

Corrosive effects from the deposition of gaseous pollutants on surfaces of cultural and artistic value inside museums

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Abstract

The objectives of the project were to assess the critical relationships between environmental factors and damage of the artefacts and other cultural property exposed inside museums, by studying: (a) the outdoor/indoor pollutant concentration and their transfer inside the museum; (b) the distribution and circulation of pollutants inside the museum influenced by various factors; (c) chemical interactions between pollutants in the gas phase leading to removal and/or formation of secondary pollutants; (d) the final deposition of the indoor pollutants on surfaces of artistic interest and the damage on them, governed by strictly defined physicochemical parameters. All the above information, together with the main factors influencing each stage, were obtained by applying the methodology developed and described in detail here. Measurements of rate constants of reactions in the gas phase, of physicochemical deposition parameters on artefacts, and the synergistic effects of pollutants on the deposition parameters, were conducted. Seven PC programmes for analysing the experimental data were written and used. The pollutants, the solid materials and the museums chosen in this programme are only examples needed to develop the necessary methodology. The numerical results obtained serve the purpose of exemplifying the procedures and not enriching the

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world's bibliography with useless empirical information. Two commercially available protectives for marble were investigated from the point of view of their reactivity towards SO_2 by using a diffusional technique. From measurements of SO_2 concentration carried out on three types of marble, the deposition velocities have been calculated. Indoor monitoring of the church of San Luigi dei Francesi and of the Museo della Civiltà Romana in Rome has shown that indoor production of nitrous acid most likely results from heterogeneous reactions indoors, on the walls and the exposed surfaces. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

This paper presents some conclusions that can be drawn from the principal results obtained within the framework of an EC project, aiming at the determination of the principal physicochemical parameters valid in the indoor environment of museums on the artworks stored and/or displayed in them. It is well known that indoor environments comprise multiphase systems in which important chemical and physical transformations of trace substances occur. It is known that an important process which contributes to the damage of artworks is dry deposition of acid species [1,2]. Acidity in the air is essentially caused by criteria pollutants, such as sulphur and nitrogen oxides, which are emitted into the atmosphere by sources related to industry, transportation and heating. These species are transformed, through complex reaction pathways, into gaseous nitric and nitrous acids (HNO_3 and HONO) and into acidic sulphates as suspended particles. Studies of the basic processes leading to these transformations are essential for understanding the role of deposition phenomena and chemical reactivity, so that the removal of aggressive chemicals is successful. Recent studies of the air quality in one of the most important Italian Museums and in a famous church of Rome have demonstrated the presence of consistent levels of HNO_3 and other aggressive species such as sulphur dioxide and ozone. High levels of indoor HONO, greatly exceeding outdoor levels, have also been measured [3,4].

The activity which has been performed can be divided in two parts: one in the laboratory for the study of the physicochemical behaviour of various materials, and the other pertaining to the study of the characteristics of indoor environments with special emphases to the formation of HONO.

The main objectives of the project were the following.

(1) To provide a better understanding of the mechanism for the dry deposition of pollutants on surfaces related to the conservation of artworks. To this end, pieces of marble from real exhibits (Kavala, Greece), three types of marble as such or protected with two protectives, pieces of ceramics and several types of pigments, were selected as model surfaces. Regarding the choice of pollutants to use in the experimental trials, it is well recognised that the oxidation of SO_2 over carbonate stones is an important pathway for the transformation of calcite into gypsum, which is the principal cause of deterioration of marble surfaces [5–8]. As pointed by Barone et al. [9], the major natural source of sulfur in the troposphere is dimethyl sulfide, $(\text{CH}_3)_2\text{S}$, emitted by oceanic phyto-

plankton. As far as pigments are concerned, it is known that they can be affected by a whole array of pollutants, among them NO_2 and C_xH_y [10].

(2) To disclose the physicochemical parameters which affect the transfer of a pollutant into the museum. To this regard, the study of the corrosion process can be considered on the basis of the following: (a) the relationship between outdoor and indoor air pollutants, and their transfer from the open atmosphere to the interior of the buildings, its main driving force being the concentration difference indoors and outdoors; (b) chemical interactions between pollutants in the gas phase leading to removal of some of them from indoor air and/or formation of other secondary pollutants; (c) the final deposition of the indoor pollutants on surfaces of artistic interest, with a finite measurable velocity and reaction probability.

After having considered the aforementioned goals of the project, the following rationale was established. Since it was recognised that the majority of the controlled environmental experiments in the laboratory had been performed in contained systems by using high concentration levels of pollutants, it was decided to use also concentrations not much dissimilar to the atmospheric concentration in urban environments. In fact, many experiments reported in the literature often pertain to concentration levels of pollutants that are at least two to three orders of magnitude higher than those characteristic of the real ambient atmosphere [5–8]. It is difficult sometimes to study mechanisms potentially important only at the low concentration region, because they may be masked by other processes occurring at higher concentration levels.

