大気汚染学会誌
J. Japan Soc. Air Pollut.
16 (5) 301 ～ 306 (1981)

The Evaluation of the Air Pollution by Sulfur Dioxide Estimated by the Lead Peroxide Method

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ABSTRACT

Concentrations of sulfur dioxide in the environmental air at Minma and Yoneizumi regions in Kanazawa city was measured with the lead peroxide method every ten days over sixty days. The two shelters made with polyvinyl chloride plate were set at each measuring point to investigate the effect of light energy $h\nu$ on the measured values. One was covered with thin aluminum film and the other was not treated. For the purpose of comparing the values obtained at different measuring points absolutely, the semi-theoretical equation is derived by using the characteristic parameter Ψ due to the difference in the environmental conditions at measuring points and the effects of several gaseous substances coexisting with sulfur dioxide and sunrays on reaction.

Key words: PbO_2 method, Evaluation for measured values, Characteristic parameter, Comparison of absolute value, Semi-theoretical equation, Surface reaction model.

Introduction

The author previously reported the theoretical[1] and experimental[1,2] researches on the PbO_2-SO_2 reaction system and it was found that the unreacted-core model corresponds closely to what really takes place in this reaction system. Furthermore, the effects of the atmospheric conditions such as gas velocity, humidity, and SO_2 and NO_2 concentrations on the reaction were proved.

In this paper, the appropriate evaluation method for the data obtained from the lead-peroxide method was studied according to the experimental results in the previous papers[1,2] and the effect of the sunrays on the PbO_2-SO_2 reaction system was investigated.

1. Theoretical analysis

As the rate expression derived from the unreacted-core model closely predicts and describes the actual kinetics, in this study the unreacted-core model is applied to the analysis of the SO_2 data in the atmosphere with the lead peroxide method.

Before going into the theoretical discussion, let us examine the difference in the operating conditions between laboratory and atmosphere. The summary is as follows;

(1) In the laboratory, the cylindrical pellet of PbO_2 powder made by manual pressurizing machine was used and in the lead peroxide method, the prepared PbO_2 paste with gum trgacanth is applied to cotton fabric wrapped around a cylindrical porcelain former. The thickness of the paste is less than 1.0 mm.

(2) The SO_2 concentration lay in the region of 20～1500 ppm (v/v) in the experiment and in the atmosphere it is less than 0.1 ppm.

(3) The average wind velocity in the atmosphere is 1～5 m/s ordinarily and the flow pattern of the wind in a instrument for the lead peroxide method is actually very complicated. In the laboratory, the gas velocity was less than 0.93 m/s and the gas flowed parallel to the axis of the cylindrical pellet.

By paying attention to the difference described above, the analytical equation to evaluate the data from the lead peroxide method was derived on the basis of the unreacted-core model.

In **Fig. 1**, the cylindrical model which axle is hollow is shown. The section taking part in the reaction of the model is very similar to that of the actual instrument. As the resistance for chemical reaction is negligible for the PbO_2-SO_2 system,[1]

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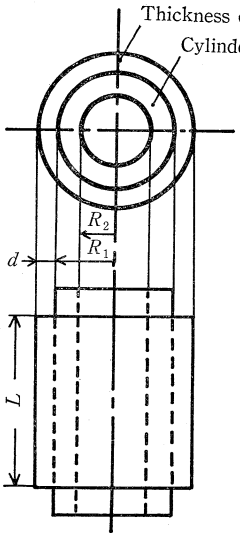

Fig. 1. Schematic model for the lead peroxide method

From Eq. (9) in the previous paper[1)]

$$-\frac{dr_c}{dt}=\frac{C_{A0}}{aC_{S0}}\times \frac{1}{\{r_c/k_f(R_1+d)\}+[r_c\ln\{(R_1+d)/r_c\}/\mathcal{D}_{eA}]}$$
$$(R_1<r_c<R_1+d) \qquad (1)$$

As mentioned above, the thickness of the PbO_2 paste applied to cotton fabric is less than 1.0 mm, and $d \ll R_1$. Equation (1) is, then, rewritten by the surface reaction model as follows;

$$-(dr_c/dt)=(C_{A0}/aC_{S0})\cdot k_f \qquad (2)$$

The mass of the lead sulfate produced by the reaction is

$$W=\pi(R_1+d)^2LC_{S0}-\pi r_c^2LC_{S0} \qquad (3)$$

By considering $d \ll R_1$, the differentiating of Eq. (3) with respect to t gives

$$dW/dt=-(2\pi R_1LC_{S0})\cdot(dr_c/dt) \qquad (4)$$

In this reaction, $a=1$ and from Eqs. (2) and (4)

$$dW/dt=2\pi R_1Lk_fC_{A0} \qquad (5)$$

and the initial condition is

$$\text{at } t=0,\ W=0 \qquad (6)$$

The integration of Eq. (5) gives

$$W=2\pi R_1L\int_0^t k_fC_{A0}dt \qquad (7)$$

In the lead peroxide method, the PbO_2 paste is left in a polluted air for a month and the SO_2 concentration and the atmospheric conditions such as wind velocity and humidity change with time or day. The integral term on the right side of Eq. (7) cannot be, then, integrated with easy.

