

New gas chromatographic instrumentation for studying the action of sulfur dioxide on marbles[☆]

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Available online 26 May 2005

Abstract

Reversed-flow gas chromatography, which is a sub-technique of inverse gas chromatography, is an experimental arrangement simulating a simple model for the action of air pollutants on buildings and monuments, in laboratory scale. By using a commercial gas chromatograph and an appropriate mathematical analysis, kinetic parameters such as rate constants for adsorption k_1 , adsorption/desorption k_R and surface reaction k_2 , as well as surface diffusion coefficients D_s , deposition velocities V_d and reaction probabilities γ of SO₂ on marble surfaces at different temperatures (303.15–353.15 K) in the presence or in the absence of protective materials (an acrylic copolymer, Paraloid B-72 or a siloxane, CTS Silo 111) were calculated. From the above mentioned physicochemical quantities the ability of the examined materials to minimize the dry deposition of SO₂ on marble is carrying out and a possible mechanism for the interaction between SO₂ and Paraloid B-72 was suggested. Both materials (CTS SILO 111 and Paraloid B-72) are good enough for protecting marble against SO₂ at low temperatures (303.15–323.15), while at high temperatures (333.15–353.15), siloxane seems to protect marble better than acrylic copolymer.
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Keywords: Sulfur dioxide; Marble; Inverse gas chromatography; Acrylic copolymer; Siloxane; Dry deposition; Deposition velocities; Reaction probabilities; Surface diffusion coefficients

1. Introduction

One of the most important effect of atmospheric pollution is the deterioration of historic monuments and buildings and generally of cultural heritage. Volatile hydrocarbons, nitric oxide and nitrogen dioxide, sulfur dioxide, aromatic hydrocarbons and suspended particulate matter, are emitted through a number of processes either anthropogenic or physical [1]. All these affects start with the deposition of air pollutants on solid surfaces. The air pollutants may arrive at the solid surface either by wet deposition (dissolved in rain or fog droplets) or by dry deposition signifying deposition in particle form, e.g. gaseous SO₂ and lead to permanent corrosion and damage [2,3].

Sulfur dioxide is one of the main decay factors of carbonate-based stones (marble, etc.) in polluted environments. SO₂ deposition on CaCO₃ of marble gives gypsum as the final product [4].

In order to study the action of SO₂ on marble is important not only to obtain results by pure chemical analysis of cultural heritage but also to clarify the mechanism of this action. This mechanism may consist of various steps in series, which are usually rate processes, with the deposition as the first step, or sometimes equilibrium states, such as the distribution of air pollutant between the solid and the nearby atmospheric environment.

In the present work a gas chromatographic technique, Reversed-flow gas chromatography (RF-GC), is introduced in the aim to calculate physicochemical parameters (rate constants as well as equilibrium constants) pertaining to the action of SO₂ on Penteli marble in Greece. In addition, the same technique was used to examine the ability of acrylic copolymers and siloxanes to protect marble against corrosion.

[☆] Presented at the 25th International Symposium on Chromatography, Paris, France, 4–8 October 2004.

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This technique which is a sub-technique of inverse gas chromatography (IGC) was developed in 1980 [5] by Katsanos and Georgiadou and has been used to measure deposition velocities and reaction probabilities through the determination of rate coefficients, namely an adsorption rate constant, an adsorption/desorption rate constant, and a surface reaction first-order rate constant [6–8]. Some of the environmental applications of RF-GC (study of action of hydrocarbon pollutants on pigments, damage measurements for the action of air pollutants on marble and monuments, study of the exchange of pollutants between the atmosphere and the water environment) have been described in a recent published book [9].

As regards the choice of Penteli marble, it is well-known that the most Greek cultural heritage objects in Acropolis of Athens and elsewhere have been constructed with this type of marble, and physicochemical parameters like those described here may throw some light on the mechanism of the deterioration of art pieces by air pollutants.

Finally, the protective materials, acrylic copolymers and siloxanes, are widely used for the formulation of protective coatings, due to their good adhesion and film forming properties. These materials have environmental stability [10] and have been largely used in conservation practice as coatings, consolidants and adhesives.

2. Experimental

2.1. Apparatus

The chromatograph used was a Pye Unicam 4500 (Cambridge, England), with a flame photometric detector (F.P.D.). The temperature of the detector in all experiments was 150 °C and the flow rates of the detector gases, in all experiments were $0.5 \text{ cm}^3 \text{ s}^{-1}$.

