Comparison of molecular contamination models based on TGA/MS experiments

Emilie Vanhove, Eudes Grosjean, Guillaume Rioland, Delphine Faye

COMPARISON OF MOLECULAR CONTAMINATION MODELS BASED ON TGA / MS EXPERIMENTS

Emilie Vanhove[(1)], Eudes Grosjean[(1)], Guillaume Rioland[(2)], Delphine Faye[(2)]

[(1)] ONERA / DPHY, Université de Toulouse, F-31055 Toulouse – France
[(2)] Centre National d'Etudes Spatiales, 18 Avenue Edouard Belin 31400 Toulouse, France

ABSTRACT

Several competing models of outgassing and reemission have been developed to describe molecular contamination. Similarly, European, American and Japanese space agencies advocate very different methods for estimating the properties of spatial contaminants. However, for flight predictions to be reliable, it is necessary to have both relevant models and good input parameters for these models (robust characterization methods).Thus, from one model to another and from one characterization method to another, the simulations very often vary by several orders of magnitude. It is therefore very important to be able to determine which methodologies provide reliable results. The coupling of the thermogravimetric and mass spectrometry analyzes makes it possible to establish the individual behavior of outgassing and of reemission of each chemical species of a spatial contaminant, separately. In this study, using these new experimental data, the most commonly used models are compared and discussed, as well as their impact on predictions of contamination levels. Alternative models are also proposed. This work may contribute to the evolution of characterization protocols and numerical models, with important consequences for simulation results.

INTRODUCTION

Accurately predicting in-flight contamination levels requires both a good description of contaminant outgassing and of contaminant reemission [1,2]. However, the assessment of models of outgassing and of reemission as well as the extraction of the parameters of these models are quite challenging because each spatial contaminant outgasses a variety of chemical species having very different properties (kinetics of outgassing and of reemission). Combining thermogravimetric analysis with mass spectrometry enables to obtain (in situ and in real time) the individual behavior of outgassing and of reemission of each chemical species (or at least of the main chemical species) of a spatial contaminant, as well as its mass spectrum [3,4]. The work presented here therefore aims to compare the most commonly used models and protocols using these new experimental data.
This paper is divided into two parts: the first part deals with outgassing and the second part deals with reemission. For each parts, the models are first presented and then compared to the TGA / MS experimental data. The impact of models and protocols on predictions is then discussed. Finally, to ease the utilization of theses models, a simplification of the equations is proposed while preserving as much as possible the physical relevance of the models.

OUTGASSING

1.1. Outgassing models

Outgassing can be described as the succession of two steps. The molecules first diffuse into the contaminant (bulk diffusion) and are then reemitted at the surface (evaporation or desorption). There is currently no doubt that both of these two phenomena occur (diffusion and reemission). The objective of this work is therefore to determine which of these two steps actually limits the overall outgassing process (or alternatively to determine whether or not the two phenomena should be taken into account in the simulations). Bulk diffusion can be described by Fick laws [5,6]:

$$\frac{\partial m_i}{S\partial t} = -C_{0i}\sqrt{\frac{D_i}{\pi t}}\left[1 + 2\sum_{n=1}^{\infty}(-1)^n \exp\left(\frac{-n^2 d^2}{D_i t}\right)\right] \quad \text{Eq.1}$$

m_i : mass of species *i* in the contaminant
C_{0i} : initial concentration
D_i : diffusion coefficient
$2d$: thickness of the contaminant
t : time
S: area

This equation has two asymptotes:
When t→0 :

$$\frac{\partial m_i}{S\partial t} = -\frac{m_{i0}}{V}\sqrt{\frac{D_i}{\pi t}} \quad \text{Eq.2}$$

m_{i0} : initial mass
V : volume of the contaminant

When t→∞ :

$$\frac{\partial m_i}{S\partial t} = -\frac{2D_i m_{i0}}{Vd} exp\left(-\frac{\pi^2 D_i t}{4d^2}\right) \quad \text{Eq.3}$$

Langmuir law can be used for evaporation:

When the mass of species i in the deposit m_i is over a monolayer:

$$\frac{1}{S}\frac{\partial m_i}{\partial t} = -\alpha_i P_{vi}\sqrt{\frac{M_i}{2\pi RT}} \qquad \text{Eq.4}$$

α_i : empirical evaporation coefficient
P_{vi}: vapor pressure of species i
M_i :molecular weight
R : gaz constant
T : temperature