2. Estimation of the gas film mass transfer coefficients

From the experimental results in the previous paper,[1)] k_f is represented by

$$J_D=(k_f/u)Sc^{2/3}=a_1H^{a_2}Re^{a_3} \qquad (8)$$

In general, the relative humidity lies in the region of 50～90% and the average wind velocity a day is more than 1 m/s under the atmospheric conditions. As is obvious from the previous paper,[1)] k_f is in proportion to $H^{0.74}$ and $u^{0.9}$. These exponents were determined by the data obtained from the experiment carried out under the different conditions from the atmosphere. Especially the exponent for the wind velocity seems to be too large. The experimental data with the lead peroxide method reported by Go et al.[3)] indicates the total amount of product was in proportion to $u^{0.5}$. The experiment was carried out under such conditions as the wind velocity was in the region of 1～4 m/s and the SO_2 concentration was in the region of 0.05～0.3 ppm. On the other hand, the PbO_2 pellet used in the previous studies[1),2)] formed by manual pressurizing machine and the surface of sample was smooth and the pellet didn't contain the different material just as gum tragacanth. Furthermore the gas contacted with the pellet directly. This phenomenon is different from that in a instrument of the lead peroxide method in which the gas velocity is reduced by the shelter.

It is, then, assumed that the degree of the effect of the gas velocity on the reaction is overestimated in the experimental study in the laboratory. To evaluate the data with the lead peroxide method, it may be suitable to use the exponent of 0.5 reported by Go et al[3)].

While the interfacial resistance at the reaction surface of the sample is affected by humidity alone according to the discussion in the previous paper[1)]. The humidity is a statistic physical factor and the wind velocity is a dynamic factor. The degree of the effect of humidity is, then, regarded as equivalent in both laboratory and atmosphere. In this analysis, the exponent 0.74 obtained from the previous study[1)] was used.

To estimate the values of k_f from the data reported by Go et al.[3)], the following equation was used

$$k_f=W/2\pi R_1LC_{A0}t \qquad (9)$$

As the experiment by Go et al.[3)] was carried out with dehumidifier and the value of humidity was not represented in their paper, it is assumed that the effect of humidity on the reaction can be ignored on their data. When k_f is in proportion to $H^{0.74}$ and $u^{0.5}$, the values of k_f by the lead peroxide method was approximately represented by

$$(k_f/u)Sc^{2/3}=0.0158H^{0.74}Re^{-0.5} \qquad (10)$$

where the diameter of a cylindrical porcelain former was used as the characteristic length.

3. Semi-theoretical equation

Now let us consider the characteristic parameter Ψ which represents the deviation from the value with the conductometric method caused by the difference in the environmental conditions at measuring points and the effect of several gaseous substances coexisting with SO_2 and sunrays on reaction. Eq. (5) is rewritten

$$dW/dt=2\pi R_1 L\Psi k_f C_{A0} \qquad (11)$$

4. The results of air pollution by sulfur dioxide measured with the lead peroxide method

4.1 Measurement

The PbO_2 sample standardized in the lead peroxide method was used. The sample was put into the shelter made with polyvinyl chloride plate which dimensions was $0.29\times0.35\times0.52$ m^3. The appearance of the shelter is shown in **Fig. 2.** The instrument was left for sixty days at two measuring points in Kanazawa city; Minma, Yoneizumi. The sides of the shelter had a numerous holes in order to go through the polluted air and in addition, to investigate the effect of sunrays on reaction, two shelters were set at each measuring point. One was covered with thin aluminum film and the other was not treated.

