

Monuments as sampling surfaces of recent traffic pollution

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Abstract

Background, aim, and scope. A new approach towards monuments, considering them as a passive sampler of pollution, is presented. Cultural Heritage objects suffer daily the damages of environmental pollution, especially in those areas interested by heavy traffic. Since monuments undergo only periodically conservation or maintenance works, surfaces are able to accumulate atmospheric deposit and to record changes in its composition. An optimised analytical protocol was developed in order to quantify platinum and rhodium at trace level on surfaces. The two elements have become tracers of automobile emissions in recent years, since the introduction of catalytic converters, and could have catalytic effects on the decay reactions of natural and artificial stone materials. As first case study, the cement mortar surfaces of a XX Century monument, the Camerlata Fountain, in Como (Italy) were investigated. Materials and methods. The surfaces of the monument were scraped in areas both exposed to atmosphere and sheltered by the architectural elements of the building. The powders were dissolved by microwave assisted mineralisation with a solution of HCl and HNO₃. The solution was filtered, irradiated and analysed by Adsorptive Cathodic Stripping Voltammetry. The powders were also analysed by Infrared Spectroscopy and X-Ray Diffraction in order to determine the chemical and mineralogical composition.

Results and discussion. An analysis protocol was set up considering the matrix effect and the expected low concentrations of the two metals. The results enlightened variable concentration values and distributions area of platinum (0.013-45 µg/Kg) and rhodium (0.55-274.4 µg/Kg) suggesting the ability of artificial stone surfaces to accumulate the two elements. The samples chemical and mineralogical composition was consistent with a typical cement plaster interested by decay phenomena.

Conclusions. This work investigated the relation between Cultural Heritage and pollution by another point of view. The analytical protocol presented in this paper was effective in determining platinum and rhodium in traces on the investigated stone surfaces with negligible matrix effects.

Recommendation and perspectives. The presence of platinum and rhodium on monuments surfaces should be of significant interest when planning Cultural Heritage conservation. A better knowledge of the two metals role in decay phenomena could impact in a positive way the artworks conservation.

Keywords: Atmospheric particulate; Monument surface; Platinum; Rhodium; Electro analytical techniques

1. Background, aim, and scope

Air quality and climate quickly changed in the last years requiring new researches focused on pollution effects, not only on environment and human health, but also on outdoor cultural heritage. As well known, the daily exposure to atmosphere in urban areas causes degradation processes on the stone monuments surfaces (natural stones, mortars, stuccoes) being soiling, concretions, films, black crusts and deposit the most diffused and investigated phenomena. A look into the literature enlightened how few is still known on the atmospheric aerosol impact on the built heritage, in particular on its content of metals coming from pollution (Hamilton et al. 1995; Schiavon et al. 1995; Rodriguez-Navarro and Sebastian 1996; Lammel and Metzsig 1997; Primerano et al. 2000; Delalieux et al. 2001; Esbert et al. 2001; Brimblecombe and Grossi 2005). For decades lead content in aerosol was the indicator of petrol vehicles, but at the present time platinum, palladium and rhodium (i.e. PGE, Platinum Group Elements) are the new markers of traffic areas. The emission of these metals as particulate particles is a consequence of the degradation of catalytic converters, chemical and physical stresses caused by oxidation and reduction reactions, high working temperatures and mechanical abrasions, mainly the wear and tear mechanism of the external layer rich in the two catalysts (Smichowski et al. 2008, Wiseman et al. 2009) being the most important causes. The mobility of aerosol and its content of PGE has been generally investigated on solid surfaces, mostly of environmental interest, e.g. snow, leaves, gullypot, soil, sediment, road dust (Smichowski et al. 2008; Dubiella-Jackowska et al. 2009; Wiseman et al. 2009). Outdoor monuments, particularly the widespread natural and artificial stone materials, may represent a new frontier. More researches concerning the metals catalytic activity and its role in the well-known degradation mechanisms would be developed (Ausset et al. 1996; Rodriguez-Navarro et al. 1996; Moropoulou et al. 1998; Boko et al. 1999; Chabas and Lefevre 2000; Primerano et al. 2000; Esbert et al. 2001; Moropoulou et al. 2001; Cultrone et al. 2008). In some cases metal species in carbon particles may act as nucleation particles for the formation of gypsum crusts, elsewhere the particulate matter catalyzes the sulfation of stone materials (Ausset et al. 1996; Rodriguez-Navarro et al. 1996; Boko et al. 1999; Primerano et al. 2000). Moropoulou et alii correlated the composition of the airborne particles detected on stone surfaces with the decay crusts formed on them observing that specific metals seemed to contribute to the decay mechanisms (Moropoulou et al. 2001). Recently Cultrone et alii observed that diesel particulate enhances the sulfation of calcitic and dolomitic mortars in simulation tests, acting as catalyzer for SO₂ oxidation and hydrolysis to sulphuric acid (Cultrone et al. 2008).