When m_i is lower than a monolayer :

$$\frac{1}{S}\frac{\partial m_i}{\partial t} = -\frac{m_i}{m_{mono\ i}}\alpha_i P_v\sqrt{\frac{M_i}{2\pi RT}} \qquad \text{Eq.5}$$

$m_{mono\ i}$: mass of one monolayer

Alternatively the desorption model is also widely used in Europe to describe outgassing [7]:

$$\frac{\partial m_i}{\partial t} = -\frac{m_i}{\tau_i} \qquad \text{Eq.6}$$

$$\tau = \tau_0 e^{\frac{E_a}{RT}} \qquad \text{Eq.7}$$

E_a : activation energy

1.2. Experimental data and simulations

These models are now compared with experimental data. The TGA / MS experiments that support this work are presented in other publications [3,4]. The species separation technique is currently under development at ONERA. This study has therefore been restricted to ion intensities (mass spectrometry measurements) whose mass to charge ratios m / z could be attributed (through gas chromatography–mass spectrometry and / or TGA / MS) to a single chemical species (or at least to a largely majority species).
Figure 1 shows the outgassing of a species issued from the contaminant EC2216 which has a very narrow reemission peak at -20 ° C. Outgassing of this species was monitored by measuring the intensity of the m / z ratio 76 (proportional to the outgassing rate of this species) over time. These experimental data cannot be reproduced using an evaporation model. Indeed according to the equation 4, when the outgassing temperature is constant, the outgassing rate is constant. This model therefore does not allow to reproduce the drop in the outgassing rate observed during each temperature step.

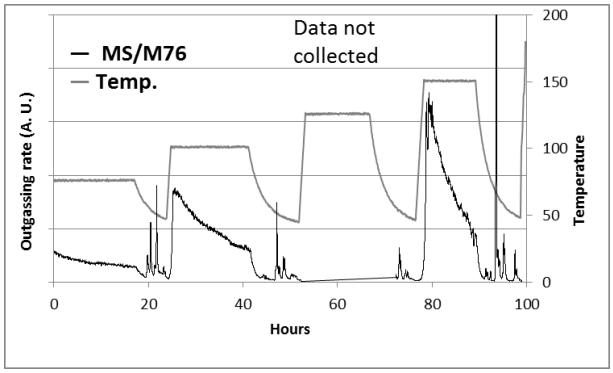

Fig. 1. Outgassing rate of a species issued by the contaminant EC2216 monitored by mass spectrometry (m/z = 76).

The desorption model does not allow to fit the experimental data either. Indeed, as shown in FIG. 2, it is not possible to reproduce both the increase in the outgassing rate observed with each increase in the outgassing temperature and the decrease in the outgassing rate during each temperature step.

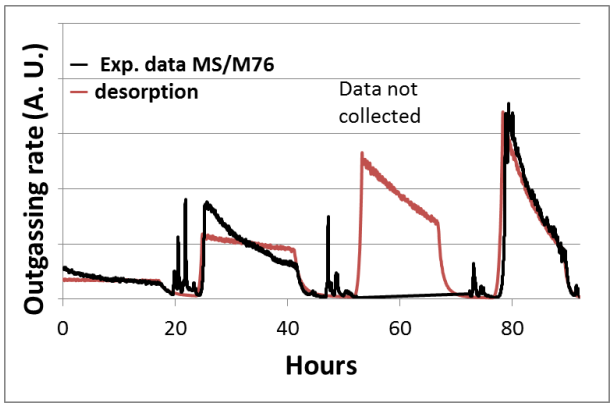

Fig. 2. Simulation of outgassing using a desorption model - EC2216 - (m/z = 76)

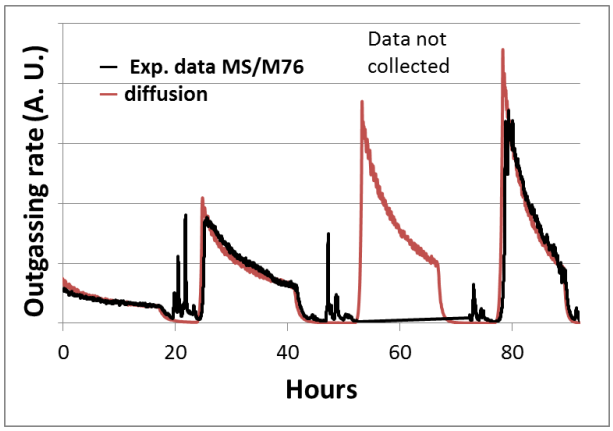

Fig. 3. Simulation of outgassing using a diffusion model EC2216 - (m/z = 76)

On the contrary, the experimental data are very well

fitted using a diffusion model (FIG 3). This work of model comparison was carried out for the outgassing of two other species emitted by EC2216: toluene [2] and 1,3-dimethoxy-5 - [(E) -2-phenylethenyl] benzene (FIG. 4 and 5). For each one of these two species the diffusion model was found to best reproduces the experimental data (FIG. 5).