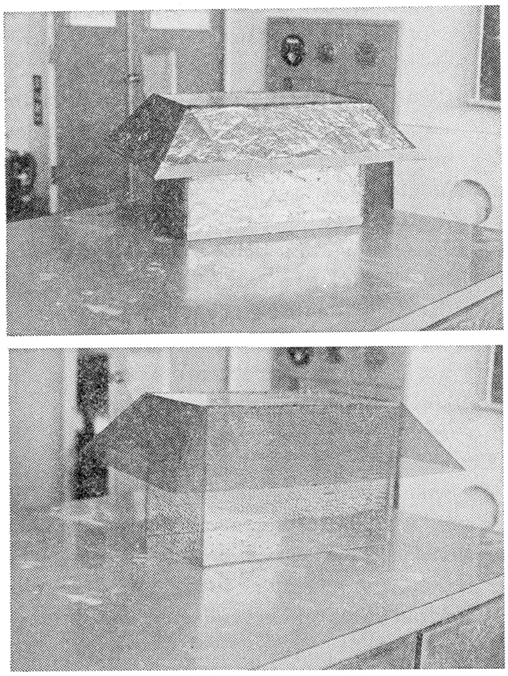

Fig. 2. Appearance of the shelters used in this experiment

In the shelter, there were six samples to investigate the air pollution by sulfur dioxide every ten days. The measurement was performed 8/9/78 to 10/9/78 and the samples were analyzed at the Environmetnal Pollution and Sanitary Research Institute, Ishikawa Prefecture.

4.2 Results and discussions

The results are shown in **Figs. 3** and **4.** The curved lines indicate the results estimated by the method described later. As is evident from these figures, the total amount of the product increases when the sunrays is applied to the sample under the identical atmospheric conditions. This result shows that the reaction between SO_2 and O_2 in the atmosphere is affected by the light energy $h\nu$.[4]

In actual, it was reported that the direct oxida-

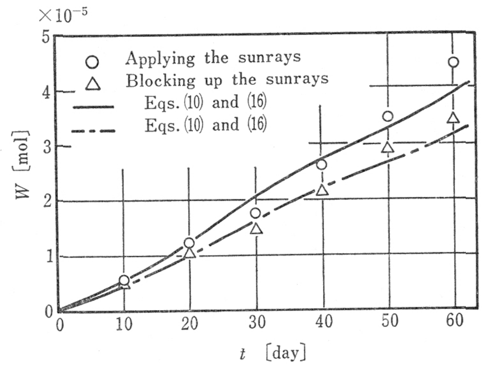

Fig. 3. Relationship between W and exposure day at Minma

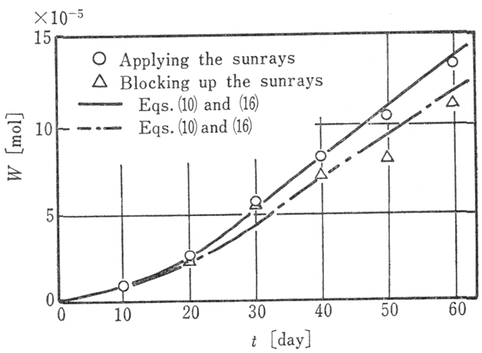

Fig. 4. Relationship between W and exposure day at Yoneizumi

tion of SO_2 by O_2 in the absence of the light energy proceeds extremely gently at atmospheric temperatures. On the other hand, Urone[5,6] reported that the oxidation in the case of applying the sunrays proceeds to some degree than that in the absence of the sunrays and its reaction mechanism was written as follows;

$$SO_2+h\nu \longrightarrow {}^1SO_2 \quad (12)$$

$$ {}^1SO_2 \longrightarrow {}^2SO_2 \quad (13)$$

$$ {}^2SO_2+O_2 \longrightarrow SO_4 \quad (14)$$

$$SO_4+O_2 \longrightarrow SO_3+O_3 \quad (15)$$

4.3 The analysis of air pollution by SO_2

Now, let us discuss the values measured with the lead peroxide method at Minma and Yoneizumi in Kanazawa city according to the semi-theoretical equation presented in this paper.

The integrating of Eq. (11) gives

$$W=2\pi R_1 L\Psi\int_0^t k_f C_{A0}dt \quad (16)$$

In performing the calculation, the atmospheric conditions at measuring points in Kanazawa City have to be considered. In this study, the averages of a day for wind velocity, relative humidity and SO_2 concentration measured by the conductometric method C_{A0} were used and W was calculated from Eqs. (10) and (16) at the time interval of a day by using the numerical integration with Simpson's formula.* Parameter Ψ is unknown value and it was evaluated by the following equation;

$$\Psi=\sum_{i=1}^{N}(W_{\mathrm{obs},i}/W_i)/N=$$

$$\sum_{i=1}^{N}\{W_{\mathrm{obs},i}/(2\pi R_1 L\int_0^{t_i}k_f C_{A0}dt\}/N \quad (17)$$

where t_i and $W_{\mathrm{obs},i}$ show the individual sampling time and the values estimated by the lead peroxide method at t_i, respectively.