In this paper a new approach towards monuments was tried. Since aerosol tends to deposit on monuments stone surfaces, and since they are seldom cleaned, they may present an integrated situation of moveable PGE species mechanisms of transport, dissolution and deposition. We focused on platinum and rhodium for some reasons. Pt is well known to be the necessary component in all types of catalytic converters because of its efficiency in transforming hydrocarbons and carbon monoxide to water and carbon dioxide, while Rh is more efficient in reducing nitrogen oxide to nitrogen. Therefore Pt can be considered as the best probe to monitor environmental pollution of all types of catalytic converters, whereas Rh traces gasoline engine 3-way converters (Fornalczyk and Saturnus 2009). Adsorptive Cathodic Stripping Voltammetry (AdCSV) was selected as the analytical method considering the very low detection limits, the low cost of the analysis (with the opportunity of portable devices) and the possibility to quantify Pt and Rh in a single analytical determination, a very important issue when dealing with Cultural Heritage as samples are often available in very small quantities (Helmerts and Mergel 1998; Barefoot 1999; Bencs et al. 2003; Pozzi et al. 2003; Locatelli 2007).

Furthermore voltammetry may overcome the spectroscopic interferences due to the high Ca and Mg content present in stone materials such as marbles and mortars (Bencs et al. 1998).

Aims of the work were the assessment of the deposition of Pt and Rh on artificial stone surfaces, in particular cement mortars, and the optimisation of an analytical procedure which allowed to determine of the two metals considering the peculiar matrix.

The new approach was tested on the Camerlata Fountain in Como (Italy), built in 1934–5. The monument (Figure 1) was designed by Carlo Cattaneo and Mario Radice, architects joining the Rationalist Movement at the beginning of the 19th century in Italy.



Fig. 1 Picture of the Camerlata Fountain

Erected for the 6th International Triennial Exhibition of Architecture and Decoration in Milan in 1936, it was later dismantled and rebuilt in 1960 in the centre of the main square of the Camerlata suburb area, at the entrance of Como. It is a nine-meter-high abstract sculpture, remarkable for the harmonic balance of four white circular shelves having a circumference of six meters and four spheres. A metallic framework with a pillar going through the axle of the spheres and rings supports the elements and the structure is covered with cement mortars. The choice of the monument was driven by its peculiarities. Firstly the building is located as a traffic island in a square crossed by four different roads and well-travelled. Secondly, as the last conservation work dated back to early Nineties, it is reasonable to find the particulate deposited over a number of years on the sheltered surfaces. Thirdly, the particular shape of the building, rich of horizontal surfaces, enhanced the deposition of particulate.

2. Materials and method

2.1 Sampling site: the Camerlata fountain

As usually when dealing with art objects, the sampling is a critical step. In this case study, the samples should in fact be representative of the deposited particulate, whose quality and quantity mainly depend on the morphology, exposure of the surfaces and, last but not least, on their conservation state. Eventually, as the building is a safeguarded artwork, the number of samples must be as lower as possible. The sampling was focused on a few areas (Figure 2), or completely

exposed to the atmosphere, i.e. on the horizontal surfaces of the rings, or sheltered by the spheres or the rings. In some cases they were characterised by an evident blackening, in others by the presence of whitish, greyish and ochre concretions (Table 1). The surface samples were scraped by the mortar by means of a small chisel.

Some small fragments of mortars were sampled near sample FC2 and cleaned from the surface layers by a small chisel in order to determine the limit of detection of the methodology and analyse the composition of the sound mortar, i.e. the nature of the binder and aggregate phases. The sampling campaign was carried out during summertime.