During the experiment shown in FIG 4 and 5, the number of temperature steps has been increased in order to be able to characterize more accurately the activation energy of the diffusion coefficient (E_a in Eq. 10). The experiment was also extended to high outgassing temperatures to assess the total mass of this benzene into the EC2216 contaminant. Overall, outgassing rate increases for each new temperature step and decreases during each step are well reproduced using a diffusion model. However some discrepancies between experimental data and simulation can be observed. In part, these differences come from the fact that, due to very strong time constraints, a simplified model of diffusion has been used to fit the experimental data (Eq. 9 and 10 instead of Eq.1).

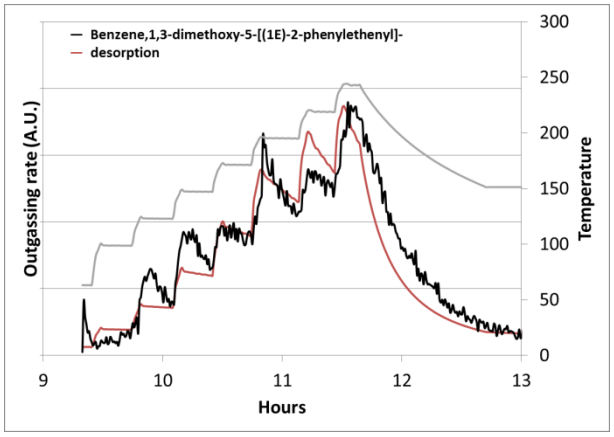

Fig. 4. Outgassing rate of 1,3-dimethoxy-5 - [(E) -2-phenylethenyl] benzene - contaminant EC2216- Experimental data and simulation – Desorption model

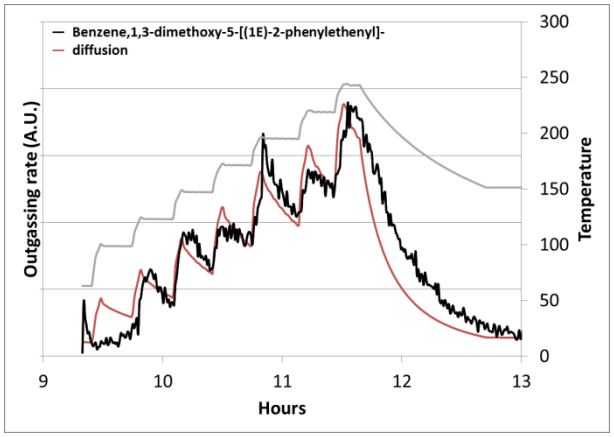

Fig. 5. Outgassing rate of 1,3-dimethoxy-5 - [(E) -2-phenylethenyl] -contaminant EC2216- Experimental data and simulation – Diffusion model

This work is still ongoing at ONERA to extend research to other materials (silicone glues, polyimides, polyetheretherketone). So far, the first results obtained confirm the relevancy of the diffusion model for the outgassing of contaminants.

1.3. Impact on predictions

Of course the simulation results vary a lot depending on the model used. Indeed, the extrapolation, from ground tests to flight contamination is very large (from a few days to a few tens of years). To illustrate these differences in predictions, the same set of data (arising from a real experiment) was fitted, once using a desorption model and another time using a diffusion model.

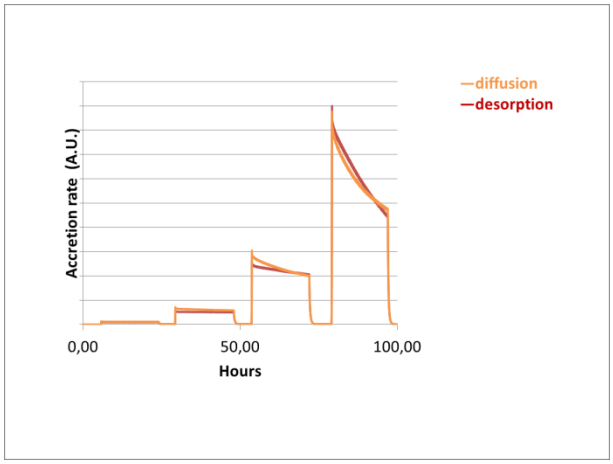

Fig. 5. Outgassing rate - A same set of experimental data was fitted using a diffusion model and a desorption model

Outgassing in flight was then extrapoled (outgassing temperature = 120°C during 12 years).

