

INNOVATIVE METHODOLOGY FOR EMISSION MODEL OF CONTAMINATION MOLECULES BASED ON DIFFUSION THEORY

Kazunori Shimazaki⁽¹⁾, Eiji Miyazaki⁽¹⁾, Yuta Tsuchiya⁽¹⁾, Fumitaka Urayama⁽²⁾, and Yugo Kimoto⁽¹⁾

⁽¹⁾ *Research Unit I, Research and development directorate, Japan Aerospace Exploration Agency,
2-1-1 Sengen, Tsukuba, Ibaraki, Japan
Email: shimazaki.kazunori@jaxa.jp*

⁽²⁾ *Space Engineering Development Co. Ltd., 5-62-1 Nakano, Nakano-ku, Tokyo, Japan
Email: urayama.fumitaka@sed.co.jp*

ABSTRACT

Contamination is always troublesome in spacecraft development and has yet to be investigated because outgassing, transportation, deposition and re-emission phenomena largely depends on the spacecraft design.

Designers and engineers analytically and empirically estimate the amount of contamination emission and deposition at each phase of designing and manufacturing. Particularly for today's sophisticated spacecraft design, the prediction and estimation of contamination effects using analytical tools are an indispensable means. Thus, current simulations need to be improved. We have consequently been addressing the improvement in the modeling of outgassing phenomena that mark the first phase in the occurrence of a contamination problem. We focused on diffusion-limited phenomena because the diffusion rate of outgassing molecules in the subject materials was considered much slower than their desorption rate at the material surface.

A new experimental technique and analytical procedure (collectively called the "JAXA test method") were originally devised for extracting the parameters of the diffusion model. In comparing the desorption model and diffusion model, we successfully modeled the emission behavior of outgassing molecules based on the diffusion theory.

1. INTRODUCTION

Molecular contaminants outgassed from organic materials are deposited on the solar arrays, thermal-control surfaces and optical components, resulting in a severe degradation of the optical performance [1-3]. To avoid such degradation, the selection and bake-out of materials for both components and spacecraft are carefully conducted. In addition, designers and engineers analytically and empirically estimate the amount of contamination deposition and the influence of contamination on optical performance. It is important for today's sophisticated spacecraft design to estimate the amount of contamination deposition in ground tests and on orbit as accurately as possible. Toward that end, several contamination analysis tools [4-8] have been developed and employed for spacecraft design. In Japan, we have developed Japan's SPacecraft Induced Contamination Environment analysis software (J-

SPICE) for use in spacecraft design [9]. However, such analytical tools for contamination analysis require constant improvement. The physical phenomena of outgassing, transportation, deposition and re-emission are generally considered in the contamination analysis, and several equations for modeling those phenomena have been employed. In the current simulations, modeling still has room for improvement. We have consequently been addressing improvement in the modeling of outgassing phenomena that mark the first phase in the occurrence of a contamination problem.

It is still open to question whether outgassing phenomena are dominated by desorption and/or diffusion. The subject contamination sources here are such organic materials as cured adhesive, coated resin of wire, thermal filler and so on. It has been reported that the theory of limitation by desorption could be a good model for explaining outgassing behavior [10]. However, we focused on diffusion-limited phenomena because the diffusion rate of outgassing molecules in the subject materials was considered much slower than their desorption rate at the material surface. In this paper, we therefore simulated the outgassing rate by using desorption and diffusion models, and then compared the result of both. It is well known that diffusion phenomena follow Fick's laws of diffusion [11]. The outgassing behavior from the inside of materials was modeled by the diffusion equations (Fick's first law and Fick's second law). In addition, the models must obtain the fitting parameters necessary for simulating the outgassing of each material. A new experimental technique and analytical procedure (collectively called the "JAXA test method") were originally devised for extracting those parameters. We successfully obtained the parameters and modeled the emission behavior of outgassing molecules based on the diffusion theory. The simulation results agreed well with the experimental ones. This paper presents the emission model of outgassing molecules and the method of parameter extraction for the calculations, together with the experiment method and results.

2. OUTGASSING MODEL

The modeling of outgassing is often discussed in a desorption model [10] or diffusion model [12]. Of course, both models could simultaneously exist. Figure 1 shows

images of the desorption and diffusion models. In the desorption model, the outgassing molecules desorb at the surface of a material, with a uniform concentration distribution of outgassing molecules in the depth direction. Conversely, the diffusion rate of outgassing molecules in the subject materials was considered slow, and the closer to the sample surface, the larger the reduction of the number of outgassing molecules in each material. Thus, the concentration distribution of outgassing molecules is not uniform. We therefore addressed which model was better to simulate the actual outgassing phenomena.

