in their matrix are considered in the literature (13) to be important catalysts of the oxidation of S(IV) into S(VI). Finally, it has been suggested that carbonaceous particles (especially in view of their high specific surface) themselves function as catalysts for the conversion of sulphur dioxide to sulphuric acid (14).

ACKNOWLEDGEMENT

This work has been supported by the Commission of the European Communities within the STEP Programme (contract no. STEP-CT90- 0107).

REFERENCES

1) N.S. Baer, C. Sabbioni and A.I. Sors, Science, Technology and European Cultural Heritage. Butterworth, Oxford, 1991.
2) S.Z. Lewin and A.E. Charola, Scanning Electron Microscopy (1978) vol. 1, 695.
3) M. Del Monte et al., Atmospheric Environment (1981), 5, 645.
4) L.A. Leysen et al., Atmospheric Environment (1987), 11, 2425.
5) P. Ausset et. al., in Science, Technology and European Cultural Heritage (ed. N.S. Baer), Butterworth (1991) 452.
6) D. Camuffo et al., Atmospheric Environment (1982), 16, 2253.
7) G. Zappia and C. Sabbioni, Material Engin. (1991) 2, 255.
8) G. Zappia et. al., J. Aerosol Science (in press).
9) P. Bacci et al., J. Aerosol Science (1983), 14, 557.
10) P. Bacci et al., J. Aerosol Science (1988), 19, 1267.

11) C. Sabbioni and G. Zappia, Proc. 4th Intern. Conference on Carbonaceous Particles in the Atmosphere. (in press).
12) M. Del Monte and C. Sabbioni, Archiv. Meteorology, Geophysics and Bioclimatology, Vol. B 35, 93.
13) L.R. Martin, in Acid Precipitation, Ann Arbor Science, Michigan, 1983
14) S.G. Chang and T. Novakov, Atmos. Environ. (1981) 15, 1287.