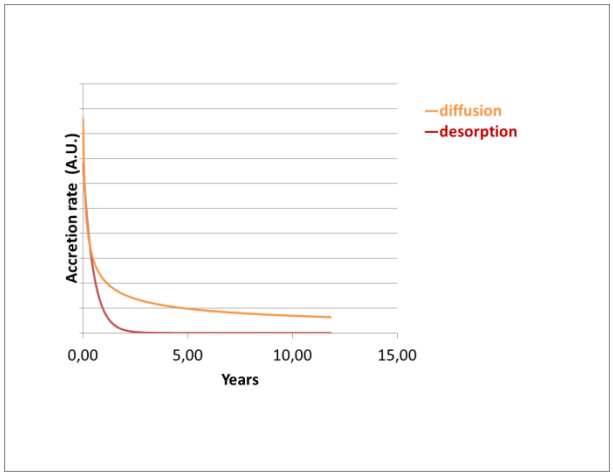

Fig. 6. Extrapolations – Outgassing temperature = 120°C – Desorption and diffusion models

The very large difference observed between the two

extrapolations is due to the fact that in the case of the desorption model the decrease of the outgassing rate observed during ground tests is attributed to the almost complete depletion of the outgassed species in the contaminant. The outgassing rate therefore drops very rapidly during the simulation of the flight case. On the other hand, in the case of the diffusion model, this decrease is attributed to the term in $\sqrt{\frac{1}{t}}$ typical of diffusion phenomena, the drop of the outgassing rate expected in flight is thus much more progressive.
Even using realistic models, the outgassing parameters cannot be extracted accurately without the help of a method of species separation. For example, the outgassing of two species with different activation energies (100 and 180 kJ) is presented in figure 7. The outgassing kinetics of species 2, which contributes less significantly to the deposit during the ground test, cannot be determined from the overall outgassing rate. This species is however predominant in flight (Fig. 8).

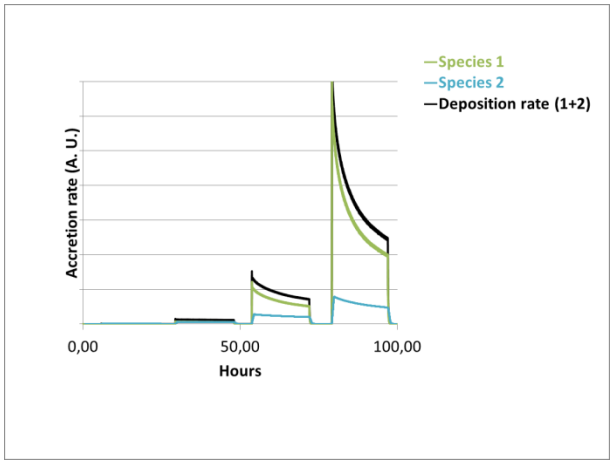

Fig. 7. Outgassing of two chemical species having two different activation energies (100 and 180 kJ)

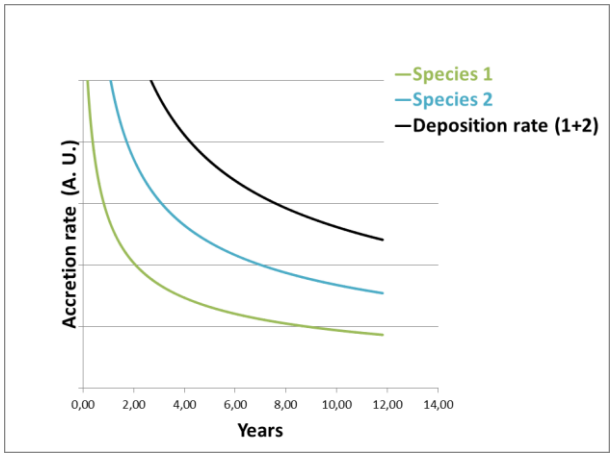

Fig. 8. Extrapolation-Outgassing temperature =125°C

1.4. Simplified model

To make quick first estimates, simplified equations can be used (Eq. 9 and 10). They capture as much as possible the physics of outgassing while being easier to handle.

$$\frac{\partial m_i}{S\partial t} = \frac{m_i}{V}\sqrt{\frac{D_i}{\pi t}}$$

Eq.8

$$t' = \int_0^t dt\, exp(-E_{a_i}/RT)$$

Eq. 9

$$\frac{\partial m_i}{S\partial t} = \frac{m_i}{V}\sqrt{\frac{D_0}{\pi t'}}e^{-\frac{E_{ai}}{RT}}$$

Eq.10

This equation has indeed the same asymptote (Eq. 2) as equation 1 for short times and presents the interest to move towards zero when the species is completely depleted. Due to very strong time constraints this equation has been used to produce the results presented here. However, at least for the validation of the models and the extraction of the parameters, it is preferable to use the equation 1.