The experimental arrangement is outlined in Fig. 1. The sampling cell consisted of the sampling column $l+l'$, the

diffusion column of length L_1 , and the lower vessel of length L_2 . The branches $l=l'=62 \text{ cm}$ were of stainless-steel chromatographic tube with 4 mm i.d. The diffusion column, was constructed from glass with 4 mm i.d. It was divided in two areas, an empty one $L_1=46.5 \text{ cm}$, and a filled with solid $L_2=4.4 \text{ cm}$. The diffusion column was connected perpendicularly to the sampling column by means of a 1/4 in. Swagelok union. The whole sampling cell was accommodated inside the oven of a usual gas chromatograph.

A four-port valve was placed inside the wall of the oven and used to connect the sampling cell to the carrier gas inlet (N_2), and to the flame photometric detector.

2.2. Materials

The marble was a Penteli marble (Athens, Greece) with a purity 97.9% (CaCO_3). It was shaped as spheres by using cutting equipments with a $3.5 \pm 0.1 \text{ mm}$ diameter. The external porosity, 0.5, and the specific surface area $100 \text{ cm}^2/\text{g}$, of the marble were determined by the mercury penetration method with a Porosimeter 2000 (Carlo Erba Instruments, Milano, Italy) with Milestone 200 software and the nitrogen-desorption method with a Sorptomatic 1900 (Carlo Erba Instruments, Milano, Italy) with also Milestone 200 software, respectively.

Sulfur dioxide was Air Liquide (Athens, Greece) product with a purity 99.99% while the protective materials namely CTS Silo 111 and Paraloid B-72 were supplied by Abio (Athens, Greece). Paraloid B-72 is an acrylic copolymer with composition of 70/30 (w/w) ethylmethacrylate (EMA) and methyl acrylate (MA) and CTS Silo 111 is a low molecule siloxane.

The carrier gas was nitrogen of 99.999% purity from Aeroskopio (Athens, Greece), dried by passing it through a gas purifier no. 452 of Matheson Gas Products (East Rutherford, NJ, USA) with a flow rate (corrected at column temperature and for pressure drop) of about $0.5 \text{ cm}^3 \text{ s}^{-1}$.

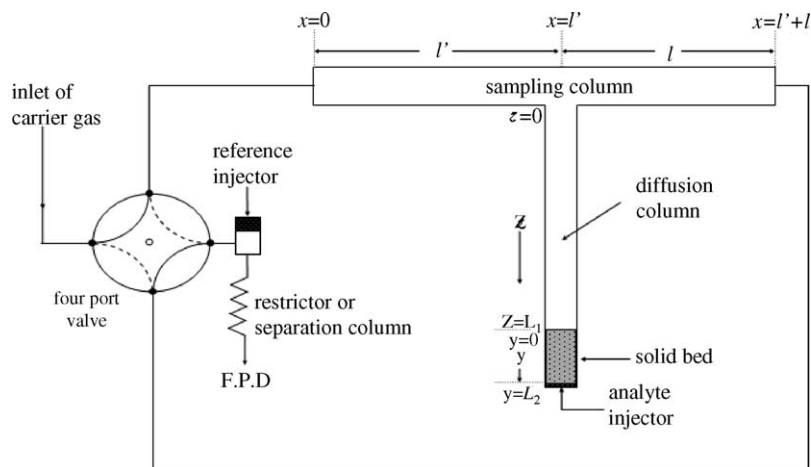


Fig. 1. Outline of the experimental arrangement for the study of the action of SO_2 on marbles.

2.3. Procedure

After conditioning of the marble (0.55 g) by heating it in situ at 523.15 K, for 20 h under a continuous carrier gas flow in order to eliminate humidity and other volatile compounds, the oven temperature was regulated to the working one. Then 5 cm³ (at atmospheric pressure) of SO₂ were introduced through the injector to establish constant surface activity.

When the chromatographic trace in the recorder had subsided to a negligible height above the baseline, a new 0.5 cm³ injection of SO₂ was made and after a time interval of about 5–10 min a continuous concentration–time curve was appeared. The rising of the concentration–time curve was due to the injection of the SO₂ and not to the contamination of the system. The later was verified by a blank run, without injecting SO₂ into the system, for which a constant base-line was observed.

After the appearance of the continuously rising concentration–time curve, the reversing procedure for the nitrogen carrier gas flow started, each reversal lasting always 6 s. This is shorter than the gas hold-up time in the sections *l* and *l'* of the cell. A symmetrical “sample peak” was created by each flow reversal. An example is given in Fig. 2. The above flow reversal procedure was repeated many times at each temperature, giving peaks corresponding to a different time from the SO₂ injection.