It is worth stressing that another potential drawback of some of the studies reported in the literature was that they overlook the fact that it is important to study the intrinsic reactivity of the surface independent or corrected for mass-transfer limitations. In fact, since the diffusion of pollutants is usually slow at atmospheric pressure, it was recognised that most of the reported corrosion rates, both in the field and in the laboratory, are presumably flawed by mass transfer limitations. In the present work gaseous diffusion and mass transfer processes, adsorption–desorption phenomena and nonlinearity of the isotherm, and chemical reactions, both in the gas phase and in the adsorbed state, are measured experimentally by analysing mathematically the results of a single experiment, as described in detail in Section 2.1.

When low pressure is adopted, as it has been done in some studies, the diffusion is faster but the corrosion rate may be different, because vacuum conditions preclude the formation of a surface H_2O film, which may be essential for corrosion processes. Therefore, it was decided to use only atmospheric pressure in the laboratory experiments, in order to be able to extrapolate the results obtained to ‘real’ atmospheres with a certain degree of confidence. Two experimental techniques, the reversed-flow gas chromatography [11–18] and the parallel plate denuder [21,22] have been used, and many physicochemical parameters related to heterogeneous reactivity of pollutants on surfaces in the laboratory, at ambient pressure and realistic concentration levels of pollutants have been measured. Also, mass-transfer phenomena and experimental isotherms were taken into account in the mathematical calculations, as explained in Sections 2.1 and 2.2.

Sections 2.1 and 2.4 are summaries of previously published papers [14–17,20,29], whereas Sections 2.2 and 2.3 are new results.

2. Results and discussion

2.1. Studies by reversed-flow gas chromatography

In a previous EC project (STEP-CT90-0108), the relatively novel technique of reversed-flow gas chromatography (RF-GC) was combined with a cylindrical denuder, used in place of the diffusion column to measure physicochemical parameters pertaining to the damage of solid objects by air pollutants [11,12]. These parameters were particularly *invariant* with respect to the geometrical characteristics, such as shape, volume, external surface area, etc. of the objects. This same arrangement was also employed in the present project to study chemical interactions between two pollutants in addition to monitoring [13]. This was extended by using both, an integration and a differential method with a combination of gases such as NO₂, SO₂, Br₂ and hydrocarbons such as benzene, toluene, ethene, propene and ethyne [14,15]. The method is characterised by simplicity and great versatility. One important aspect which has been evidenced concerns the suitability of the method when analytical calibration is a major problem, particularly with unstable species. No calibration is needed with this method, which is an absolute rate constant technique. The system is neither a static nor a flow one like the more traditional ones. Of particular interest is the study of the reactivity of NO₂ with ethane, ethene, ethyne, propene and 1-butene.

2.1.1. Integration method and results

The theoretical analysis including the mathematical model, the solution of the resulting system of partial differential equations, and the PC programme written for the calculation of the physicochemical parameters mentioned above have been published [14], together with the necessary experimental details for carrying out the measurements. The results obtained include second-order rate constants for various gaseous reaction systems with various amounts of reactants.

Changing the amount, and therefore the concentration of the second reactant, has a small or big effect on the value of the rate constant k , showing that the reaction is not a true second-order one.

In some systems, changing the amount of the second reactant causes a big change in the rate constant k , but leaves the value of kn_B virtually constant, as judged from the error of the mean value. This points to a zero-order dependence of the reaction on the concentration of the second reactant. A comparison of the rate constant k with the diffusion parameter $\alpha_A = \pi^2 D_A / 4L^2$ in some reactions shows that the first is considerably bigger than α_A . By changing the length L of the diffusion column, the parameter α_A can be varied at will within wide limits making the reaction diffusion controlled at will. The above method is an absolute rate constant technique, and a diffusion controlled system with the parameters α_A and α_B varying at will within wide limits. The central physicochemical parameter pertaining to these studies was the rate constant of the various chemical reactions, being usually non-first-order reactions, and falling in the regions between first- and second-order kinetics or between second- and third-order laws.

2.1.2. Differential method and results

Both, experimental arrangement and procedure followed are the same as those of the integration method. The theoretical analysis starts from Fick's second law of diffusion and goes over to a linear logarithmic expression, through the calculation of the concentration c_A and the derivative dc_A/dt of the pollutant A [15]. By means of these, the apparent rate constant of the bimolecular reaction of two pollutants $A + B \rightarrow$ products, and the relative reaction order are calculated, using the PC programme published therein (Ref. [15], Appendix). These kinetic parameters for seven systems of solute hydrocarbons, with nitrogen dioxide at different mol ratios are given in Tables 1–5 of Ref. [15]. These results must again be taken as examples of application of the method rather than as literature kinetic data enriching the stock of existing data.

A comparison of the results obtained for the same systems by the two methods (integration and differential) shows that they are comparable in most cases.

2.1.3. Measurement of physicochemical deposition parameters on artefacts

A significant advancement was the simple determination of the experimental adsorption isotherm of a gaseous pollutant on the surface of solids, and therefore on the surface of the artistic objects [16].

Together with the local adsorption parameter k of the isotherm, the method gives the value of the desorption rate constant k_{-1} of the pollutant from the surface of the object, the rate constant k_2 of a possible first-order or pseudo-first-order surface reaction of the adsorbed analyte, and the chromatographic detector calibration factor g for the pollutant. The method was applied to the systems: ethene/marble, ethyne/marble, propene/silica gel, propene/marble, sulfur dioxide/marble, cyclohexane/graphitized carbon black, and benzene/graphitized carbon black.