REEMISSION

1.5. Reemission models

Like outgassing, reemission can be described in first approach by a diffusion step followed by an evaporation step (Eq. 1, 4 and 5). Alternatively the desorption model (Eq. 6 and 7) is very widely used in Europe. We have also studied in detail more complex phenomena in previous studies (phase change, phase separation ...) [8]. The objective pursued here is to determine what is the limiting step of the reemission process.

1.6. Experimental data and simulations

What most clearly distinguishes the models of reemission is their dependence on the mass of contaminant m_i that remains in the deposit. Indeed, according to the desorption model, the reemission rate is proportional to this mass. To the contrary, according to the evaporation model the reemission rate does not depend on m_i. To compare these two models, reemission peaks corresponding to various deposit thicknesses were studied. As it can be seen in Figure 9, according to the desorption model, the emission peak does not shift when the thickness of the deposit varies (reemission rate proportional to the mass m_i) whereas

according to the evaporation model the reemission peak describes an exponential law as a function of temperature (Eq. 4 FIG.10)

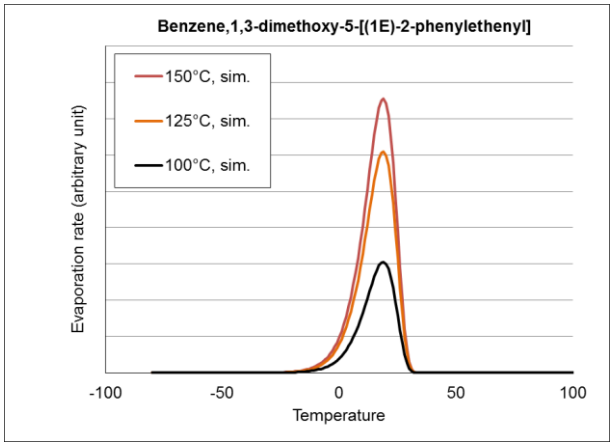

Fig. 9. Simulation - Desorption model - Reemission of benzene - Contaminant EC2216 – TGA performed after each outgassing steps (100, 125 and 150°C)

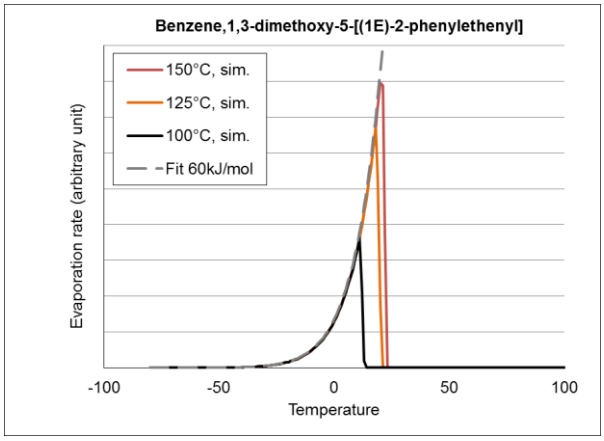

Fig. 10. Simulation - Evaporation model- Reemission of benzene - Contaminant EC2216 – TGA performed after each outgassing steps (100, 125 and 150°C)

The reemission peaks of 1,3-dimethoxy-5 - [(E) -2-phenylethenyl] benzene (deposits issued from the outgassing of contaminant EC2216 after outgassing steps at 100 ° C FIG. 13 and 16, 125 ° C FIG. 12 and 15. and 150 ° C FIG. 11 and 14.) were thus simulated using a desorption model (equations 6 and 7) and an evaporation model (equation 12). Experimental data are better fitted using an evaporation model. The same work was repeated for another species from outgassing of EC2216 (not yet identified by comparison with a mass spectrometry databank-work in progress- FIG 17 to 20). Again a shift of the reemission peak very consistent with the evaporation model is observed.

