1. Introduction

Several papers have been published on the monitoring of environmental conditions inside museums and galleries. There are also some works regarding air quality in churches, which are relevant for cultural heritage (CH). Historical buildings and castles, that have nowadays been turned into museums, where precious CH items are exhibited, should be studied as well. However, in such historical buildings, which are CH objects themselves, preservation techniques requiring significant interventions into the environment surrounding the exposed objects are not always possible. This applies not only to storage of CH objects in high-technological showcases with improved microclimatic conditions, but also to installations and drastic changes of the constructions. In the case of modern museum premises, the construction can be planned according to the requirements imposed by art conservators, such as hermetic sealing of the windows, limitations regarding daylight and light in general and stable microclimatic
conditions assured by sophisticated air conditioning systems. In the case of historical buildings, advanced changes in construction are limited. This may lead to some compromises, including more intensive exposure to atmospheric air pollution, which can be introduced by tourists, or by air exchange through windows.

The deposited atmospheric particulate matter, such as soot, organic material and gypsum particles adsorbing soot, can cause significant soiling of works of art. Oxidation of sulphur-rich particles to sulphuric acid can cause discolouration of paintings. This process can be catalyzed by iron-rich particles. Therefore, an appropriate knowledge of the chemical composition of particulate pollutants is crucial for conservation.

The aim of this study was to investigate the composition of particulate matter inside the museum of the Wawel Castle in Cracow, Poland. The Wawel Castle, the Polish Acropolis and Pantheon, is the most important place in Polish history and culture. For 500 years, this place was the country's political and cultural centre, and after Poland's loss of independence, it became the heart of the cult of the past, determining and reinforcing national awareness.

This paper presents chemical characteristics of atmospheric aerosol particles collected inside the museum, as a function of their size. During this study two micro- and trace analytical techniques were applied. Automated electron probe micro-analysis (EPMA) with energy-dispersive X-ray detection allows characterisation of large numbers of individual particles in a fast, automated way and can give detailed information about their elemental composition and size distribution. Micro-Raman spectrometry (MRS), a technique of molecular fingerprinting based on the unique position and symmetry of Raman shift bands, has lately become rather popular in the field of CH. There are numerous papers on the recognition of materials used for paintings, ceramics, pottery, wallpapers, textiles etc. MRS, considered to be non-destructive, can sometimes give a fast and conclusive answer about the composition of the investigated art object. However, its application to particulate matter still remains challenging. Only a few papers have been published on this aspect within the last couple of years. They are mainly devoted to optimisation of MRS analysis of individual particles and to the substrate contribution to the molecular spectrum. A preliminary study on the recognition of ambient and indoor aerosols was described by Potgieter-Vermaak and Van Grieken, who pointed out the relative simplicity of the detection of inorganic components, as well as the severe limitations in the case of organic species. Hereby we would like to present a novel approach to the analysis of the aerosol particles, involving automated EPMA followed by numerical data analysis.

2. Experimental

2.1 Sampling

Samples of particulate matter were collected inside the Royal Museum in the Wawel Castle in Cracow, Poland, in the wintertime (January, 2006). Samples were taken in a room situated on the second floor, called Senators' Hall. This large room has eight unsealed windows (double wooden frames) and the walls are mostly covered with panels and huge 16th century Flemish tapestries ("Arrases"). In Figure 1, we show the sampling set-up in the Senators’ Hall, with one of the tapestries and the Royal Throne.

For spectroscopic analyses (EPMA and MRS) of individual particles, samples were collected by a cascade Berner impactor equipped with a low-volume vacuum pump (30 L min⁻¹). Such strategy allows size segregation of the particles according to their aerodynamic diameter, based upon their inertial properties. For particles deposition, non-organic substrates (Si, Ag) were used. The particle size ranges (cut-off aerodynamic diameters) for the stages (3, 4, 5, 6, 7 and 8) of the Berner cascade impactor used, were equal to 0.25, 0.5, 1, 2,
4 and 8 µm, respectively. The samples were collected when no tourists were present.