2.1.4. Results with a new theoretical advancement

During the project, another arrangement of the gaseous/solid phase resembling that of a heterogeneous fluid bed catalysis, was studied. The mathematical modelling now was considerably different than before, but the solution of the resulting partial differential equations led again to mathematical relations for the calculation of the same physicochemical parameters, except for the calibration factor g of the detector, namely:

- The local adsorption parameter k_1 of the analyte pollutant A and its experimental isotherm on the surfaces of artistic value.
- The rate constant of desorption k_{-1} from the surface.
- The rate constant k_2 of a possible first- or pseudo-first-order surface reaction.

The main lines of the necessary mathematical analysis was based on a nonlinear adsorption isotherm. For this purpose, it was not necessary to determine the isotherm equation as before. Only the basic definition of the local adsorption equation was adopted, thus incorporating the nonlinear isotherm in the mathematical calculations. The nonlinearity is automatically taken care of [17,18,20]. From the parameters k_1 , k_{-1} and k_2 calculated, the deposition velocity V_d of the gaseous pollutants on the surfaces of artistic value, and the reaction probability γ with them are calculated by simple mathematical relations. Both parameters V_d and γ are independent of molecular diffusion, being related only to the local adsorption isotherm (k_1), the desorption rate

constant (k_{-1}) and the surface reaction rate constant (k_2). The necessity for correcting reaction probabilities by means of such rate constants was first pointed out by Judeikis and Stewart [19] 22 years ago, but, to the best of our knowledge, this has never been done before, except by us in the frame of the previous EC program (STEP-CT90-0108).

2.1.5. Synergistic effects of pollutants on the deposition parameters

Chemical interactions between two pollutants in the gas phase above the pieces of art may be called chemical synergistic effects of air pollutants acting on solid surfaces. Linear adsorption isotherms or real experimental isotherms, without any restriction regarding the adsorption equation were used. The first effort was based on axial diffusion in a denuder tube having a wall coating. The result was to determine deposition velocities V_d and reaction probabilities γ of pollutants with a simultaneous chemical reaction in the homogeneous gas phase above the solid surface, thus placing the synergistic effects on a quantitative scientific basis.

The mathematical modelling and the solution of the system of partial differential equations have been published [13], and two simple PC programmes permit: (a) the computation of reaction order n and the rate constant k_{app} of an apparent first-order chemical reaction in the gaseous phase, in the absence of the solid coating in the denuder tube; (b) the calculation of deposition velocity V_d and the reaction probability γ , by conducting the same experiment in the presence of a solid wall coating, and using n and k_{app} found before.

The effects of the homogeneous reaction on V_d and γ are then acknowledged.

Last, but not least, came the measurement of chemical synergistic effects taking into account the real experimental isotherms, with an arrangement similar to a catalytic bed, used in the previous subsection. The mathematical analysis, which has been published recently [20], is an extended version of the previous one, including now a homogeneous reaction in the gas phase with an apparent first-order rate constant again (k_{app}).

All calculations were carried out by a PC programme given in the Appendix of Ref. [20] and lead to the physicochemical parameters k_1 , k_{-1} , k_2 , V_d , γ and k_{app} in the gas phase. The systems studied comprised C_2H_2 , C_2H_4 , C_2H_6 , C_3H_6 , $1-C_4H_8$, and $(CH_3)_2S$, and solid surfaces of Cr_2O_3 , ZnO , Penteli marble and samples from three statues exhibited in the National Archaeological Museum of Kavala, Greece.

The experiments were conducted in the absence and in the presence of a second pollutant very abundant in the atmosphere, namely nitrogen dioxide, in three main concentrations, at temperatures 27° – $50^\circ C$.

Table 1 is an overview of the findings described in this subsection, including those of Section 2.4.

2.2. Studies by parallel plate denuder

Denuder diffusion techniques have developed into an established analytical technique which is now widely used for air sampling [21]. The use of a particular type of diffusion denuder for studying the reactivity of marble (the parallel plate or ‘flat’ denuder) results from the basic assumption that the surface reaction is the limiting step for mass transport to the walls. Under this condition, verified in the case of moderately reactive coatings,

uptake rates are independent of diffusion and a surface removal constant, dimensioned as a deposition velocity, can be determined [22]. A flat diffusion denuder consists of an enclosed polyethylene box containing two parallel briquettes of the marble under investigation (12 cm long \times 5 cm high \times 0.8 cm thick). The marble samples, after being polished with 400-grit silicon-carbide powder were washed with distilled water in an ultrasonic bath, and conditioned in a sealed container for > 24 h at the same relative humidity to be used in the test. The briquettes are placed horizontally face to face and spaced 0.3 cm apart. A Viton O-ring which assures airtightness, constitutes an additional spacer which increases the distance between the plates. Air is drawn into the box and flows in the space between the plates. Air is admitted through a circular opening that gradually widens in order to insure a uniform distribution of flow at the inlet and outlet. This permits full development of laminar flow (Reynolds number less than 50) before heterogeneous wall removal occurred. The flat denuder is contained in a temperature controlled chamber.