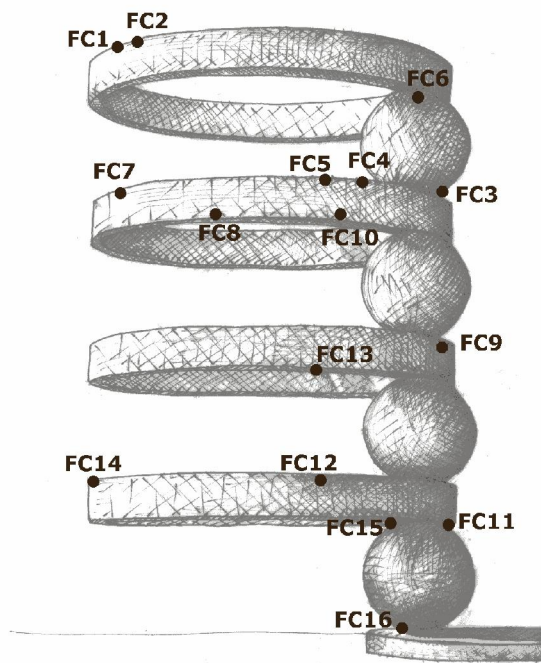


Fig. 2 Sketch of the Camerlata Fountain showing the sampling points

Sample	Height of sampling (m)	Description	Exposure	Rh ($\mu\text{g}/\text{Kg}$)	Rh SD ($\mu\text{g}/\text{Kg}$)	Pt ($\mu\text{g}/\text{Kg}$)	Pt SD ($\mu\text{g}/\text{Kg}$)
FC 1	9	Black deposit	Not sheltered	89	8.3	<LOD	-
FC 2	9	Black deposit	Not sheltered	7.4	0.47	11	1.3
FC 3	6.8	Black deposit	Sheltered	<LOD	-	500	45
FC 4	6.8	Whitish concretion	Not sheltered	<LOD	-	11.2	0.55
FC 5	6.8	Greyish concretion	Not sheltered	<LOD	-	1.40	0.054
FC 6	8.4	Whitish concretion	Sheltered	<LOD	-	3.1	0.23
FC 7	6.8	Black deposit	Not sheltered	38.1	0.94	21.9	0.47
FC 8	6.2	Black deposit	Not sheltered	<LOD	-	2.50	0.061
FC 9	4.6	Greyish concretion	Not sheltered	60	18	33.8	0.37
FC10	6.2	Whitish concretion	Not sheltered	0.55	0.036	1.20	0.013
FC11	1.8	Black deposit	Sheltered	<LOD	-	39	3.7
FC12	2.4	Ochre concretion	Not sheltered	<LOD	-	4.60	0.016
FC13	4	Ochre concretion	Sheltered	274.4	0.34	33.6	0.92
FC14	2.4	Ochre concretion	Not sheltered	41.92	2.5	18	1.8
FC15	1.8	Whitish concretion	Sheltered	6.940	0.0061	4.1	0.075
FC16	0.20	Black deposit	Sheltered	<LOD	-	140	15

[SD= Standard Deviation; LOD=Limit of Detection]

Table 1 Samples description and Pt and Rh concentrations.

2.2 The sample treatment

Dissolution

The acid dissolution step of solid samples was carried out as follows. The samples (around 100 mg) were powdered in an agate mortar and dried for 24h in an oven at 80°C. A weighed amount of dried powder was transferred into a PTFE vessel with 1.5 mL of 37% HCl, 0.5 mL of HNO₃ (suprapur grade) and sonicated for few minutes in order to remove CO₂ and avoid over pressure during the acid attack. The high-pressure digestion was carried out in sealed Teflon vessels by a Milestone MLS-1200 microwave system equipped with a temperature control unit. The experimental parameters are shown in Table 2.

After mineralisation samples were heated on hot plate to dryness and residues were treated with 2 mL of HCl 2% in order to re-solubilise platinum and rhodium.

The solutions were then filtered on Millipore nitrocellulose filters 0,45 μm and the residue carefully dried and weighed. The solutions were then quantitatively transferred into 100 mL volumetric flasks and aliquots irradiated for the UV-digestion. This dilution allows to reach a pH value compatible with the voltammetric determination.

<i>Step</i>	<i>Temperature (°C)</i>	<i>Power (W)</i>	<i>Time (min)</i>
Pre-heating	75	250	3
Thermalisation	-	0	1
Mineralisation	150	500	10
Cooling down	-	0	10

Table 2- Microwave program for samples digestion

UV-digestion

Voltammetric metals determination requires samples free from organic matter (Locatelli 2007). Samples were irradiated in a Metrohm 705 UV Digester employing a 500 W high pressure mercury vapour lamp, for three hours.

Pt and Rh analyses

10 mL of the sample were transferred in the voltammetric cell, 162 μ L of 37% HCl and 10 μ L of formaldehyde were added and finally rhodium was analysed. Afterwards, 15 μ L of hydrazine sulphate were added to enable the platinum determination. The quantification of both analytes in the same solution was performed through the standard addition method.