2.2 Single particle analysis by EPMA

The size-segregated samples were analysed by means of a JEOL (Tokyo, Japan) 733 electron probe micro-analyser equipped with a super-atmospheric thin-window energy-dispersive X-ray detector (Oxford Instruments, Scotts Valley, CA) under the control of self-made software. This setup allows determination of also low-Z elements, like carbon, nitrogen and oxygen, which are required for rough chemical analysis at the single particle level. The applied measurement conditions are described elsewhere. For the samples collected on Si substrate (impactor stages 3 and 4), one hundred particles were measured manually. Approximately 300 particles deposited on Ag foils were analysed in an automated mode (for impactor stages 5-8). To avoid beam damage of the particles, 5000 particles were measured manually. Particles from different impactor stages were all treated independently. In stage 4 (Table 2), two abundant groups identified by EPMA contained relatively large amounts of carbon, i.e., they were mainly soot (partially oxidized), as shown in Table 1. MRS indeed confirmed that most particles contained mainly amorphous carbon. All this indicates that fine soot particles can easily penetrate inside the Hall from outdoors since no indoor sources can be considered. For preventive conservation, such particles are very dangerous, since they cause blackening of the surface.

Moreover, soot particles are very good sorbents for other organic species. The particle type #2 in Table 1 probably refers to soot agglomerated with ammonium sulphate: this compound is a well-known outdoor background aerosol derived from the reaction of sulphur compounds with ammonia. Cluster #3 was identified as agglomerates of sodium chloride, aluminosilicates and soot. The molecular identification of this combination was confirmed by MRS for aluminosilicates but not for sodium chloride since this compound gives a very weak response to laser exposure and the Raman scattering is not evident.

3. Results and Discussion

In order to identify the chemical properties and the possible interactions between particulate pollutants, the particles were classified by HCA into representative groups. The results, containing the elemental composition of the recognized particle types (clusters) for each impactor stage, are shown in Tables 1-6. The abundance of each cluster and its average composition expressed as "elemental composition" are given. Clusters with abundance below 1% were not considered in the further evaluation. It should be noted that the particles from stages 3 and 4 were collected on Si wafers (in view of their smooth surface properties, necessary for the smallest particles). Therefore, the contribution of Si in the X-ray spectra was not taken into account during clustering. A direct identification of aluminosilicates was derived from the contributions of oxygen and aluminium (since the occurrence of pure aluminium oxides did not seem reasonable).

Of the smallest particles, stage 3, almost all contained large amounts of carbon, i.e., they were mainly soot (partially oxidized), as shown in Table 1. MRS indeed confirmed that most particles contained mainly amorphous carbon. All this indicates that fine soot particles can easily penetrate inside the Hall from outdoors since no indoor sources can be considered. For preventive conservation, such particles are very dangerous, since they cause blackening of the surface. Moreover, soot particles are very good sorbents for other organic species. The particle type #2 in Table 1 probably refers to soot agglomerated with ammonium sulphate: this compound is a well-known outdoor background aerosol derived from the reaction of sulphur compounds with ammonia. Cluster #3 was identified as agglomerates of sodium chloride, aluminosilicates and soot. The molecular identification of this combination was confirmed by MRS for aluminosilicates but not for sodium chloride since this compound gives a very weak response to laser exposure and the Raman scattering is not evident.