The use of the continuity equation gives for a parallel plate denuder (with dimension a corresponding to half depth and b corresponding to the long dimension of the channel) the following equation

$$\frac{c}{c_0} = \exp\left(\frac{-2L(2a + b)K}{Q}\right) \quad (1)$$

with c = outlet concentration, c_0 = inlet concentration, K = surface removal constant, L = length of the channel, Q = flowrate.

Eq. (1) has been used to investigate the reactivity towards SO_2 of Thassos, Penteli and Carrara marbles as such and when coated with two protectives. From the measurements of SO_2 concentrations, a surface removal constant and the corresponding deposition velocity have been calculated. The parallel plate denuder can be assimilated to a flow reactor coated with the solid of interest. Deposition velocities obtained in this manner are independent of mass transport and reflect the rates of heterogeneous removal of the trace species by interaction with the surface. These deposition velocities represent maximum values that would be obtained under turbulent atmospheric conditions.

Preliminary blank runs (parallel plate denuder and no specimens) indicate that losses inside the flat denuder due to the heterogeneous removal on the surfaces (and, in principle, to gas phase reaction during the transit time) are negligible. Permeation tubes were used to generate SO_2 which was diluted at the inlet with purified ambient air. The humidity of the air was controlled by using a humidity generator.

Fig. 1 presents the results obtained at 90% relative humidity (RH) on specimens of three marbles (Thassos, Penteli and Carrara) coated with the two protectives P1 and P2. These protectives have been chosen because they are normally used in the specialized practice. They have shown a considerable protective influence on the marbles. It is worth noting that coating of differently reactive surface involves the same degree of protection as a final result. This is demonstrated by the fact that Penteli marble, which is characterized by the highest V_d value (about 0.2 cm/s), shows V_d values of about 0.05 cm/s when coated with the protectives P1 and P2. Since mass transport by diffusion has been taken expressly into account in the data analysis, the values of V_d found apply to the environment under turbulent atmospheric conditions and represents the maximum

Table 1
Overview of integration and differential methods in the gas phase, measurement of deposition parameters, and synergistic effects in adsorption/desorption phenomena

Method	Gas	Substrate	Results	Reference	Notes
Integration method by RF-GC ^a	SO ₂ + NO ₂	–	Rate constants k , changing with the amount of NO ₂ and falling in the regions between first- and second-order kinetics or between second- and third-order laws	Ref. [14]	Experimental determination of such rate constants of non-linear processes in the ppb region is a very difficult task
	SO ₂ + Br ₂	–			
	C ₆ H ₆ + NO ₂	–			
	C ₇ H ₈ + NO ₂	–			
	C ₃ H ₆ + NO ₂	–			
	C ₂ H ₄ + NO ₂	–			
Differential method by RF-GC ^a	C ₂ H ₂ + NO ₂	–	Apparent rate constant of bimolecular reactions and reaction order	Ref. [15]	Comparison of this method with the integration one shows that they are comparable in most cases
	C ₂ H ₆ + NO ₂	–			
	C ₂ H ₄ + NO ₂	–			
	C ₂ H ₂ + NO ₂	–			
	C ₃ H ₆ + NO ₂	–			
	1-C ₄ H ₈ + NO ₂	–			
	C ₆ H ₆ + NO ₂	–			
C ₇ H ₈ + NO ₂	–				
Physicochemical deposition parameters on solids by RF-GC, using a diffusion denuder tube	C ₂ H ₄	marble	Local adsorption parameter k_1 , desorption rate constant k_{-1} , first-order surface reaction rate constant k_2 , irreversible extent of adsorption	Ref. [16]	The method computes experimental adsorption isotherms directly, without an a priori specification of an isotherm equation
	C ₂ H ₂	marble			
	C ₃ H ₆	marble, SiO ₂			
	SO ₂	marble			
	C ₆ H ₆	graphitized carbon black			
	C ₆ H ₁₂	graphitized carbon black			

Physicochemical deposition parameters on solids by RF-GC, using gaseous diffusion through a solid bed	C ₂ H ₂	Cr ₂ O ₃ , ZnO	Local adsorption parameters k_1 , desorption rate constant k_{-1} , first-order surface reaction rate constant k_2 , deposition velocities V_d , and reaction probabilities γ	Ref. [17] Ref. [18] Ref. [20]	It was not necessary to determine the isotherm equation separately. Only the basic definition of the local isotherm was required
	C ₂ H ₄ C ₂ H ₆ C ₃ H ₆ 1-C ₄ H ₈ (CH ₃) ₂ S	Cr ₂ O ₃ Cr ₂ O ₃ , ZnO Cr ₂ O ₃ Cr ₂ O ₃ marble, pieces from statues			
Synergistic effects of pollutants on the deposition parameters by RF-GC, using gaseous diffusion through a solid bed	C ₂ H ₂ + NO ₂ C ₂ H ₄ + NO ₂ C ₂ H ₆ + NO ₂ C ₃ H ₆ + NO ₂ 1-C ₄ H ₈ + NO ₂	Cr ₂ O ₃ , ZnO Cr ₂ O ₃ Cr ₂ O ₃ , ZnO Cr ₂ O ₃ Cr ₂ O ₃	Local adsorption parameters k_1 , desorption rate constant k_{-1} , first-order surface reaction rate constant k_2 , deposition velocities V_d , reaction probabilities γ , and apparent gaseous reaction rate constant k_{app}	Ref. [20]	The real experimental isotherms are incorporated into the mathematical model analysis, placing the synergistic effects on a scientific basis
	(CH ₃) ₂ S + NO ₂	marble, pieces from statues			
Synergistic effects in competitive adsorption and surface reaction, by a master equation with transition probabilities in the Arrhenius form	CO CO ₂ O ₂ O ₃ NO _x	various	Analysis of the influence of surface heterogeneity on multistability. With two kinds of adsorption sites, the degree of multistability can increase up to three stable steady states; hence, three reaction rates can be found	Ref. [29]	Multistability can produce hysteresis loops when environmental conditions are changed and restored later