2.3 Analytical techniques

The surface samples and the sound mortars were finely ground and analysed with a diffractometer Bruker AXS D8 ADVANCE with the following conditions: 40 kV; 40 mA; slit DS 1.0; RS 0.2 mm; R=217.5mm; radiation Cu-K α ; λ = 1.5418 Å; pyrolytic graphite monochromator with diffracted ray; geometry θ : θ ; soller slits 2.3°; continuous scan 1°/min; $\Delta 2\theta$ = 0.02°; scan range 5-55°; deep quarter sampler 200 μ m. The results were compared with search libraries provided by the EVA Bruker software.

The powders were lately analysed as KBr pellets by a FTIR spectrophotometer Nicolet Nexus, in the transmission mode (400 to 4000 cm^{-1} , 4 cm^{-1} resolution). The samples were carefully collected under a stereomicroscope by means of a needle-sampler. The spectra were compared with standard references (Wilson 1994).

Pt and Rh AdCSV determinations were carried on the dissolved and opportunely diluted surface samples by Metrohm 746 VA Analyzer, equipped with an HMDE as working electrode, a glassy carbon auxiliary electrode and Ag/AgCl reference electrode. The solutions were analysed in a Teflon cell in order to minimise adsorption phenomena on the walls. The instrumental settings are described in Table 3.

A standard EDTA 0.01M solution was employed to perform the complexometric titration for the determination of the total amount of calcium and magnesium in the dissolved samples, with the aim to determine the binder/aggregate ratio (B/A ratio).

Instrumental parameter	Rhodium	Platinum
Drop Size (a.u.)	5	5
Deposition Potential (V)	-0.7	-0.7
Deposition Time (sec.)	60	60
Start Potential (V)	-1	-0.7
End Potential (V)	-1.2	-1
Voltage Step (mV)	2	2

Table 3- Instrumental settings employed for Pt and Rh determination

3. Results and discussion

3.1 Chemical and mineralogical characterisation of the samples

FTIR and XRD analyses were carried out both on the sound mortar fragments and on the powders scraped off the monument surfaces. The fragments were finely ground and the powders were analysed. All the samples contained both carbonatic and silicatic fractions as expected in cement mortars. In particular, FTIR spectra presented the peculiar absorbance peaks of calcite, around 1420, 875 and 712 cm^{-1} . The signal around 1028 cm^{-1} and the doublet at 798-780 cm^{-1} indicated respectively the presence of silicates and quartz ascribable to the aggregate phase. XRD spectra identified the silicatic content as illite.

The mortars binder/aggregate ratio (B/A ratio) was also determined. Several sound fragments were weighted, dissolved as described in paragraph 3.2, and the insoluble fraction carefully dried and weighted. The B/A ratio was calculated as ratio between the binder and the aggregate weights, ascribing the carbonatic content only to the binder fraction. The B/A value was also determined by complexometric titration of Ca and Mg with standard solution EDTA 0.01M. An average value of 1:2 was obtained for both approaches.

Coming to the surface powders, FTIR and XRD analyses confirmed everywhere the patterns observed for the sound mortar, i.e. calcite, small quartz amounts and silicates, identified by XRD spectra as illite. Ettringite was also identified by XRD analyses, probably related to the sulphation of cementitious phases. Moreover, traces of organic compounds were indicated by FTIR absorbance around 2957, 2875 and 1728 cm^{-1} . The peaks were consistent with the presence of residues of acrylic resins used during the conservation work occurred in the Nineties. In a few cases gypsum (samples FC13 and FC16) was identified in FTIR spectra (absorbance peaks at 3545, 3408, 1620, 1140 and 1116 cm^{-1}) as minor component, probably ascribed to the well known sulphation of the cement mortar carbonatic fraction.

3.2 Dissolution and sample pre-treatments

According to literature (Pozzi et al. 2003; Rauch et al. 2001) an *aqua regia* acid attack micro-wave assisted was chosen to dissolve the sample. The nitric acid excess was eliminated by heating the samples to dryness since it could interfere with the voltammetric analysis. During the dissolution step, the sample dissolution percentage was very various, from a minimum of 47% up to 100%, depending on the fraction of mortar scraped with particulate deposits. On the basis of previous works (Pozzi et al. 2003; Rampazzi et al. 2003) the MW parameters were set up to assure the dissolution of both PGE and “acid soluble” mortars fraction.