We adopted the ‘function’ and ‘equation’ of each model. Here, ‘function’ is a solution of a differential equation of each model, and ‘equation’ is a differential equation itself. Although ‘equation’ is accurate, it is extremely time-consuming to numerically solve and difficult to estimate the probable fitting parameters described later without the appropriate initial values. Although ‘function’ is limited in use, its calculation speed is faster than that of ‘equation’. Thus, we initially used ‘function’ to estimate the initial fitting parameters, and then employed ‘equation’ to obtain the final fitting parameters and simulate the outgassing behavior.

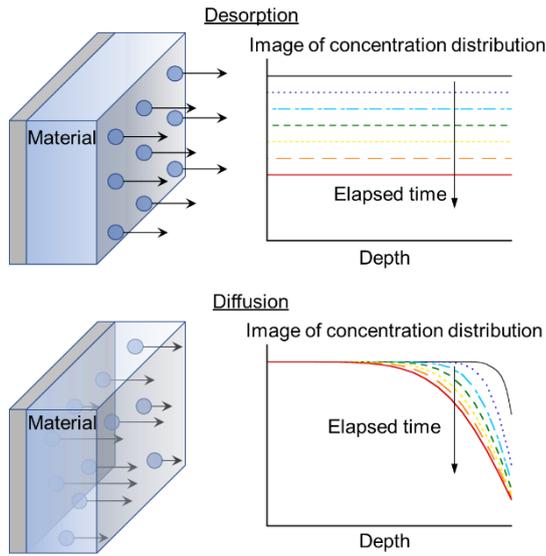


Fig. 1. Images of desorption and diffusion phenomena.

2.1 Desorption model

2.1.1 Function of desorption

In this study, we consider the emission phenomena of outgassing molecules from a material as a contamination source by elevated heating. When the heating rate of the material is constant regardless of time, the function of desorption for an arbitrary component is expressed by the following functions (1) and (2) [13]. The functions hold when the heating is started from absolute zero temperature. The functions were fitted to experimental outgassing data described later to estimate the fitting

parameters. The fitting parameters are M_0 , τ_0 , and E .

$$\begin{aligned} \dot{M}_i(T) &= \frac{1}{\tau_{0i}} \exp\left(\frac{-E_i}{RT}\right) \\ &\cdot M_{0i} \exp\left\{-\frac{RT^2}{\tau_{0i}\beta E_i} \exp\left(\frac{-E_i}{RT}\right) \Psi_i(T)\right\} \end{aligned} \quad (1)$$

$$\Psi_i(T) = \sum_{j=1}^{\infty} j! \left(-\frac{RT}{E_i}\right)^{j-1} \quad (2)$$

where,

\dot{M}	: Outgassing rate	[g/cm ² /s]
M_0	: Initial amount of adsorption at material surface	[g/cm ²]
τ_0	: Arrhenius pre-exponential factor of surface residence time	[s]
E	: Desorption energy	[J/mol]
R	: Gas constant	[J/K/mol]
T	: Temperature of contamination source	[K]
β	: Heating rate of contamination source	[K/s]
i	: Number of component	

2.1.2 Differential equation of desorption

When temperature elevation begins from an arbitrary temperature, the differential equation of desorption for an arbitrary component is expressed by the following equations [14].

$$\dot{M}_i = \frac{dM_i}{dt} = -\frac{M_i}{\tau_i} \quad (3)$$

$$\tau_i = \tau_{0i} \exp\left(-\frac{E_i}{RT}\right) \quad (4)$$

where,

M	: Amount of adsorption at material surface	[g/cm ²]
τ	: Outgassing time constant	[s]

2.2 One-dimensional diffusion model

2.2.1 Function of 1D diffusion

When the heating rate of the material is constant regardless of time and the material has much larger area compared to the thickness, the function of a one-dimensional diffusion model for an arbitrary component is expressed by the functions (2) and (5) [13]. The functions hold when heating is started from absolute zero temperature. This function was used to estimate the parameters for fitting to experimental data described later. The fitting parameters are C_0 , D_0 , and E .