^aReversed-flow gas chromatography.

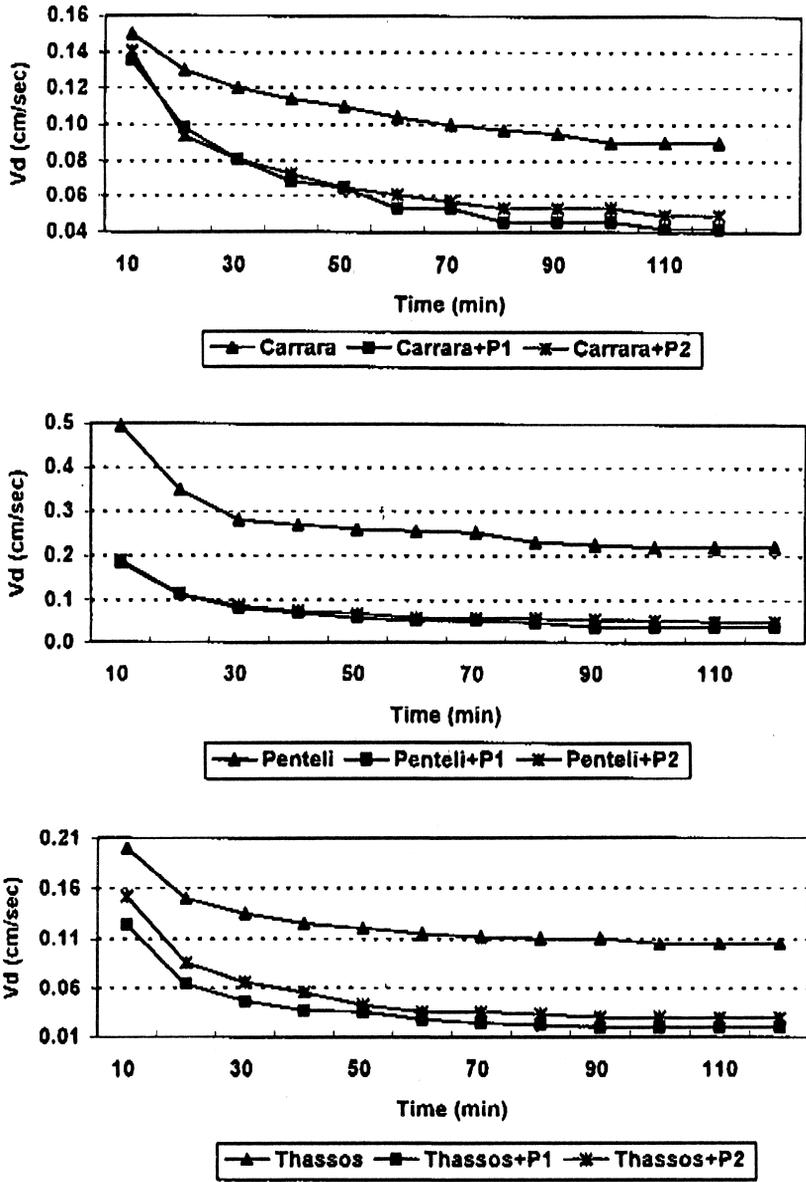


Fig. 1. Deposition of SO₂ at 90% RH on protectives P1 and P2.

rates of dry deposition. The small differences found can probably be attributed to the different physicochemical properties of the materials deriving from their porosity and pore size distribution. It is also apparent that protective P1 is slightly better than protective P2.