Organic compounds present in samples can affect the analytical determinations either directly by interactions with the electrode or indirectly by complex formation with metal ions. In order to overcome interferences effects, a UV-digestion step to be applied prior to the voltammetric analysis was optimized. UV irradiation of the dissolved compounds enhances the decomposition of the organic matter by the formation of several highly reactive oxidative species. The advantage of this approach is the minimal sample contamination risk as no reagents are added to the sample solution. Small amounts of hydrogen peroxide could accelerate in any case the degradation of organic substances.

For this reason, the irradiation time influence and the presence of hydrogen peroxide were studied using one of the samples collected on the Fountain (sample FC7). The sample was dissolved and properly diluted. 10 mL aliquots of the solution were then irradiated with and without 150 μ L of hydrogen peroxide keeping the temperature between 80°C and 90°C and employing a 500 W high pressure mercury vapour lamp. As a result, after three hours irradiation no meaningful differences were observed between the concentration values of both metals. Furthermore, the hydrogen peroxide presence was considered non influential. Finally the optimized digestion procedure was carried out for three hours irradiation time without any hydrogen peroxide addition prior to any voltammetric determination.

3.3 Blank analysis and Limit of Detection

It is worthwhile to remind that when dealing with Cultural Heritage only limited sample amounts are generally available and this affects the limit of detection (LOD) of the whole analytical procedure. According to IUPAC formula (International Union of Pure and Applied Chemistry) LOD was calculated starting from the blank standard deviation, i.e. a sound mortar sample.

Almost 100 mg of sample were finely powdered and dried, dissolved and diluted according to the procedure previously described. No voltammetric signals were registered for both metals, confirming that there was no contamination during the whole procedure and that the mortar coming from Camerlata Fountain did not contain any appreciable amounts of platinum and rhodium. Platinum and rhodium standard additions were then performed. Eventually, LODs on liquid were calculated according to the IUPAC formula on the standard deviation of a sample with Pt and Rh concentrations near to the LOD. The values of LOD determined for the solutions translated to concentrations of 0.44 μ g/kg for platinum and 0.48 μ g/kg for rhodium in the solid samples.

The very low values allowed the determination of platinum and rhodium at trace levels in most of the samples.

3.4 Determination of Pt and Rh in the samples

First of all the effects of the high amounts of calcium and magnesium coming from the plaster surface on the voltammetric determination were evaluated. Known amounts of platinum and rhodium (final concentration 2 ng/L, a value comparable with those found in environmental samples) were added to a synthetic solution resembling the maximum concentration that Ca^{2+} and Mg^{2+} can assume in mortar samples (final concentration 0,053 g/L for Ca^{2+} and 0,014 g/L for Mg^{2+} , considering 100 mg of a mortar sample with 1:2 B/A and 40% w/w of calcium carbonate and 15% of magnesium carbonate, diluted to 100 ml). Pt and Rh were then quantified in this solution. Recoveries obtained for three replicates were above 90% for both analytes. Thus, it was possible to affirm the absence of matrix effect on the quantitative determination of Pt and Rh.

As usual in the Cultural Heritage field there is a lack in specific Standard Reference Materials. Thus, the whole analytical procedure, starting from the dissolution step to the quantitative platinum and rhodium determination, was tested on a sample coming from the Camerlata Fountain (sample FC7 as it was available in a sufficient quantity). It was divided into three aliquots after an adequate grinding and homogenization. The three aliquots were then dissolved and analysed. The standard deviation was finally calculated considering the three obtained rhodium and platinum values. Authors considered these values as an estimate of the whole procedure standard deviations: they resulted less than 5% for both analytes.

Platinum and rhodium quantitative determination together with the standard deviation provided by the instrument (thus obtained considering the five instrumental repetitions for a given sample), are summarised in Table 1. It is worthwhile to note that the average standard deviation (mean of the standard deviations of all the analysed samples) for both platinum and rhodium is about 5% (only sample FC9 showed an high variability in the instrumental repetitions resulting in a standard deviation of about 30%).

As mentioned in paragraph 3.2, the dissolution percentage of the investigated samples was very various. This could be ascribed to the fraction of plaster scraped together with the particulate deposit. While the binder fraction is acid soluble, the aggregate fraction remained as precipitate (authors considered that other insoluble fractions, e.g. silicates and carbon particles normally present in the particulate matter, gypsum and organic matter were negligible with respect to the insoluble residue coming from aggregate fraction of the plaster). As the B/A ratio of the plaster is known, it is simple to derive the weight of the mortar fraction dissolved by the acid attack (the binder fraction) from the weight of the residue after the acid attack. These two quantities, subtracted to the total amount of weighed samples, allowed to determine the quantity of the analysed particulate deposit. Platinum and rhodium concentrations were then referred to the amount of the particulate deposit fraction of each sample.