First, by using uncovered marble spheres, the physicochemical parameters for the action of SO₂ on pure marble can be determined.

After that, the same marble spheres were soaked by immersing them twice in each protective material (each impregnation was lasted for 20 min and the interval between them was 10 min according to the manufacturers manuals). Then coated marble spheres were placed into the diffusion column and heated at 383.15 K for 20 h under a continuous carrier gas flow. After this treatment the same physicochemical parameters were determined in the purpose to compare the ability of each material to protect marble against corrosion.

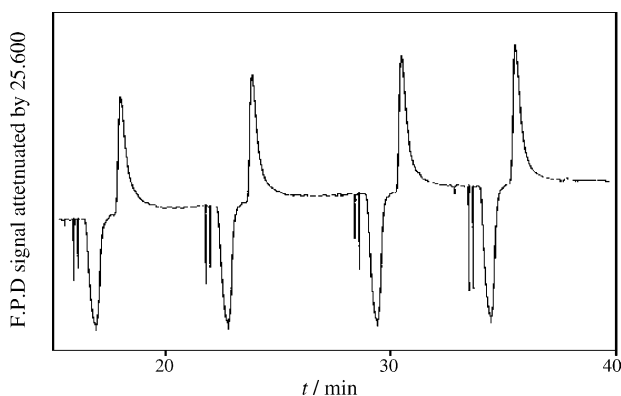


Fig. 2. Sample peaks of SO₂ obtained by reversed-flow procedure during action on marble at 323.15 K.

In all experiments the pressure drop along the cell was negligible and the solid bed was under a pressure of 1 atm.

3. Theoretical

The theoretical analysis relevant to the present work, dealing with physicochemical parameters determination, has been published elsewhere [11]. All these parameters such as rate constants for adsorption k_1 , adsorption/desorption k_R , and surface reaction k_2 , as well as surface diffusion coefficients D_y , deposition velocities V_d and reaction probabilities γ of SO₂ on marble surfaces describe the interaction between SO₂ and marble. Only the absolutely necessary mathematical equations are quoted here to help the reader understand how the parameters pertaining to the action of SO₂ on marble follow the experimental data.

Four basic equations are mentioned.

First the local adsorption isotherm of SO₂:

$$c_s^* = \frac{n_s}{a_s} \delta(y - L_2) + \frac{a_y}{a_s} k_1 \int_0^t c_y(\tau) d\tau \quad (1)$$

Second, the mass balance equation for SO₂ in the gaseous region z of the diffusion column:

$$\frac{\partial c_z}{\partial t} = D_z \frac{\partial^2 c_z}{\partial z^2} \quad (2)$$

Next the mass balance equation for SO₂ in region y of the diffusion column, filled with the marble (coated or uncoated):

$$\frac{\partial c_y}{\partial t} = D_y \frac{\partial^2 c_y}{\partial y^2} - k_R \frac{a_s}{a_y} (c_s^* - c_s) \quad (3)$$

Finally, the rate of change of the adsorbed concentration:

$$\frac{\partial c_s}{\partial t} = k_R (c_s^* - c_s) - k_2 c_s \quad (4)$$

with the symbols above denoting at the end of the text:

It is known [12] that the calculation of physicochemical parameters based on a theoretical analysis of the diffusion band obtained by plotting $H^{1/M}$ or $(1/M) \ln H$ against t in (min), where M (dimensionless) is the response factor for the detector (1.914 for the F.P.D.) and t the time when the respective flow reversal was made.

The height H (in arbitrary units, lets say cm) is proportional to the concentration $c(l', t)$, $H^{1/M} = gc(l', t)$, where $c(l', t)$ is the concentration of the pollutant, mol cm⁻³, measured at the junction of the sampling column with the diffusion column (Fig. 1) and g the calibration factor of the detector, cm per mol cm⁻³.

By taking into account the initial conditions (cf. Eq. (126) of Ref. [13]), and the boundary conditions (cf. Eqs. (16), (18) and (19) of Ref. [14]) the system of the above differential Eqs.

(1)–(4) was solved [14] leading to the function:

$$H^{1/M} = gc(l', t) = \sum_{i=1}^4 A_i \exp(B_i t) \quad (5)$$

which describes the diffusion bands.

The physicochemical parameters previously defined, k_1 , k_R , k_2 , and D_y are hidden under the exponential coefficients of time B_1, B_2, B_3 and B_4 of Eq. (5), while the pre-exponential factors A_1, A_2, A_3 and A_4 have not be used in the calculations of the physicochemical parameters.