The device studied for the mentioned experiments can be also utilised for performing studies on the formation of HONO on surfaces. A brief introductory comment is in order at this point. A study on the air quality in one of the most important Italian Museums—the Uffizi Gallery, Florence—has demonstrated the presence of consistent levels of HNO_3 and other aggressive species such as SO_2 and O_3 [23], which have been ascribed to penetration from outdoors. In the same study, high levels of indoor HONO, greatly exceeding those outdoors, have also been measured. These high levels suggest indoor production by secondary reactions. Although the exact mechanism of formation of this species is still not completely understood, there are sound indications [23–25] that its

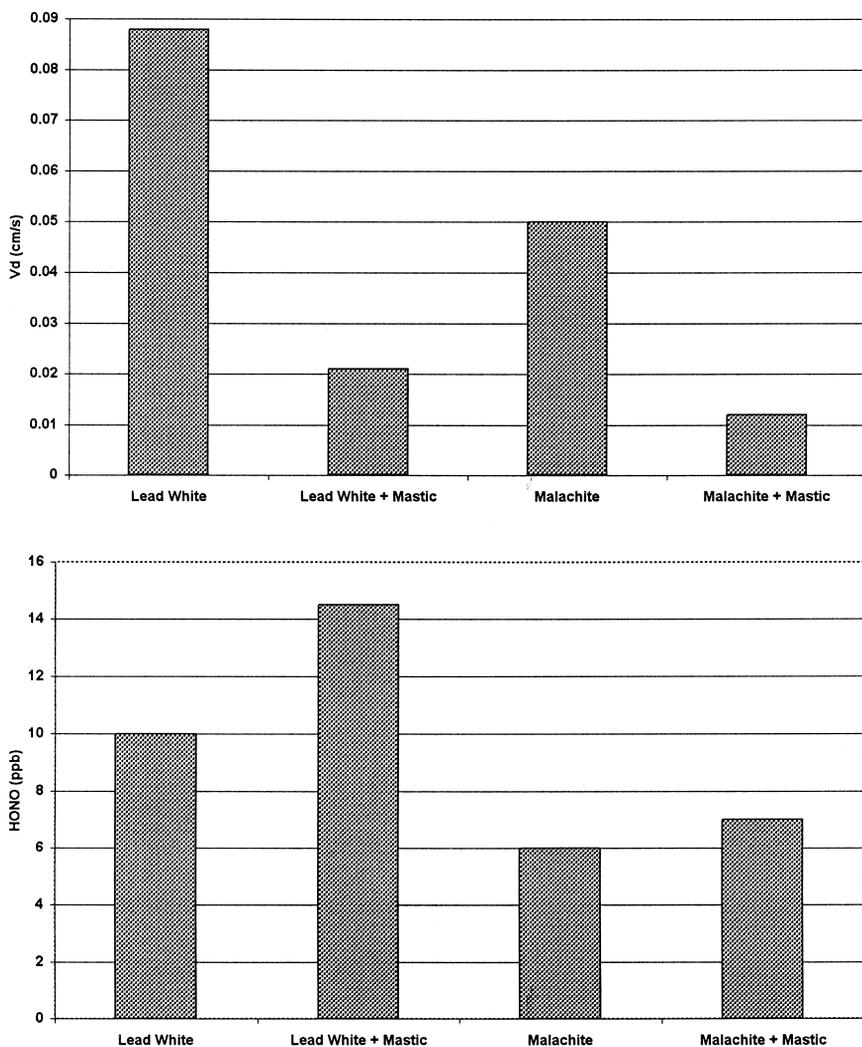


Fig. 2. Deposition of NO_2 and formation of HONO on two pigments.

presence indoors may proceed quite rapidly on the surface of materials having high surface roughness. The presence of this species indoors could be indicative of a major hazard to the artworks in consideration of the fact that HONO production is coupled with the heterogeneous formation of HNO_3 on surfaces, most likely including artworks.

Laboratory studies [26] have conclusively shown that HONO produced and adsorbed on the surfaces is released in the gas phase, while HNO_3 tends to remain adsorbed on the surfaces. As an example, the distribution of the products of the above reaction on a Pyrex glass surface was that more than 98% of nitrous acid was released in the gaseous phase while HNO_3 was entirely retained on the glass walls of the reactor.

In the framework of the project, a laboratory study which has been carried out on some model surfaces that can be of interest in the protection of paintings, has been performed. These surfaces have been investigated from the point of view of their reactivity towards NO_2 and of their tendency to form HONO on the basis of the aforementioned heterogeneous reaction, by using the already mentioned parallel plate denuder. The device has been used to investigate the reactivity of two pigments (lead white and malachite) as such and when treated with a protective (mastic) to decrease the reactivity. By measuring the inlet and outlet concentrations of NO_2 it is possible to relate the decrease of concentration with the reactivity expressed as a function of the surface removal constant, and therefore with the deposition velocity. From Fig. 2 it can be deduced that the protective shows a considerable influence on the reactivity. It is also interesting to note that a considerable production of HONO takes place in the parallel plate denuder

2.3. Measurements in indoor environments

In the framework of the project, the observations and analysis of HONO in a church and in a museum of Rome (the church of San Luigi dei Francesi and the Museo della Civiltà Romana) have been carried out. The main objective of the campaigns was to study the formation of HONO indoors and its relationship with the other pollutants of the nitrogen cycle.

Fig. 3 displays the mixing ratios of HONO in the San Luigi dei Francesi church during the period under study. By itself, nitrous acid is only slightly acidic and, though a specific study on the effect on surfaces has not been done yet, it is likely that it does not have, as such, any major effect on pigments and sensitive surfaces typical of artworks. Previous investigations on indoor HONO have shown that formation reactions in homogeneous phase such as:



are of negligible importance due to their slow kinetics [27,28]. The surface-catalyzed heterogeneous reaction of NO_2 with water may however be more important [24]. Therefore, the presence of nitrous acid in the indoor air of the church could be indicative of the concurrent formation of nitric acid, according to Eq. (3) in heterogeneous phase.