Table 1: Particle characteristics derived from EPMA for impactor stage 3, aerodynamic diameter: 0.25 - 0.5 µm.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Abundance</th>
<th>Elemental composition (m/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>48%</td>
<td>C (74%); O (17%)</td>
</tr>
<tr>
<td>2</td>
<td>46%</td>
<td>C (67%); O (21%); N (3%); S (3%)</td>
</tr>
<tr>
<td>3</td>
<td>3%</td>
<td>C (57%); O (15%); Al 10%; Cl (8%); Na (2%)</td>
</tr>
<tr>
<td>4</td>
<td>3%</td>
<td>C (48%); O (32%); N (6%)</td>
</tr>
</tbody>
</table>

In stage 4 (Table 2), two abundant groups identified by EPMA contained relatively large amounts of copper, which is quite unexpected. The recognition of its source requires further investigations. However, since copper and gold floss was used in the production of tapestries, the deterioration of the numerous tapestries exhibited in the investigated room can be considered. Our EPMA system was not set to detect gold (although this will be done in subsequent research in the Castle).
Deterioration of the tapestries may be a reason for crumbling of the copper-rich threads and appearance of these tiny particles. Besides, in the cleansing liquids regularly applied to the tapestries, both elements were detected abundantly.

The second particle type in Table 2 is probably soot with some organic contribution. The molecular interpretation by MRS indicated again some contribution of soot for nearly all the particles in this size range.

The particles collected in impactor stage 5 (cut off 1.0 µm), shown in Table 3, seem to be the most differentiated (by the EMPA procedure) of all particle fractions. In fact, particle type #1, containing carbon/oxygen/sulphur/nitrogen, was split up by the EMPA approach into four groups but we have averaged these here.

MRS showed these abundant particles to consist of soot agglomerated with either ammonium sulphate (see RMS spectrum in Fig. 2) or sulphur bound to organic compounds. It is generally known that ammonium sulphate particles are hazardous to artworks, mainly paintings, because they attack the varnish layer. The question is whether their deteriorative impact increases, if they are agglomerated with soot.

MRS showed an exceptionally strong signal for amorphous carbon, which dwarfs other signals. The identification of cluster #2 in Table 4 was complicated due to the unusual composition. From MRS results, it could be concluded that a combination of copper oxides and carbonates agglomerated with amorphous carbon is present (see Figure 3). It can be supposed, that these species are products of oxidation and agglomeration processes of small metallic copper particles, found in smaller fractions.

In impactor stages 7 and 8 (Tables 5 and 6, respectively), more agglomerated species appeared. But as we examine larger particles, mineral components like calcite (probably from the limestone building walls), aluminosilicates and iron oxides (soil dust particles, passing along the windows or brought in by visitors), and even sodium chloride (probably from the de-icing of the courtyard) start to dominate the picture. The unusual presence of copper (which, as discussed above, might be from the deterioration of tapestries) is still confirmed, but occurs now more as oxide and carbonate, together with soot. In case of particle

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Abundance</th>
<th>Elemental composition (m/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>49%</td>
<td>Cu (93%); C (6%)</td>
</tr>
<tr>
<td>2</td>
<td>33%</td>
<td>C (78%); O (15%); N (3%)</td>
</tr>
<tr>
<td>3</td>
<td>18%</td>
<td>Cu (84%); C (13%)</td>
</tr>
</tbody>
</table>

Table 2: Particle characteristics derived from EPMA for impactor stage 4, aerodynamic diameter: 0.5 - 1 µm

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Abundance</th>
<th>Elemental composition (m/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70%</td>
<td>C (35%); O (35%); S (11%); N (10%)</td>
</tr>
<tr>
<td>2</td>
<td>9%</td>
<td>O (44%); C (15%); S (10%); Ca (8%); N (6%); Na (6%)</td>
</tr>
<tr>
<td>3</td>
<td>6%</td>
<td>C (64%); O (17%); S (6%)</td>
</tr>
<tr>
<td>4</td>
<td>6%</td>
<td>C (77%); O (9%)</td>
</tr>
<tr>
<td>5</td>
<td>5%</td>
<td>O (41%); C (20%); Si (13%); Al (7%)</td>
</tr>
<tr>
<td>6</td>
<td>3%</td>
<td>O (34%); Fe (32%); C (16%)</td>
</tr>
</tbody>
</table>