By introducing the auxiliary parameters X, Y, Z and W , we have the relations between the physicochemical parameters and the exponential coefficients of time:

$$X = a_1 + a_2 + a_2 Q + k_R + k_2 = -(B_1 + B_2 + B_3 + B_4) \quad (6)$$

$$Y = (a_2 + a_1 + a_2 Q)(k_R + k_2) + a_1 a_2 + k_1 k_R \\ = B_1 B_2 + B_1 B_3 + B_1 B_4 + B_2 B_3 + B_2 B_4 + B_3 B_4 \quad (7)$$

$$Z = a_1 a_2 (k_R + k_2) + a_1 k_1 k_R + k_1 k_R k_2 + a_2 Q k_R k_1 \\ = -(B_1 B_2 B_3 + B_1 B_2 B_4 + B_1 B_3 B_4 + B_2 B_3 B_4) \quad (8)$$

$$W = (a_2 Q + a_1) k_1 k_R k_2 = B_1 B_2 B_3 B_4 \quad (9)$$

where

$$a_1 = \frac{2D_z}{L_1^2}; \quad a_2 = \frac{2D_y}{L_2^2}; \quad Q = 2a_y L_2 / a_z L_1 \quad (10)$$

It has been referred [11] that the physicochemical parameters mentioned above can not be calculated only from the four Eqs. (6)–(9) and an other mathematical approach had to be adopted [11]. This led to the same Eq. (5) with $i=5-7$. Instead of Eqs. (6)–(9) above, the following relations are valid:

$$X_1 = \frac{a_2 a_1}{a_1 + a_2 + a_2 Q} + k_R + k_2 \\ = -(B_5 + B_6 + B_7) \quad (11)$$

$$Y_1 = \frac{\alpha_1 a_2 (k_R + k_2) + (a_1 + a_2 Q) k_1 k_R}{a_1 + a_2 + a_2 Q} \\ = B_5 B_6 + B_5 B_7 + B_6 B_7 \quad (12)$$

$$Z_1 = \frac{a_1 + a_2 Q}{a_1 + a_2 + a_2 Q} k_1 k_R k_2 = -(B_5 B_6 B_7) \quad (13)$$

4. Results and discussion

Using a non-linear regression analysis PC programs in GW-BASIC [11], the exponential coefficients of time and from them the auxiliary parameters $X, Y, Z, W, X_1, Y_1, Z_1$ can be calculated. Through these with the help of Eqs. (6)–(13), all four physicochemical constants k_1, k_R, k_2 and D_y are computed. The α_1 value can be calculated by the means of a known value of D_z obtained from the literature [15]. Finally, through the following Eqs. (14) and (15) of Ref. [6] the overall deposition velocity, which is equivalent to an overall mass transfer coefficient of SO_2 to the marble, corrected for the activated adsorption/desorption and surface reactions, and the reaction

Table 1

Kinetic parameters, diffusion coefficients, deposition velocities and reaction probabilities for the systems SO_2 + pure marble and SO_2 + coated marble with acrylic copolymer or siloxane at various temperatures

Solid adsorbent	T (K)	k_1 (10^3 s^{-1})	k_R (10^3 s^{-1})	k_2 (10^4 s^{-1})	V_d (10^7 cm s^{-1})	γ (10^{11})	D_y ($10^3 \text{ cm}^2 \text{ s}^{-1}$)
Pure marble		3.352	5.971	1.201	1.661	2.099	3.775
Marble + Paraloid B-72	303.15	3.157	9.341	1.275	1.068	1.325	5.146
Marble + CTS SILO 111		2.724	5.386	1.127	1.402	1.770	3.811
Pure marble		4.745	7.651	1.290	1.976	2.451	12.850
Marble + Paraloid B-72	313.15	3.192	5.270	1.391	1.772	2.239	3.758
Marble + CTS SILO 111		3.331	5.932	1.248	1.724	2.136	5.741
Pure Marble		5.176	1.892	1.381	8.847	3.082	50.590
Marble + Paraloid B-72	323.15	3.071	9.537	1.487	1.185	1.386	2.096
Marble + CTS SILO 111		3.359	6.172	1.286	1.722	2.107	3.860
Pure Marble		4.847	1.577	1.418	10.040	11.000	93.390
Marble + Paraloid B-72	333.15	3.883	5.701	1.476	2.462	3.012	7.160
Marble + CTS SILO 111		2.298	12.790	1.333	0.595	0.717	2.257
Pure Marble		5.445	1.849	1.426	9.795	11.630	228.000
Marble + Paraloid B-72	343.15	4.582	7.266	1.493	2.317	2.835	9.003
Marble + CTS SILO 111		2.891	8.838	1.314	1.214	1.441	2.673
Pure Marble		5.755	2.005	1.499	10.050	11.760	326.000
Marble + Paraloid B-72	353.15	4.486	1.608	1.541	9.858	11.690	47.880
Marble + CTS SILO 111		3.901	7.847	1.425	1.614	1.887	4.748