It is interesting to note that when HONO is produced on a surface, it can react with the substrate or can be released in the atmosphere as a function of the acid–base

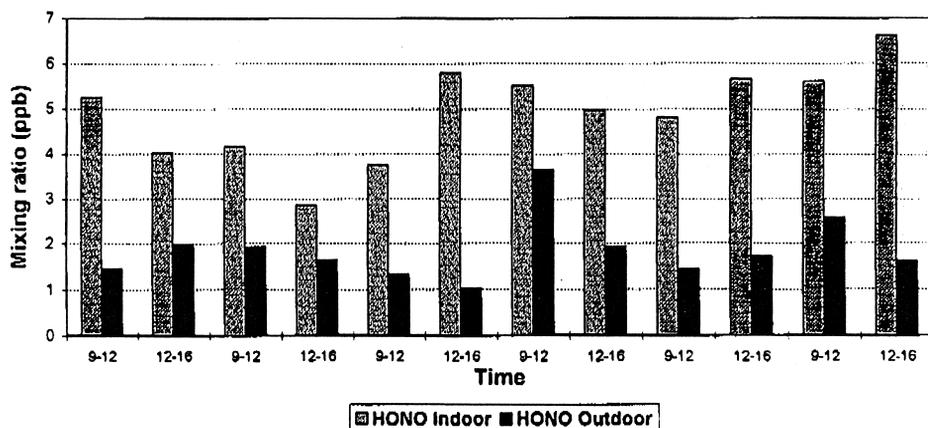


Fig. 3. A typical diurnal trend of indoor and outdoor HONO.

characteristics of the surface, whereas HNO_3 , which is much more reactive, tends to 'stick' to the surface. As a consequence, although HNO_3 and HONO are formed in equimolecular amounts, the indoor concentration of the first is much lower than that of the second. Assuming an average concentration of NO_2 of $228 \mu\text{g}/\text{m}^3$, a surface volume ratio of 0.7 and using two different values of formation constants for HONO, of $6 \times 10^{-6} \text{ m/s}$ (from Ref. [3]) on pyrex glass, and of $5 \times 10^{-5} \text{ m/s}$ (from Ref. [26]) on a porous material like nylon, the formation rates of HONO are calculated to be $0.4 \mu\text{g}/\text{h}$ and $3.8 \mu\text{g}/\text{h}$, respectively. These values underestimate the experimental concentration values measured in this study. Performing a reverse calculation on the experimental data, a surface formation constant of $5 \times 10^{-4} \text{ m/s}$ which is an order of magnitude greater than that of nylon can be found. This indicates that the complex nature of the actual surfaces present in the church (consisting of wood, marbles, plaster, textiles, paintings, etc.) can not be simplified by resorting to simple laboratory studies on a specific surface. Fig. 4 reports the daily indoor trend of NO, NO_2 and HONO in the Museo della Civiltà Romana. As can be seen, while NO concentrations exhibited strong diurnal variations, NO_2 and HONO concentrations, on the contrary, they were relatively stable during the whole period under study. The concentrations of HONO are within the range we have previously measured in the Church of San Luigi dei Francesi. In general, the concentration–time behaviour of HONO tended to follow that of NO_2 with temporary minima and maxima occurring at the same time as NO_2 minima and maxima. This again suggests that HONO is produced according to an heterogeneous reaction on surfaces from NO_2 and H_2O . It is interesting to note that, apparently, no effect of the presence of NO on the formation of HONO can be inferred from the figures. This is another indirect indication that the homogeneous reaction (2) is not an important source of HONO indoors.

2.4. Synergistic effects in competitive adsorption and surface reactions

In adsorption–desorption phenomena and reactions catalyzed by a surface, an important factor is heterogeneity caused by impurities, defects or polycrystallinity, and others.