Table 3: Particle characteristics derived from EPMA for impactor stage 5, aerodynamic diameter: 1 - 2 µm

Figure 2: Raman spectra of selected particles representative for clusters identified by EPMA
such as actinolite Ca_2(Mg,Fe^{II})_5Si_8O_{22}(OH)_2 (part-agglomerates of calcium-rich aluminosilicates type #1 in Table 5, we can see indications for significant result.

of collection, which still assures a statistically sig-manted EPMA, it is possible to scan the whole area due to low particle concentration. During the auto-

8, the manual analysis by MRS was quite difficult in case of stage 8, with calcite. In case of stage 7, with hematite, and in cluster # 4 of stage 7 and cluster # 3 of stage 8 with calcite. In case of stage 6, aerodynamic diameter: 2 - 4 µm.

Table 4: Particle characteristics derived from EPMA for impactor stage 6, aerodynamic diameter: 2 - 4 µm.

Cluster Abundance Elemental composition (m/m)
1 21% C (37%); O (33%); Ca (6%); N (4%)
2 14% C (61%); O (18%); Cu (8%)
3 13% C (76%); O (15%)
4 13% O(44%); C (20%); N (15%); S (14%)
5 13% O(36%); C (16%); N (5%); Na (15%); Cl (9%); S (6%)
6 12% O (42%); C (14%); Al (12%); Si (15%)
7 12% O (45%); C (19%); Ca (18%); S (8%)
8 12% O (46%); C (19%); Ca (18%); S (8%)

Table 5: Particle characteristics derived from EPMA for impactor stage 7, aerodynamic diameter: 4 - 8 µm.

Cluster Abundance Elemental composition (m/m)
1 26% O (29%); Cu (10%); Ca (9%); Al (8%); Cl (6%); Na (5%); C (4%); Mg (2%); FeO(2%)
2 21% Ca (40%); O (29%); C(9%)
3 20% Cu (52%); C (14%); O (9%)
4 19% Cu (31%); Ca (24%); O (20%); C (8%)
5 10% C (39%); O (20%); Ca (11%); Si (6%); Cl (6%); Al (4%)
6 4% Fe (73%); O (9%); Cu(7%)

Table 6: Particle characteristics derived from EPMA for impactor stage 8, aerodynamic diameter: >8 µm.

Cluster Abundance Elemental composition (m/m)
1 29% Cu (56%); C (16%); O (6%)
2 29% O (29%); C (15%); Si (9%); Ca (68%); Cu (9%); Al (6%)
3 18% Ca (46%); O (25%); Cu (15%); C (4%)
4 11% C (49%); Ca (14%); O (14%); Cl (6%)
5 6% Fe (79%); O (9%)
6 5 5 Al (36%); Si (26%); O (25%)
7 2 2 Cl (52%); Na (31%)

4. Conclusions

The application of EPMA for identification of sus-pended particulate matter enables us to discrimi-nate particles rich with certain elements, but a complementary image can be achieved by simulta-neous molecular analysis by MRS. However, the results should be treated with caution. From the analytical point of view, even a combination of these powerful techniques may not give a conclusive identification of the species. The number and type of elements gathered in one particle type recognised by the EPMA procedure reflects the averaged data of individual particles classified according to their similarity. During the molecular interpretation, it turned out that the high carbon content in the particles, which masked other components, was most problematic. Still, this points to the overall abundance of outdoors soot in the Wawel Castle, which is a major concern for preventive conservation. On the other hand, unquestionable progress in data interpretation was achieved in case of mixed aerosol species and agglomerates, which also predominate in the larger particles in the museum. The finest particle fraction consists mostly of amorphous carbon (soot from combustion), while, in the micrometer-size fraction, significant amounts of amorphous carbon agglomerated with ammonium sulphate were found. An unambiguous identification was obtained in case of Ca/C/O-rich particles. The unexpected Cu-rich particles require further attention.

Acknowledgements

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References