probability γ of SO₂ with the marble (coated or uncoated) are found:

$$V_d = \frac{k_1 V'_G(\text{empty})\varepsilon}{A_S} \frac{k_2}{k_R + k_2} \quad (14)$$

$$\frac{1}{\gamma} = \left(\frac{R_g T}{2\pi M_B} \right)^{1/2} \frac{1}{V_d} + \frac{1}{2} \quad (15)$$

where A_S (cm²) is the total surface area of the marble, V'_G (cm³) is the gaseous volume of the section y of the experimental cell (cf. Fig. 1), R_g (J K⁻¹ mol⁻¹) is the ideal gas constant, ε is the external porosity of the solid, M_B (kg mol⁻¹) is the molar mass of SO₂ and T (K) is the absolute temperature.

The results from the above calculations are listed in Table 1. These refer to the heterogeneous interactions SO₂ + pure marble, SO₂ + marble + Paraloid B-72 and SO₂ + marble + CTS SILO 111.

From the listed results we can observe the following:

(1) The values of k_2 in all cases where the marble was coated by an acrylic copolymer (Paraloid B-72) were bigger than those for pure marble while the values of k_2 in all cases where a siloxane protective material was used (CTS SILO 111) were smaller than those for pure marble. This may happen because the sulfur dioxide interacts with the acrylic copolymer and not with the siloxane. These results are plotted in the Fig. 3.

The interaction between sulphur dioxide and Paraloid B-72 may occur because of the MA, which is a constituent of the acrylic copolymer but not of the siloxane. The other constituent of the Paraloid B-72, EMA, does not interact with SO₂, due to the presence of -CH₃ group instead of -H.

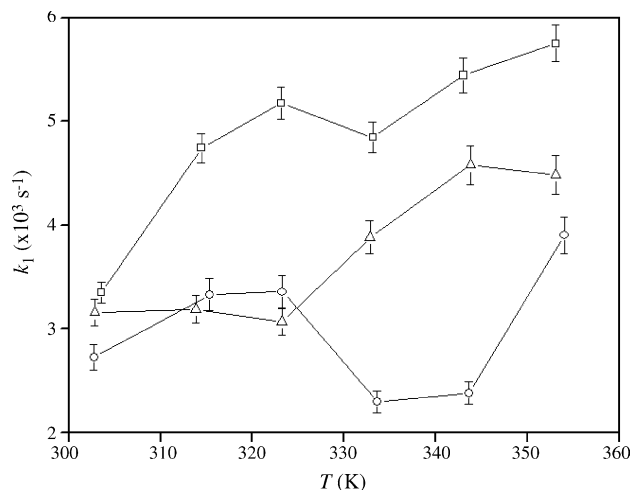
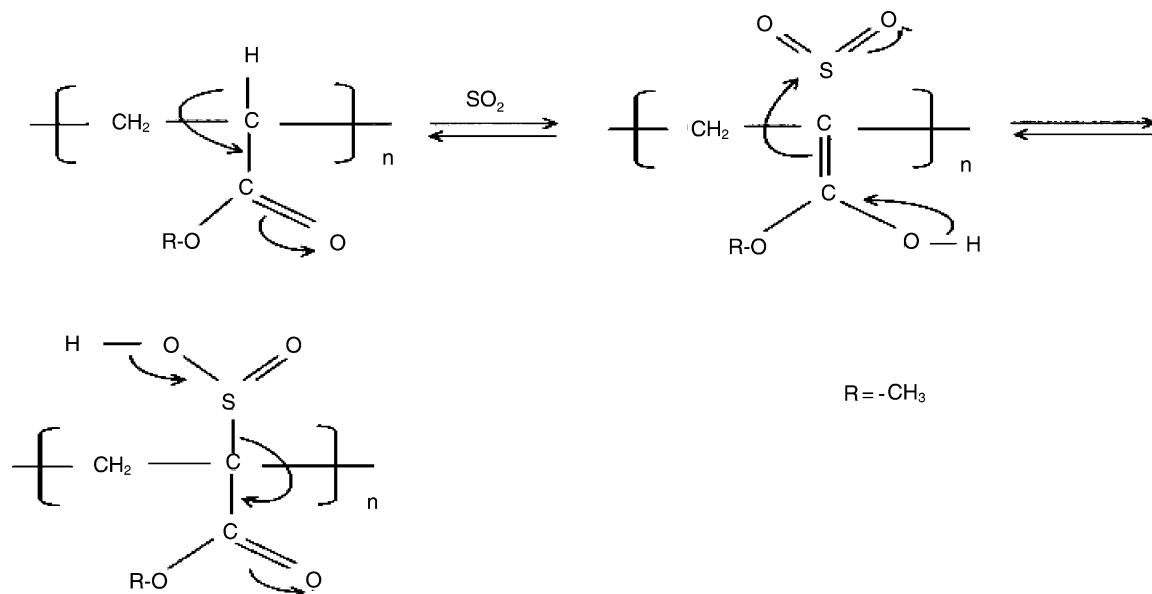