$$\begin{aligned} \dot{M}_i(T) &= \frac{2C_{0i}D_{0i}}{d} \exp\left(\frac{-E_i}{RT}\right) \\ &\times \sum_{m=0}^{\infty} \exp\left[-\left\{\frac{(2m+1)\pi T}{2d}\right\}^2\right] \\ &\cdot \frac{RD_{0i}}{\beta E_i} \exp\left(\frac{-E_i}{RT}\right) \Psi_i(T) \end{aligned} \quad (5)$$

where,

C_0	: Initial amount of outgassing concentration in material	[g/cm ³]
d	: Sample thickness	[cm]
D_0	: Arrhenius pre-exponential factor of interdiffusion coefficient	[cm ² /s]
E	: Interdiffusion energy	[J/mol]

2.2.1 Differential equation of 1D diffusion

When temperature starts to rise from an arbitrary temperature and the material has much larger area compared to the thickness, the differential equation of diffusion for an arbitrary component is expressed by the following equations [11].

$$\dot{M}_i = -\frac{d}{dt} \int C_i dx \quad (6)$$

$$\frac{\partial C_i}{\partial t} = D_i \cdot \frac{\partial^2 C_i}{\partial x^2} \quad (7)$$

$$D_i = D_{0i} \cdot \exp\left(-\frac{E_i}{RT}\right) \quad (8)$$

where,

C	: Outgassing concentration in material	[g/cm ³]
x	: Distance from sample surface ($0 < x < d/2$)	[cm]
D	: Interdiffusion coefficient	[cm ² /s]
t	: Elapsed time	[s]

2.3 Outgassing rate experiment with constant heating rate

For applying the above-mentioned equations, it is necessary to obtain the unknown fitting parameters. Those parameters are obtained by fitting the functions or equations to the outgassing rate data. Therefore, outgassing rate tests were carried out using the apparatus pictured in Fig. 2. The configuration of this apparatus is compliant with ASTM E1559 [15]. A shroud cooled by liquid nitrogen is installed in the chamber, and an effusion cell containing a contamination source is installed in the shroud. By heating the effusion cell, outgassing molecules are effused from the open orifice on the top of the cell and adheres to a quartz microbalance crystal (QCM) set at a height of 150 mm. The QCMs are

cooled to about -193°C (see Fig. 3). The outgassing rate is calculated from the adhesion rate of outgassing molecules on the QCM surface. As previously mentioned, the desorption and diffusion functions hold when the heating rate of contamination source is constant. A lower heating rate is desirable in order to distinctively separate the outgassed components due to differences in temperature. Considering the apparatus restriction and experiment time, the heating rate was determined to be 1°C/h .

The sample used as a contamination source was a two-part silicone adhesive (RTV S-691: Wacker Chemie AG). The sample measured 40 mm^2 in size and 2.0 mm in thickness. The sample was installed in the effusion cell to outgas from both surfaces.



Fig. 2. Photo of outgassing rate measurement apparatus.

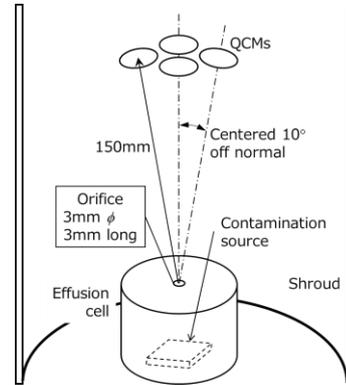


Fig. 3. Schematic illustration of effusion cell and QCM locations.

3. EXPERIMENTAL AND MODEL FITTING RESULTS

Shape and configuration of orifice and QCMs were modeled for calculating the outgassing rate. We simulated the rate of outgassing effused from the orifice and deposited on a QCM.

3.1 Determination of fitting parameters

3.1.1 Desorption model

Curve fitting was performed using functions (1) and (2) on the measured outgassing rate data to obtain M_0 , τ_0 , and E as initial values. Figure 4 shows the results. The measured outgassing rate decreased rapidly right after the experiment was started, but later increased toward at around 60 °C. The outgassing rate was reduced again at around 80 °C, and the continued to rise as the temperature elevated. Thus, two peaks were assumed in this calculation to correspond to each outgassed component. Peak 1 was assumed to exist above 125 °C, while peak 2 was at around 60 °C.

At the next step, the final M_0 , τ_0 , and E of all peaks, that is, all components, were determined by the nonlinear least squares method while numerically solving equations (3) and (4) using M_0 , τ_0 , and E previously obtained as initial values. Figure 4 shows the fitting result, and Table 1 lists the final fitting parameters obtained. As can be seen in Fig. 4, the fitting result and measurement result agreed well except for data less than 50 °C. The fitting was performed on the data greater than 50 °C, so as to improve the fitting accuracy above the temperature. The fitted results deviated extremely from a measurement result of less than 50 °C. In addition, the fitted initial amount of adsorption (M_0) was approximately 0.1 g/cm², which corresponds to about 1 mm in thickness. This is a physically impossible value. This result indicated that the desorption model did not to correctly express the outgassing behavior.