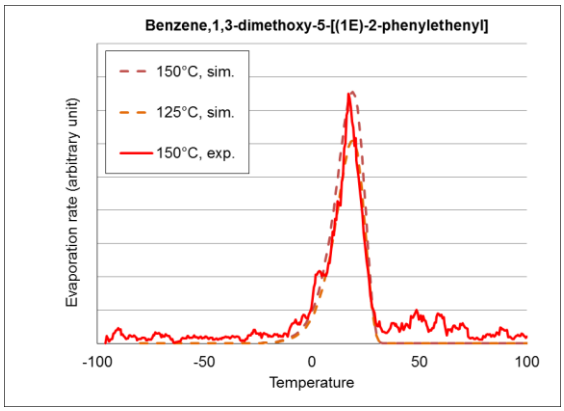

Fig. 11. Experimental data and simulation - Desorption model - Reemission of benzene (TGA performed after the outgassing step at 150°C - Contaminant EC2216)

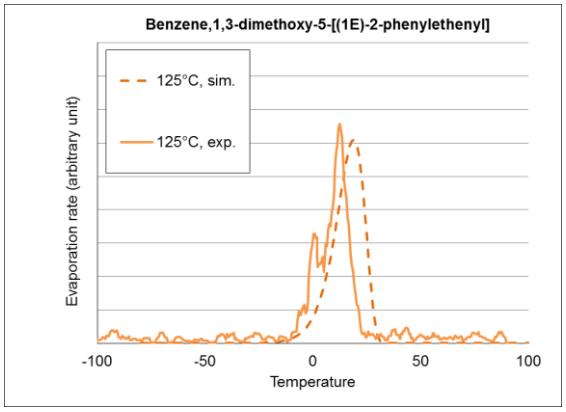

Fig. 12. Experimental data and simulation - Desorption model - Reemission of benzene (TGA performed after the outgassing step at 125°C - Contaminant EC2216)

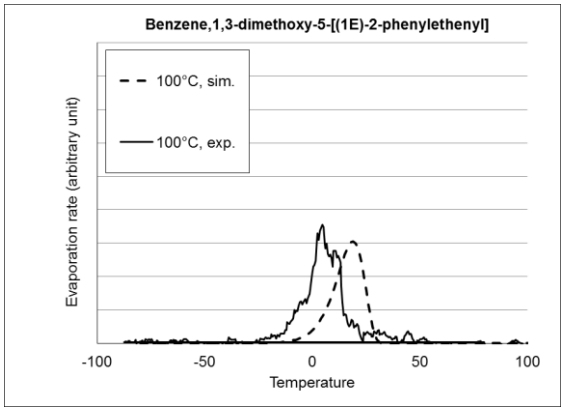

Fig. 13. Experimental data and simulation - Desorption model - Reemission of benzene (TGA performed after the outgassing step at 100°C - Contaminant EC2216)

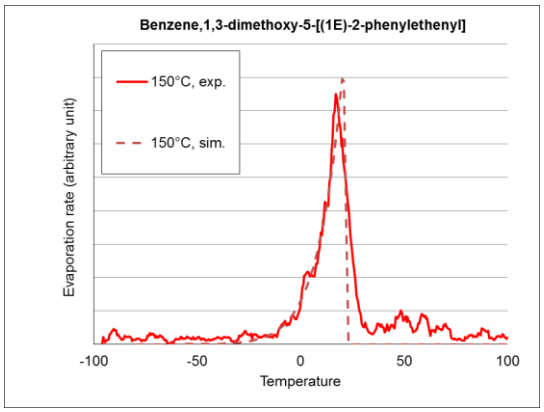

Fig. 14. Experimental data and simulation - Evaporation model - Reemission of benzene (TGA performed after the outgassing step at 150°C - Contaminant EC2216)

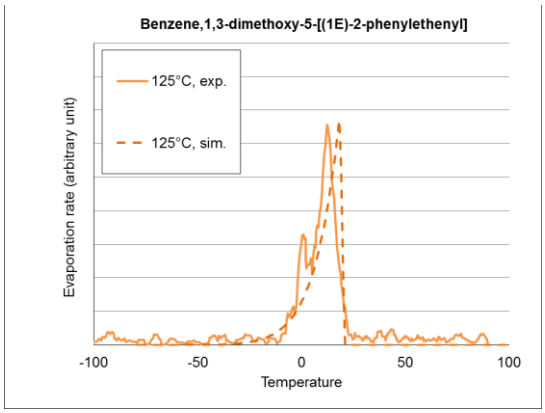

Fig. 15. Experimental data and simulation - Evaporation model - Reemission of benzene (TGA performed after the outgassing step at 125°C - Contaminant EC2216)