Fig. 3. Temperature dependence of k_2 for the systems SO₂ + marble (□), SO₂ + marble + Paraloid B-72 (◇) and SO₂ + marble + CTS Silo 111 (○).

For this interaction the above mechanism was suggested. In this mechanism the first step is the intermolecular shifting of -H and then the addition of SO₂ to the double bond. All the above steps are reversible and the whole mechanism is under further investigation.

On the other hand all the values of k_1 for the system (SO₂ + marble) are bigger than those for the systems (SO₂ + coated marble) (cf. Fig. 4). From the above it seems that the adsorption of SO₂ is more difficult in the case of coated marble than in the pure marble.

(2) The values of V_d and γ in most cases where the marble was coated by an acrylic copolymer (Paraloid B-72) or siloxane protective material (CTS SILO 111) were smaller than those for pure marble. The only exception was at temperature 353.15 K where the differences



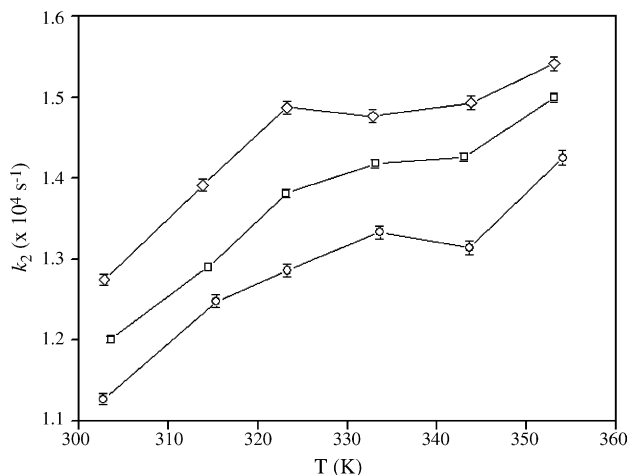


Fig. 4. Temperature dependence of k_1 for the systems SO_2 + marble (□), SO_2 + marble + Paraloid B-72 (◇) and SO_2 + marble + CTS Silo 111 (○).

between the values of V_d and γ for the systems SO_2 + marble and SO_2 + marble coated with acrylic copolymer were negligible (cf. Fig. 5). This could be attributed to the fact that at this temperature SO_2 interacts with a relatively high rate with Paraloid B-72.

- (3) All listed values of V_d were four to six orders of magnitude smaller than those from the literature. Judeikis and Stewart [16] reported values for deposition velocities of SO_2 on selected buildings materials which varying between 0.04 and 2.5 cm s^{-1} depending on the surface material. On the other hand Cobourn et al. [17] had measured deposition velocities of SO_2 on marble and dolomite stones which varied between 0.06 – 0.1 cm s^{-1} and 0.02 – 0.1 cm s^{-1} , respectively. More recent work of Grøntoft and Raychaudhuri [18] illustrated values for the deposition velocity of SO_2 on marble equal to 0.009 and 0.088 cm s^{-1} for the deposition velocity of SO_2 on limestones.

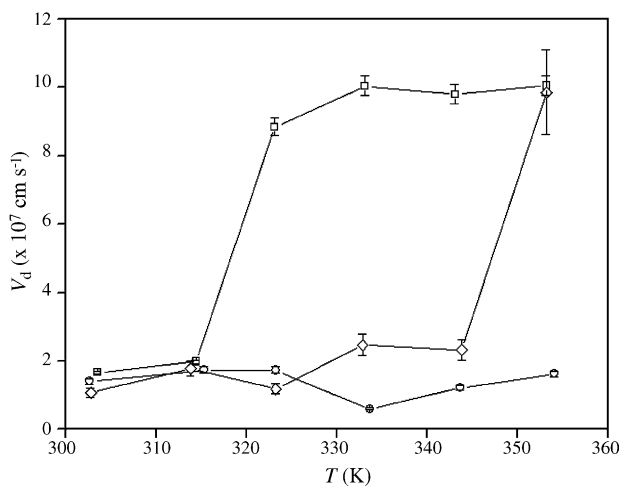


Fig. 5. Temperature dependence of V_d for the systems SO_2 + marble (□), SO_2 + marble + Paraloid B-72 (◇) and SO_2 + marble + CTS Silo 111 (○).