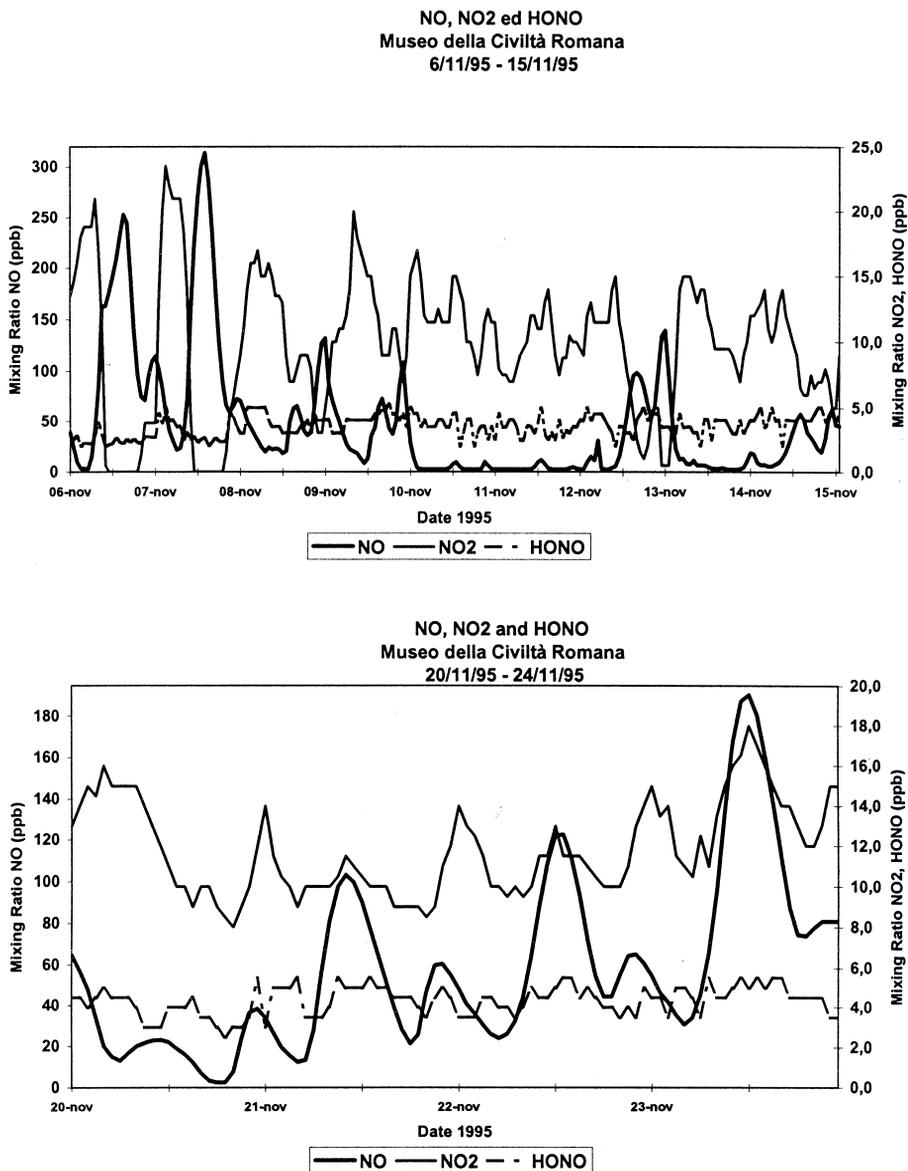


Fig. 4. NO, NO₂ and HONO at the Museo della Civiltà Romana (Rome).

Starting from a master equation, with transition probabilities in the Arrhenius form, a number of cases of competitive adsorption of two species and reaction catalyzed by an adsorbent surface has been analyzed, considering different degrees and distributions of heterogeneities. Depending on the values of frequency factors, activation energy and interaction among adsorbates, multiplicity can exist, with two stable steady states (and

hence, two different reaction rates), which can be reached for the same conditions, depending on the initial concentrations. The values of these reaction rates can differ by several orders of magnitude. When the adsorbent surface becomes saturated, the reaction process stops. Multiplicity arises for values of the relevant parameters which exceed certain critical values, particularly when adsorbate interaction is greater than a critical limit. This depends on the other parameters, but we have obtained that for an energy of 0.1 kcal/mol multiplicity is possible even at room temperature. Mobility of adatoms on the surface does not destroy multistability, although it increases slightly the critical value of interaction energy. As in real cases, typical values of this interaction energy may be of the order of 1 kcal/mol and multiplicity can occur at room temperature. A detailed study has been applied to processes of adsorption and reaction of CO, CO₂, O₂ and can be extended to others as O₃ and NO_x.

Also, we have analyzed the influence of surface heterogeneity on multistability. In general, when there are two kinds of adsorbent sites, the degree of multistability can increase up to three stable steady states and hence three different reaction rates can be found. An 'excess' of heterogeneity destroys multiplicity [29].

The analysis performed makes it possible to determine in what range the species concentrations should be maintained to speed up, to delay or even to inhibit certain processes. Also, multistability can produce hysteresis loops when environmental conditions are changed and restored later. These general results can be applied to certain processes of adsorption and surface reaction of water and some pollutants on surfaces, which act as catalysts or are damaged. Phenomena of this kind could be detected in catalyzed oxidation reactions involving compounds as CO, CO₂, O₂, O₃ and NO_x, although not always at room temperature.

3. Conclusions

The main and general conclusion drawn from Section 2 is that the objectives described in Section 1 under (1) and (2) can be substantiated by defining and measuring some basic physicochemical parameters, like those described in Sections 2.1, 2.2 and 2.4, all belonging in the domain of rate constants and deposition velocities. These parameters, although strict in definition, can be easily and accurately measured by performing simple experiments with denuders and catalytic like solid beds, containing surfaces of artistic value or similar to those.

From such measurements, the mechanism of corrosive effects on cultural surfaces inside museums can be approached, including synergistic effects of two pollutants in the gaseous phase. Thus, by performing simple laboratory and/or field experiments, the corrosion effects are placed on a purely scientific basis, and this makes the designing of protection of artistic value surfaces easier and more effective.

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