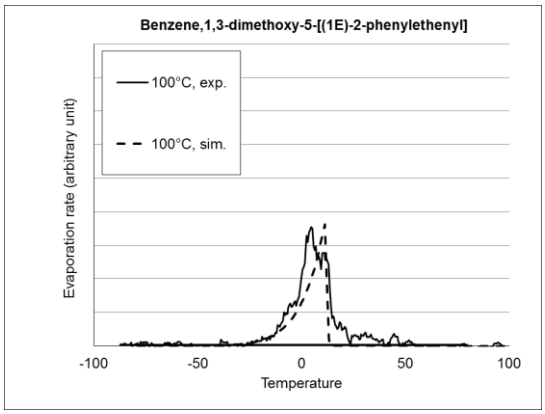

Fig. 16. Experimental data and simulation - Evaporation model - Reemission of benzene (TGA performed after the outgassing step at 100°C - Contaminant EC2216)

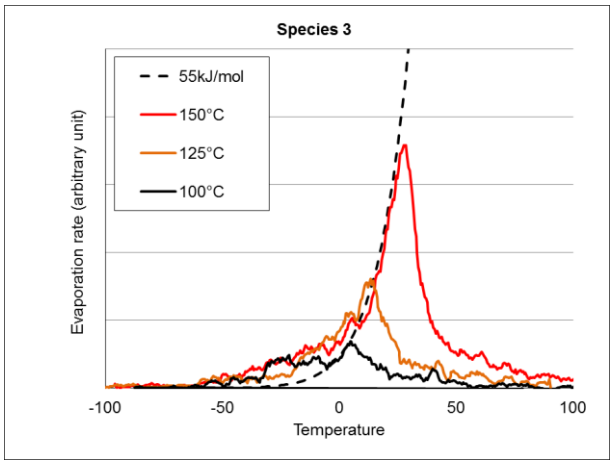

Fig. 17. Experimental data and simulation - Evaporation model - Reemission of species 3, m/z = 128 (TGA performed after the outgassing steps at 100, 125 and 150°C - Contaminant EC2216)

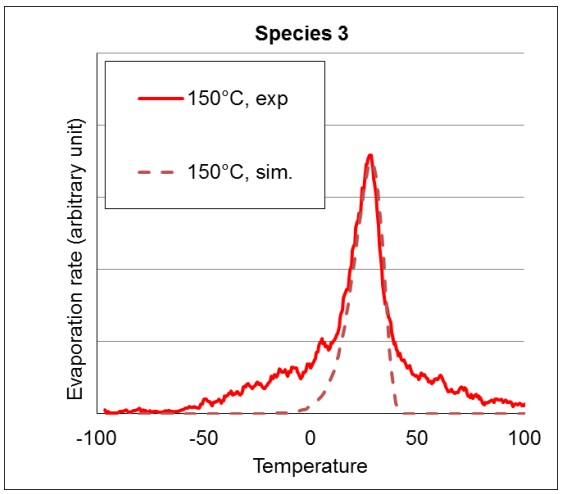

Fig. 18. Experimental data and simulation - Desorption model - Reemission of species 3, m/z = 128 (TGA performed after the outgassing step at 150°C - Contaminant EC2216)

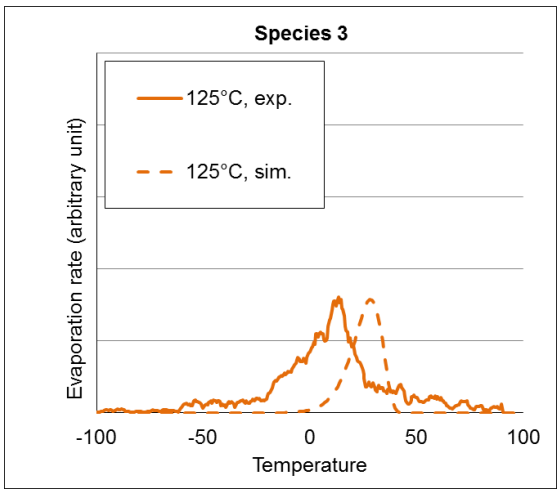

Fig. 19. Experimental data and simulation - Desorption

model - Reemission of species 3, m/z = 128 (TGA performed after the outgassing step at 125°C - Contaminant EC2216)