An explanation is that the listed values of V_d in Table 1 were obtained from a steady state system (RF-GC is a steady state technique because all phenomena occur in the diffusion column where the carrier gas is stagnant), while those in the literature [16–18] from a dynamic one (a gas steam flows over the solid surfaces). In addition, V_d values in the present work are not only refer to a surface deposition but also to a deposition in the porous of the material and so are smaller than those for surface deposition. This is obvious from the definition of V_d (cf. Eq. (14)) where the rate constants for adsorption, adsorption/desorption and surface reaction are involved.

- (4) From the D_y values the effect of the protective materials is obvious (cf. Fig. 6). In the absence of protective materials the D_y values, at extreme temperatures, higher than 333.15 K , had the same order of magnitude with those for diffusion of SO_2 in pure N_2 . This may lead to the conclusion that at high temperatures (over than 343.15 K) the porous of the marble are being destroyed and so surface diffusion coefficients are equivalent to diffusion coefficients in the gas phase (according to the literature [15] the theoretical calculated values for the diffusion coefficient of SO_2 in N_2 at 343.15 K is $0.161 \text{ cm}^2 \text{ s}^{-1}$ and at 353.15 K is $0.169 \text{ cm}^2 \text{ s}^{-1}$). In the presence of protective materials the later does not happen due to the shrink of the porous size of the marble [19].
- (5) Finally, an explanation of the abnormal behavior of the k_R values may be the fact that k_R is a complex rate constant pertaining to adsorption and desorption of SO_2 on marble.

From all the above, it seems that both materials (CTS SILO 111 and Paraloid B-72) cut down the dry deposition of SO_2 on marble at low temperatures (303.15 – 323.15) while at high temperatures (333.15 – 353.15), siloxane acts better as a protective material than acrylic copolymer.

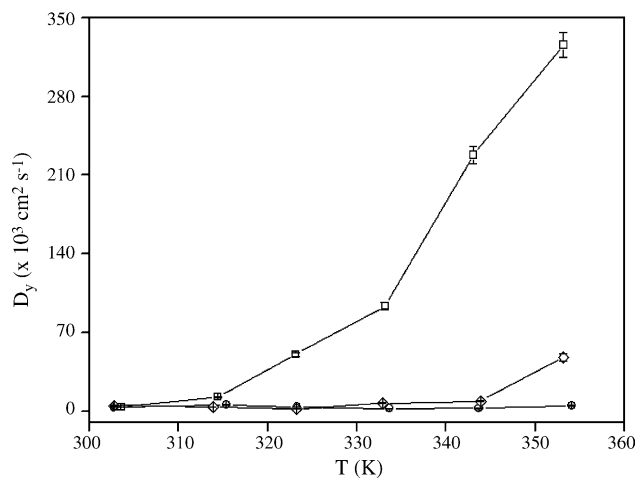


Fig. 6. Temperature dependence of D_y for the systems SO_2 + marble (□), SO_2 + marble + Paraloid B-72 (◇) and SO_2 + marble + CTS Silo 111 (○).

Table 2
Mean values of kinetic parameters (rate constants for adsorption, k_1 adsorption/desorption, k_R and first or pseudo-first order surface reaction, k_2), diffusion coefficients (D_y), deposition velocities (V_d) and reaction probabilities (γ) with their corresponding standard deviation (σ) and percent precision for the three under study systems at 323.15 K