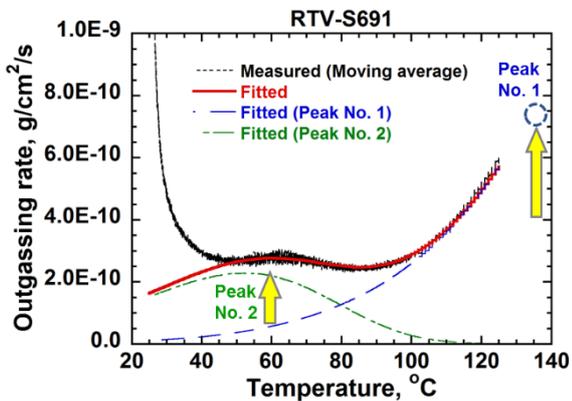


Fig. 4. Fitting results of differential equations of desorption to measurement result. Blue dot circle is pointed only as a guide for a position of Peak No.1.

Table 1. Fitted parameters by desorption model.

Peak #	M_0 , g/cm ²	τ_0 , s	E , J/mol
1	1.46×10^{-1}	1.95×10^3	3.90×10^4
2	4.46×10^{-5}	2.37	2.91×10^4

3.1.2 1D diffusion model

Curve fitting was performed using functions (2) and (5) on the measured outgassing rate data to obtain C_0 , D_0 , and E as initial values. Two peaks were assumed in this calculation to correspond to each outgassed component. Peak 1 was assumed to exist above 125 °C, while peak 2 was at around 60 °C.

At the next step, final C_0 , D_0 , and E of all peaks, that is, all components, were determined by the nonlinear least squares method while numerically solving equations (6-8) using C_0 , D_0 , and E previously obtained as initial values.

Figure 5 shows the fitting results, and Table 2 lists the final fitting parameters obtained. Although, the fitting was performed on data greater than 50 °C, each fitting result and measurement one agreed well except for data less than 20 °C. Unlike the desorption model, the temperature dependence of an outgassing rate of less than 50 °C shows behavior similar to that indicated by the measurement result. This point is explicitly different from the desorption model result.

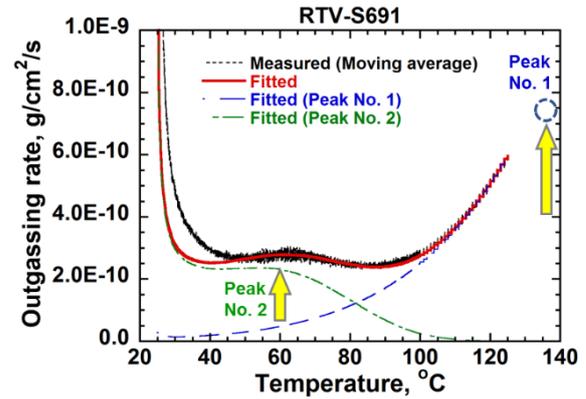


Fig. 5. Fitting results of differential equations of diffusion to measurement result. Blue dot circle is pointed only as a guide for a position of Peak No.1.

Table 2. Fitted parameters by diffusion model.

Peak #	C_0 , g/cm ²	D_0 , cm ² /s	E , J/mol
1	3.21×10^{-2}	5.91×10^1	9.19×10^4
2	7.88×10^{-4}	5.27×10^{-3}	3.24×10^4

3.2 Simulation of outgassing behavior

To investigate the validity of the model and the fitting parameters obtained, it was examined whether the outgassing behavior by multi-stepwise method [14] can be simulated. Using the apparatus shown in Fig. 2, the outgassing rate was obtained by heating the contamination source at the temperature steps given in Fig. 6. The sample used as a contamination source was RTV S-691. The sample measured was 40 mm² in size and 1.5 mm in thickness. The sample was installed in the effusion to outgas from both surfaces.

3.2.1 Desorption model

Equations (3) and (4) were numerically solved using the obtained fitting parameters listed in Table 1 and compared with the measured outgassing rate. Figure 6 shows the results. At a heating temperature of 25 °C, the simulation results remarkably deviated from the measured one. At a heating temperature between 50 °C and 125 °C, the simulation result was less than half of the measured one. And at a constant heating temperature of 125 °C, the simulated rate was constant though the measured rate continued to decrease. This is attributed to the considerably large initial amount of adsorption of peak 1. This finding suggests that the desorption model does not properly simulate the outgassing behavior according to the multi-stepwise method.