The fountain was sampled in areas very different one from each other, i.e. different exposure and height, in order to represent in the most complete way the deposition variability. Thus, the data confirmed the expected results.

As first result, no correlation between the degradation type and the concentration values of both metals was found.

Platinum was found in almost all the investigated samples while rhodium concentration was below LOD in several cases. No correlation between the two metals was found: e.g. the sample that showed the highest value for platinum had a value below the LOD for rhodium. Literature confirms that the Pt and Rh ratios in solid matrices are not constant and may vary in a large range.

A very high variability in the found values for both analytes arose from the study. Nevertheless it is worthwhile to note that the platinum highest concentration values were found in samples collected at the bottom part of the monument.

Two samples showed peculiar values: sample FC3 presented a very high concentration of platinum (500 µg/kg) while sample FC13 showed the highest concentration of rhodium (274.4 µg/kg). It is worthwhile to note that these two samples were placed in areas particularly sheltered by rain runoff, thus high amounts of particulate could be accumulated.

This high variability could be ascribed to the presence of two mechanisms that may be involved in such distribution pattern, i.e. the deposition of particulate matter on to cement mortar surface that should be constant over the monument, and the particulate matter and/or pollutants removal via precipitations or more in general via meteorological events.

Moreover, Rh and Pt removal and/or remobilisation within the monument surface could also be caused by their solubilisation in the percolating water. It is in fact suggested by various authors that a non negligible Pt and Rh fraction in the particle matter near roads and motorways is water soluble.

4. Conclusions

In this work a new approach towards the relation between monuments and pollution was undertaken. On one hand, the opportunity of determining platinum and rhodium on mortars was verified, and their distribution over the monument was evaluated. Secondly, the whole analytical protocol was optimized for the determination of platinum and rhodium deposited on monument surfaces. The choice of the cases study was of primary concern, by the point of view of sampling opportunity and by its urban position. Of significant interest from these results is that the whole procedure proved very effective for the determination of platinum, particularly in terms of detection limits and negligible matrix interferences, notwithstanding an expected variability of concentrations. The amounts of rhodium were even more variable, being absent in some of the samples and more concentrated than platinum elsewhere. Whether it was a matter of sampling, being a matter of analytical procedure requiring greater amounts of sample, or mirror of the inequality of the actual distribution of rhodium on surfaces, needs to be enlightened in a new dedicated analytical campaign.

Besides these criticisms, the work gained a twofold purpose.

By the environmental point of view, the stone surfaces of the Camerlata Fountain actually suffered the contamination of modern pollutants such as platinum and rhodium, particularly in those areas sheltered by rain runoff and able to accumulate atmospheric deposit. The approach here proposed suggests the ability of artificial stone surfaces to give an integrated evaluation of modern pollutants such as Pt and Rh in the particulate matter, in view to the comparison of air quality among areas characterised by different kinds of pollution.

The occurrence of platinum and rhodium on monuments surfaces should be of significant interest when planning Cultural Heritage conservation as well. Thus, besides the decay phenomena traditionally considered and investigated on outdoor monuments (e.g. gypsum crusts, efflorescence, incrustations, films, and blackening), the presence of catalytic metals specifically coming from the vehicular pollution has to be seriously considered. A better knowledge of the metals role in degradation mechanisms could in fact impact in a positive way the artworks conservation and contribute to the answering of questions about the pedestrianisation of urban historic areas.

Thus, Voltammetry should be the key analytical technique for such determinations in conservation science, considering the advantages previously discussed. This issue is only the preliminary step, necessary to stress the critical points of an

articulate monitoring, i.e. the sampling and the acid attack steps, the analytical problems, interferences of the stone matrix. Taking a step beyond, the Authors have started the investigations of other monuments by the optimised analytical procedure, focusing also on the comprehension of the role of platinum and rhodium in the decay processes of natural and artificial stone surfaces.

Acknowledgments

The Authors would like to thank the Municipality of Como for the permission of sampling the monument, Dr. Francesca Roncoroni for the sketch of the Camerlata Fountain, and Dr. Marcello Marelli for the picture of the monument.

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