The results estimated are shown in Fig. 3 and 4 as curved lines. As is evident from these figure, good agreement is recognized between observed and estimated values. The values of Ψ were 0.24 and 0.28 at Minma measuring point in the cases of blocking up the sunrays and applying the sunrays, respectively. On the other hand, at Yoneizumi the former was 1.3 and the latter was 1.6. The degree of the effect of the sunrays on the reaction can be evaluated by the comparison of the Ψ values at individual measuring points. The ratio of Ψ value obtained by applying the sunrays to that by blocking up the sunrays was 1.17 at Minma and 1.23 at Yoneizumi. In this study, it was observed such a tendency as the measured value in the case of applying the sunrays was 1.2 times than that in the case of blocking up the sunrays.

* refers to Appendix

5. Evaluation of the meausred values of air pollution by SO_2 with the lead peroxide method

The lead peroxide method has been used as a measurement of the SO_2 concentration in the air in Japan. The measured values, however, are affected by the atmospheric conditions and the environmental conditions, and the values obtained at the different measuring points are not compared with each other absolutely.

When the semi-theoretical equation proposed in this paper is used, the reliability of the values measured with the lead peroxide method is improved as follows; The average concentration $\overline{C}_{A0}$ is calculated from the total amount of the product W_{obs} with the lead peroxide method.

$$\overline{C}_{A0}=W_{\mathrm{obs}}/\{2\pi R_1 L\Psi\int_0^t k_f(H,u)\,dt\} \quad (18)$$

In this case, the wind velocity and relative humidity used for the estimation of k_f are the average of a day. The values of Ψ at various measuring points are estimated by the similar way described above with the average SO_2 concentration of a day by the conductometric method.

In **Table 1**, the results calculated from the method proposed here** are shown with the averages measured with the lead peroxide method and conductometric method. As is evident from this table, the calculated results are faily in agreement with the values measured with the conductometric method. It is, then, concluded that the values measured with the lead peroxide method at various measuring points can be evaluated absolutely by using the method in this paper. The values of Ψ should be estimated at the interval of several months, for example, four seasons and further, the average for several years should be used for calculation in practice.

Conclusion

To evaluate precisely the air pollution by SO_2 measured with the lead peroxide method, the semi-theoretical equation was proposed by considering the atmospheric conditions such as wind velocity. relative humidity, and several gaseous substances

** The simpson formula was used. In this case $F(i)$ expressed by Eq. (A-4) is as follows;
$F(i)=H(i)^{0.74}u(i)^{0.5}Sc(i)^{-2/3}\nu(i)^{0.5}$

Table 1. Comparison of measured values with calculated ones for average SO_2 concentrations at Minma and Yoneizumi

Time [day]	Lead peroxide method [mg-SO_3/day/100cm^2-PbO_2]				Conductometric method $\times 10^7$ [mol/m^3]		Calculated value $\times 10^7$ [mol/m^3]			
	Minma		Yoneizumi		Minma	Yoneizumi	Minma		Yoneizumi	
	A	B	A	B			A	B	A	B
8/9–8/18	4.71×10^{-2}	3.83×10^{-2}	0.77×10^{-1}	0.61×10^{-1}	1.74	0.685	1.99	1.99	0.686	0.635
8/9–8/28	4.76	4.12	1.03	0.88	2.01	0.841	2.02	2.15	0.888	0.889
8/9–9/7	4.52	3.57	1.51	1.51	2.10	1.10	1.85	1.81	1.26	1.46
8/9–9/17	5.16	4.12	1.61	1.42	2.11	1.21	2.09	2.06	1.34	1.38
8/9–9/27	5.64	4.69	1.64	1.24	2.12	1.49	2.33	2.39	1.42	1.26
8/9–10/7	5.97	4.60	1.75	1.46	2.10	1.60	2.46	2.32	1.57	1.51

A: Applying the sunrays, B: Blocking up the sunrays

coexisting with SO_2 and further, the effect of light energy $h\nu$ on PbO_2-SO_2 reaction was investigated. The following became clear in this study;

1) The values measured with the lead peroxide method are affected by the light energy $h\nu$ and the amount of reaction product in the case of applying the sunrays is larger than that in the case of blocking up the sunrays.

2) The surface reaction treatment based on the unreacted-core model presents closely the actual kinetic for the reaction on the lead peroxide method.

3) The semi-theoretical equation proposed in this paper is very useful for the evaluation of the values measured with the lead peroxide method.