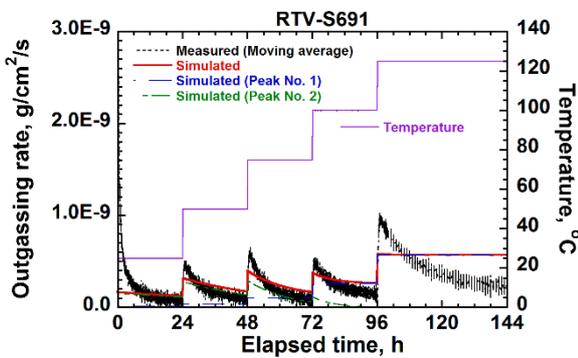


Fig. 6. Comparison of simulation results by desorption model with outgassing rate data obtained by multi-stepwise method.

3.2.2 1D diffusion model

Equations (6-8) were numerically solved using the obtained fitting parameters listed in Table 2 and compared with the measured outgassing rate. Figure 7 shows the results.

In contrast to the desorption model, temporal changes in the outgassing rate agreed well between the simulation and measurement results. At a heating temperature of 25 °C, the simulation result is similar to the measurement result, although the fitting was performed on the data greater than 50 °C. In addition, the outgassing behavior agreed well with the experiment at a constant heating temperature of 125 °C. This result suggests that the diffusion model is preferable for simulating outgassing phenomena. Moreover, it is possible to simulate the outgassing behavior of each component in this model. In Fig. 7, it can be seen that component 1 (peak 1) is outgassed above 75 °C, and that component 2 (peak 2) is almost completely outgassed at below 75 °C.

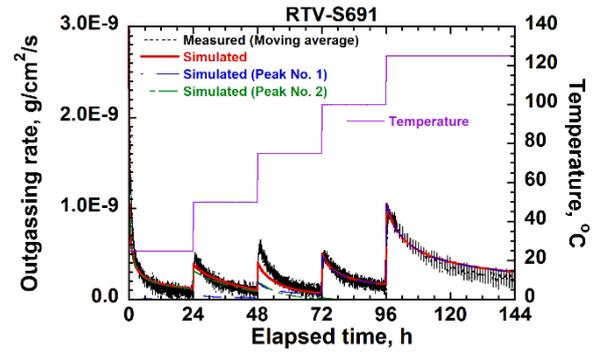


Fig. 7. Comparison of simulation results by diffusion model with outgassing rate data obtained by multi-stepwise method.

4. ORIGINAL OUTGASSING RATE MEASUREMENT FOR IMPROVING PARAMETER FITTING

The diffusion model properly simulated the outgassing behavior compared with the desorption model. However, the fitted total initial amount of outgassing concentration (ΣC_0) listed in Table 2 was one order of magnitude larger than the value estimated by ASTM E1559. ΣC_0 estimated by ASTM E1559 was 1.51×10^{-3} . ASTM E1559 is a simple and alternative test method to estimate ΣC_0 . The reason why is that C_0 of peak 1, which is outgassed at high temperature, was not correctly estimated. It is thus necessary to obtain a more precise initial concentration (C_0).

A new experimental technique and analytical procedure (collectively called the “JAXA test method”) were originally devised for extracting the parameters. As previously mentioned, the adopted diffusion model holds when the heating rate of the contamination source is constant. A lower heating rate is desirable to separate the outgassed components due to differences in temperature. And to improve the estimation accuracy of C_0 of the component outgassed at high temperature, after reaching the upper-limit temperature, the contamination source was held at that maximum temperature for a certain period. The experimental conditions were determined due to the apparatus restrictions and experiment time as follows. The heating rate was 1°C/hour and the maximum temperature of the contamination source was 125 °C. The holding period at 125 °C was approximately three days.

The outgassing rate tests were carried out using the apparatus shown in Fig. 2 according to the above-mentioned conditions. The sample used as a contamination source was RTV S-691. The sample measured 40 mm² in size and 1.887 mm in thickness. The sample was installed in the effusion to outgas the outgassing molecules from both surfaces.

4.1 Determination of fitting parameters

Curve fitting was performed by following the same procedure described in subsection 3.1.2. Two peaks were assumed in this calculation to correspond to each outgassed component. Peak 1 was assumed to exist above 125 °C, while peak 2 was at around 60 °C. The fitting was performed on data greater than 50 °C. Data less than 50 °C and during a constant heating temperature of 125 °C were not used for the fitting.