System under study	$k_1 \pm \sigma_{k_1}$ (10^3 s^{-1})	$k_R \pm \sigma_{k_R}$ (10^3 s^{-1})	$k_2 \pm \sigma_{k_2}$ (10^4 s^{-1})	$V_d \pm \sigma_{V_d}$ (10^7 cm s^{-1})	$\gamma \pm \sigma_\gamma$ (10^{11})	$D_y \pm \sigma_{D_y}$ ($10^3 \text{ cm}^2 \text{ s}^{-1}$)
SO ₂ + pure marble	5.176 ± 0.157 (96.97%) ^a	1.892 ± 0.077 (95.93%) ^a	1.381 ± 0.005 (99.64%) ^a	8.847 ± 0.257 (97.09%) ^a	3.082 ± 0.207 (93.28) ^a	50.590 ± 0.690 (96.66) ^a
SO ₂ + marble + Paraloid B-72	3.071 ± 0.126 (95.90%) ^a	9.537 ± 0.085 (99.11%) ^a	1.487 ± 0.008 (99.46%) ^a	1.185 ± 0.149 (87.43) ^a	1.386 ± 0.165 (88.10) ^a	2.096 ± 0.130 (93.81) ^a
SO ₂ + marble + CTS SILO 111	3.357 ± 0.154 (95.41%) ^a	6.172 ± 0.178 (97.12%) ^a	1.286 ± 0.008 (99.38%) ^a	1.722 ± 0.093 (94.60) ^a	2.107 ± 0.122 (94.21) ^a	3.860 ± 0.180 (95.34) ^a

^a Where the numbers in parentheses denoting the percent precision calculated by the Eq. (16).

(6) All the calculated physicochemical parameters, k_1 , k_R , k_2 , D_y , V_d and γ in Table 1 are given without errors because it is difficult to estimate the final errors since they come out as a result of complex algebraic equations based on Eqs. (6)–(16). The application of the law of propagation of errors in a relatively long but not complex sequence of steps like that does not give reliable final errors [14].

In order to test the precision of the method, three replications at each temperature for the three systems namely, pure marble + SO₂, pure marble + Paraloid B-72 + SO₂ and pure marble + CTS SILO 111 + SO₂, were performed. In Table 2 the obtained results for the mean values of the physicochemical parameters with their corresponding standard deviation at the intermediate temperature, 323.15 K are presented. The results for the other temperatures are of the same order.

From the listed values an estimation of the precision of the method for the calculation for each physicochemical quantity can be obtained. The precision for each quantity are computed from the relation:

$$\text{precision (\%)} = 100 - 100 \times \frac{\text{standard deviation}}{\text{mean value}} \quad (16)$$

The percent precision values for each physicochemical parameter for the three systems are also illustrated in Table 2.

From Table 2 is obvious that although the results were coming out through complex algebraic equations, which means that accuracy or uncertainties couldn't be calculated, method seems to have a good precision (92–99%).

The statistical analysis (*t*-test) of the mean values of all parameters shows that the observed differences between them for the systems SO₂ + pure marble and SO₂ + marble + Paraloid B-72 or SO₂ + pure marble and SO₂ + marble + CTS Silo 111 are statistically significant in the 0.05 level of significance.

5. Conclusions

1. An inverse gas chromatographic method was introduced for studying the interaction between SO₂ and marble as well as for the physicochemical characterization of protective materials.
2. Kinetic parameters, surface diffusion coefficients as well as deposition velocities and reaction probabilities of SO₂ on coated or uncoated marble were determined in order to clarify the ability of protective materials (acrylic copolymers—Paraloid B-72 and siloxane CTS SILO 111) to cut down the dry deposition of SO₂ on marble.
3. It seems that both materials are good enough at low temperatures (303.15–323.15), while at high temperatures (333.15–353.15) siloxane acts better as protective material than acrylic copolymer.

6. Nomenclature

a_s	amount of the marble per unit length of column bed (g cm^{-1})
a_y	free cross sectional area in the solid bed in region y (cm^2)
c_s	concentration of SO_2 adsorbed on the solid (mol g^{-1})
c_s^*	local adsorbed equilibrium concentration of SO_2 at time t (mol g^{-1})
c_y	gaseous concentration of SO_2 in region y (mol cm^{-3})
c_z	gaseous concentration of SO_2 in the region z (mol cm^{-3})
D_y	effective diffusion coefficient of SO_2 in the solid bed ($\text{cm}^2 \text{s}^{-1}$)
D_z	diffusion coefficient of SO_2 into the carrier gas (nitrogen) ($\text{cm}^2 \text{s}^{-1}$)
k_1	dynamic adsorption rate constant (s^{-1})
k_2	rate constant of a possible first-order or pseudo first-order surface reaction of SO_2 (s^{-1})
k_R	rate constant for adsorption/desorption on the solid bulk (s^{-1})
n_s	initially adsorbed concentration of SO_2 (mol)
y	length coordinate along section L_2 (cm)
$\delta(y - L_2)$	Dirac's delta function for the initial condition of the bed, when the SO_2 is introduced as an instantaneous pulse at the point $y = L_2$ (cm^{-1})
τ	dummy variable for time (s)

Acknowledgement

The authors wish to thank the University of Patras for funding the above work by CARATHEODORY program.

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