Acknowledgement

The author would like to thank Mr. A. Kawashima for providing the data and Mr. K. Suzuki for his help in the experiment.

Appendix

Considering $2\pi R_1 L=100$ cm^2, one obtains from Eqs. (10) and (16).

$$W=100\Psi\int_0^t C_{A0}k_f dt$$
$$=1.58(2R_1)^{-0.5}\int_0^t Sc^{-2/3}\nu^{0.5}H^{0.74}u^{0.5}C_{A0}dt \qquad \text{(A-1)}$$

When the time interval is a day, the integration term in Eq. (A-1) is rewritten

$$(60\times 60\times 24/3)\times \int_0^{ti} Sc(i)^{-2/3}\nu(i)^{0.5}H(i)^{0.74}u(i)^{0.5}C_{A0}(i)\,dt \qquad \text{(A-2)}$$

By using the Simpson formula, the integration term in Eq. (A-2) is as follows;

$$\int_0^{ti} H(i)^{0.74}u(i)^{0.5}C_{A0}(i)\,Sc(i)^{-2/3}\nu(i)^{0.5}dt$$
$$=F(0)+\sum_{i=1}^{N/2-1}\{4F(2i-1)+2F(2i)\}+4F(N-1)+F(N) \qquad \text{(A-3)}$$

where

$$F(i)=H(i)^{0.74}u(i)^{0.5}C_{A0}(i)\,Sc(i)^{-2/3}\nu(i)^{0.5} \qquad \text{(A-4)}$$

and N is the days of exposure interval.

From Eqs. (A-1) to (A-4), then, the value of W is calculated.

REFERENCES

1) Hayashi, Y.: The study on mass transfer mechanism for PbO_2-SO_2 reaction system, *J. Japan Soc. Air Pollut.*, **16**(5), 285(1981)
2) Hayashi Y.,: Effect of nitrogen dioxide on the measurement of sulfur dioxide concentration with the lead peroxide method, *ibid.*, **16**(5), 296(1981),
3) Go, F. and A. Ohshino: Studies on the measurement of atmospheric sulfur dioxide pollution by lead peroxide, *Osaka-fu Koshu Eisei Kenkyusho Ho*, **6**, 69 (1969)
4) Koballa, T. E. and M. P. Dudukovic: Sulfur dioxide adsorption on metal oxides supported on alumina, *AIChE Symp. Ser.*, **73**, 199 (1977)
5) Urone, P. and J. P. Smith: Static studies of sulfur dioxide reactions, Effect of NO_2, C_3H_6, and H_2O.
6) Suzuki, S.: Atmospheric chemical reaction—sulfur dioxide—, *Sekiyu Gakkaishi*, **18**, 62 (1975)

Literature cited

a	=stoichiometric coefficient	[—]
C_{A0}	=concentration of gaseous reactant in bulk phase	[mol/m^3]
$\bar{C}_{A0}$	=average concentration of gaseous concentration in bulk phase defined by Eq. (18)	[mol/m^3]
C_{S0}	=initial concentration of solid reactant	[mol/m^3]

d	=thickness of PbO_2 paste on cylinder	[m]
$F(i)$	=function defined by Eq. (A-4)	
H	=relative humidity	[%]
k_f	=overall gas film mass transfer coefficient	[m/s]
L	=height of PbO_2 paste on cylinder	[m]
N	=days of exposure interval	[day]
R_1	=outside radius of cylinder	[m]
Re	=Reynolds number ($=2R_1u/\nu$)	[—]
r_c	=distance from the axis of cylinder to unreacted-core surface	[m]
Sc	=Schmidt number	[—]
t	=exposure time	[day], [s]
u	=mean wind velocity	[m/s]
W, W_i	=total amount of solid product	[mol]
Ψ	=characteristic parameter defined by Eq. (11)	[—]

Subscript

obs	=observed value with the lead peroxide method	

二酸化鉛法による亜硫酸ガスの大気汚染評価

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金沢市の三馬および米泉地域で，大気中の亜硫酸ガス濃度を二酸化鉛法を用いて10日毎に60日間にわたって測定した。測定値に及ぼす光エネルギー $h\nu$ の影響を調べるために，塩ビ製の2つのシェルターを各々の測定点に設置した。一つは薄いアルミ箔をシェルター内にはったものであり，他方は何の処理も施さないものである。異なった測定点で得られた値の絶対量を比較するため，測定点での環境条件の差異ならびに反応に及ぼす大気中の共存ガスや太陽光線の影響による特性パラメータ Ψ を用いて半理論式を導いた。

(昭和56年6月8日受付)