Figure 8 shows the fitting results, and Table 3 lists the fitting parameters obtained. The fitted total initial amount of outgassing concentration (ΣC_0) was 2.33×10^{-3} and close to the value estimated by ASTM E1559. Conversely, D_0 of peak 1 is one order of magnitude larger than the result listed in Table 2. The increase of D_0 might compensate for the decrease of C_0 . Given the reasonable ΣC_0 , however, this fitting result is better than the result in Table 2.

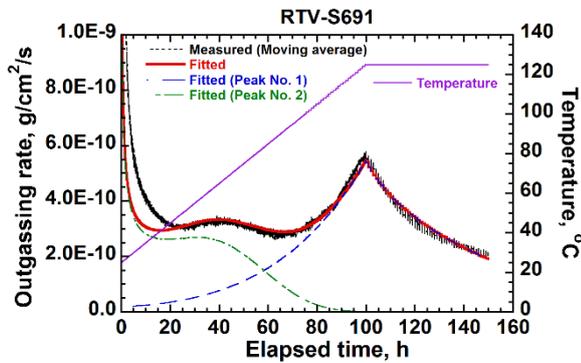


Fig. 8. Outgassing rate data and fitting results using diffusion equations.

Table 3. Fitted parameters by diffusion model.

Peak #	C_0 , g/cm ²	D_0 , cm ² /s	E , J/mol
1	1.64×10^{-3}	4.72×10^2	7.92×10^4
2	6.93×10^{-4}	3.22×10^{-3}	3.14×10^4

4.2 Simulation of outgassing behavior

To check the validity of the obtained fitting parameters in Table 3, we simulated the outgassing behavior obtained by using a multi-stepwise method. Figure 9 shows the results. The only difference is the parameters used. Temporal changes in the outgassing rate agreed well between the simulation and measurement results. The temperature dependence of each component on the outgassing rate was similar to that shown in Fig. 7. The results indicated that the fitting parameters determined by “JAXA test method” and diffusion model were very plausible analytical approach to simulate the emission behavior of outgassing molecules from inside the material.

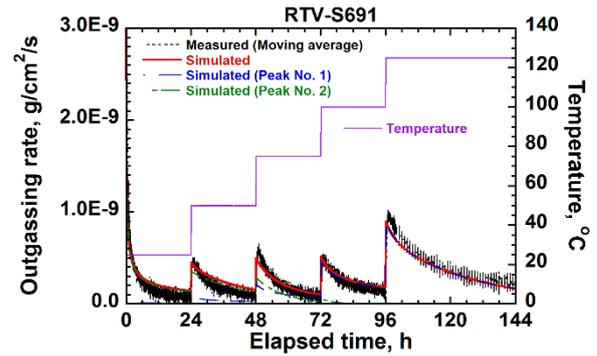


Fig. 9. Simulation results using fitted parameters and diffusion equations. Simulation and the experiment were performed according to a multi-stepwise method.

5. SUMMARY

We addressed improvement of the modeling of outgassing phenomena. The outgassing behavior was modeled based on desorption and diffusion theory. The desorption model did not properly simulate the outgassing behavior. In contrast with the desorption model, the diffusion model correctly simulated the outgassing behavior. The results suggested that the diffusion model was preferable to the desorption model in simulating outgassing phenomena.

In addition, a new experimental technique and analytical procedure (collectively called the “JAXA test method”) were originally devised for extracting the parameters of the diffusion model, and can be summarized as follows. The outgassing rate is measured using the original procedure for the heating contamination source as slowly as possible, and after reaching the upper-limit temperature, the contamination source is held at that maximum temperature for a certain period. The diffusion functions and equations are used to analyse the outgassing rate data obtained, and acquire the fitting parameters. By using these parameters, we can simulate the emission behavior of outgassing molecules by using diffusion equations. The “JAXA test method” is an innovative methodology to model outgassing phenomena, and could significantly improve the accuracy in simulating outgassing behavior. We have developed a Japan’s Spacecraft Induced Contamination Environment analysis software 2 (J-SPICE2) that incorporates a diffusion model. J-SPICE2 has a module for fitting and extracting the parameters of the diffusion model and simulating outgassing behavior based on the diffusion theory. In the future, we will apply the diffusion model to other contaminations and obtain the parameters for modeling the emission behavior of various outgassing molecules.

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