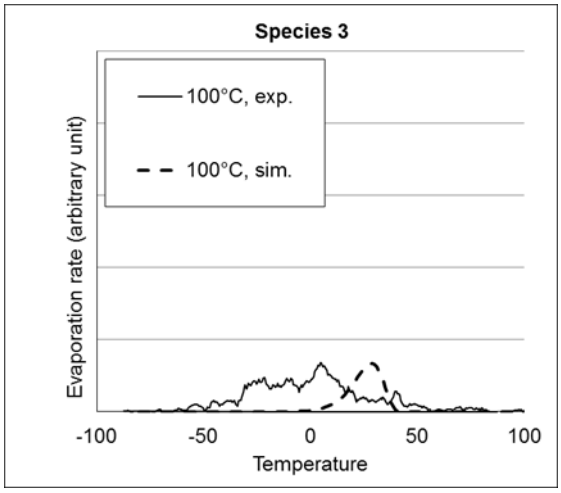

Fig. 20. Experimental data and simulation - Desorption model - Reemission of species 3, m/z = 128 (TGA performed after the outgassing step at 100°C - Contaminant EC2216)

1.7. Impact on predictions

In the desorption model, the reemission rate is proportional to the mass of contaminant remaining in the deposit, whereas in the evaporation model this rate does not depend on this mass. Therefore, if a desorption model is used instead of an evaporation model to predict the in-flight reemission of a thinner deposit, the latter will be underestimated by a factor : mass of the species in the ground test deposit/ mass of the species in the in-flight deposit.
It is very difficult to extract the reemission parameters from a TGA experiment due to peak overlaps [3,4]. Even assuming that this extraction was possible, it would in any case not be possible to link without the help of a species separation method the outgassing and reemission properties of the same chemical species (and of course even less to identify it), which has a very strong impact on flight predictions. It is therefore strongly recommended to use a species separation technique to characterize outgassing and reemission.

1.8. Simplified model

Equations 4 and 5 can be simplified as follows:

$$\frac{\partial m_i}{\partial t} = -\frac{\frac{m_i}{m_{i\,mono}}}{\frac{m_i}{m_{i\,mono}} + 1} A e^{-\frac{E_a}{RT}}$$

Eq.11

And even :

$$\frac{\partial m_i}{\partial t} = A e^{-\frac{E_a}{RT}}$$

Eq.12

When mi >> $m_{i\,monolayer}$(for example in the case of a TGA). All data presented here have been processed using this last equation because of very strong time constraints. Nevertheless for the extraction of the parameters, it is recommended to preferably use the equations 4 and 5.

CONCLUSION

TGA/MS data was used to evaluate outgassing and reemission models and protocols. So far, outgassing seems to be governed by diffusion while reemission seems to be better described by evaporation. However, this work is still ongoing. The models but also the methods used to extract the parameters of these models have a very large impact on the flight simulations (several orders of magnitude). Species separation is therefore strongly recommended to assess the contamination kinetics

REFERENCES

1. Roussel J.-F., Tondu T., Paulmier T. Faye D., van Eesbeek M. and Rampini R., "Progress on the Physical Approach to Molecular Contamination Modeling", *Journal of Spacecraft and Rockets*, 48 (2), pp. 246–255 2011.

2. J.F. Roussel, E. Vanhove, E. Grosjean, D. Faye, G. Rioland, R. Rampini., O. Ergincan "Progress in a physical approach to contamination in Europe" *SPIE*, San Diego 2018

3. E. Vanhove, T. Tondu, J.F. Roussel, D. Faye, P. Guigue, "In Situ Real-Time Quantitative and Qualitative Monitoring of Molecular Contamination", *Journal of Spacecraft and Rockets*, Vol. 53, No. 6, November-December 2016.

4. E. Grosjean, E. Vanhove, J.F. Roussel, G. Rioland, D. Faye, "Molecular Contamination from Space Materials: Species Characterization by TGA / MS" *ISMSE 2018*, Biarritz

5. Liu C. K. and Gassford A. P. M., "Kinetics data for diffusion of outgassing species from RTV 560 silicone rubber", *J. Vac. Sci. Technol*., 15(5), pp 1761-1768 (1987).

6. J. F. O'Hlanlon "A User's Guide to Vaccuum Technology", Chapter 4, 3rd edition, 2003 John Wiley and Sons Inc.

7. R. Rampini, E. Ftaka, M. Van Eesbeek, "Dynamic Outgassing Testing: A Revisited Mathematical Approach" in 11th ISMSE, France, 2009

8. Tondu T., Vanhove E., Roussel J.-F. and Delphine Faye, "Mixture Effects in Contaminant Reemission", Journal of Spacecraft and Rockets, Vol. 53, No. 6, pp. 1172-1177 (2016) https://doi.org/10.2514/1.A33507