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Improvement of Bake-Out Prediction thanks to Realistic Species Separation

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Abstract. A new approach to material outgassing modelling based on chemical species separation was applied to Bake-Out modelling. The outgassing of the Scotchweld EC-9323-2 epoxy glue was first characterized experimentally, both before and after Bake-Out. Based on the former, the latter was modelled, following the classical approach on the one hand and the new approach on the other hand. The MS-based species separation of this new approach allowed measuring the emitted flux of each species individually, even during the outgassing phase. The evolution of these fluxes all along the outgassing tests, during the five classical 24 h plateaus was successfully modelled by diffusion-limited outgassing laws, while it proved inconsistent with a desorption-limited outgassing. Their modelling by diffusion laws allowed a very consistent modelling of the total mass measurements in TML and CVCMS, with a small number of chemical species of different volatilities. The effect of a preliminary Bake-Out on this outgassing was finally modelled and compared to the experimental characterization of the baked material. The modelling accuracy still remains comparable to that of the traditional modelling based on mathematical species. Yet, the realistic species separation of the new approach allows simpler assumptions on water regain (its first species) than the traditional one, which needs to assess the amount of water contained in each mathematical species. Progress in the new method should come from an improved species separation and a direct characterisation of the water flux.

1. Introduction

Baking-out materials before integrating them on spacecraft is a widespread technique to reduce their condensable contaminant content. Predicting this contaminant reduction before actually performing the Bake-Out (BO), in order to specify its duration and temperature to fulfil contamination requirements, is another interesting and common practice. In Europe, this assessment is usually done following the residence time approach defined in the 1980s [1], including thermal activation of species desorption. However, this approach is now thought to be closer to a mathematical fit by “mathematical pseudo-species” than an actual separation of different chemical species. This may reduce the accuracy of the model predictions, and make the assessment of water regain after BO a bit more complex to model.

This is one of the reasons why a new approach to contamination assessment, aiming at a realistic species separation, was started in the late 2000s years by ONERA and other teams [2][3]. The principle consists in performing Thermogravimetric Analyses (TGA) by ramping up deposits temperatures to (partially) separate condensed contaminant species, and identify them by mass spectrometry (MS). This coupled



TGA-MS method, somewhat similar to a gas chromatography-mass spectrometry (GC-MS) that would be performed in situ (with poorer separating power yet), was already presented with increasingly accurate results (see e.g. [4], [5] or [6]). Once chemical species and their mass spectra are identified this way, MS data acquired during the initial outgassing phase can be processed to also track their outgassed flux. The simplest way is through mass fragments than only show in the spectrum of one single species, usually heavy ones (with mass-to-charge ratio m/z close to, or larger than 100 unified atomic mass unit (a.m.u.)). Otherwise, combinations of species spectra during outgassing must be pursued, which may induce more uncertainties, depending also on data accuracy.

This experimental and theoretical protocol were implemented on several space-used materials. In another communication made during this 15th ISMSE [5] by some of these authors (from ONERA and CNES, in collaboration with other ESA authors), species separation achievements were reviewed, with a special focus on recent results on the epoxy glue EC9323-2, presented quite in details.

TGA/MS-based species separation was then applied to the analysis of other physical processes, such as outgassing. The principle simply consists in tracking m/z fragments specific of a species during outgassing, to determine its outgassing law. This was also performed on a few other materials, and reviewed in [7].

In this communication, we go one step further. On the basis of mass spectrometry measurements acquired at ONERA during the outgassing, we first analyse and model the outgassing of the seven species that were separated and identified in reference [5]. Next, based on this physical modelling, we add a Bake-Out step to the outgassing history, to see how the forthcoming outgassing was reduced by BO. This is reported in section 3.

Before that, in section 2, the classical approach to BO modelling, as performed by industry and CNES, is reported as a basis for comparison. All of these modelling results are compared to experimental outgassing data obtained at CNES on baked materials.

2. State of the art approach

2.1. Introduction

In order to model the material outgassing and predict the induced molecular contamination on a spacecraft, dynamic outgassing test has been performed. This test consists in applying temperature steps on the tested material, usually four from 25°C to 125°C, and to measure the outgassing from the deposited mass on at least one cold Quartz Crystal Microbalance (QCM), typically -170°C. For desorption modelling, fitting of deposited mass is performed using several mathematical species coupled to Arrhenius law, linearized or not. Finally, each mathematical species is characterized by the mass that can emit, also called emittable mass, an emission time constant and a reemission time constant.

Up to now, simulated bake-out is obtained by recalculating the emittable mass of each species from the mass emitted during bake-out. To take reabsorption of water vapour into account after the bake-out, the emittable mass of the first species is reintroduced i.e. the emittable mass before and after bake-out is considered equal.

2.2. Reintroduction of the first species

As explained previously, the current method consists of recalculating the emittable mass of each species, commonly known as W_0 , from the emitted mass during the bake-out except for the first specie:

$$W'_0 = W_0 \exp[-t_{BO}/\tau_e(T_{BO})] \quad (1)$$

$$\tau_e(T) = A_d \exp[-E_d/RT] \quad (2)$$

$$\tau_e(T) = \tau_{e0}(T_0) \exp[k_e(T - T_0)] \quad (3)$$

where W'_0 is the emittable mass after bake-out in %, W_0 is the emittable mass before bake-out in %, t_{BO} is the bake-out duration in h, τ_e is the emission time constant at a temperature T in h, T_{BO} is the bake-out temperature in K, A_d is the Arrhenius pre-exponential factor in h, E_d is the desorption activation energy in J.mol⁻¹, R is the gas constant in J.K⁻¹.mol⁻¹, T is the temperature in K, τ_{e0} is the emission time

constant at reference temperature T_0 in hours, k_e is the residence time-temperature dependency coefficient in K^{-1} and T_0 is the reference temperature of the material in K.

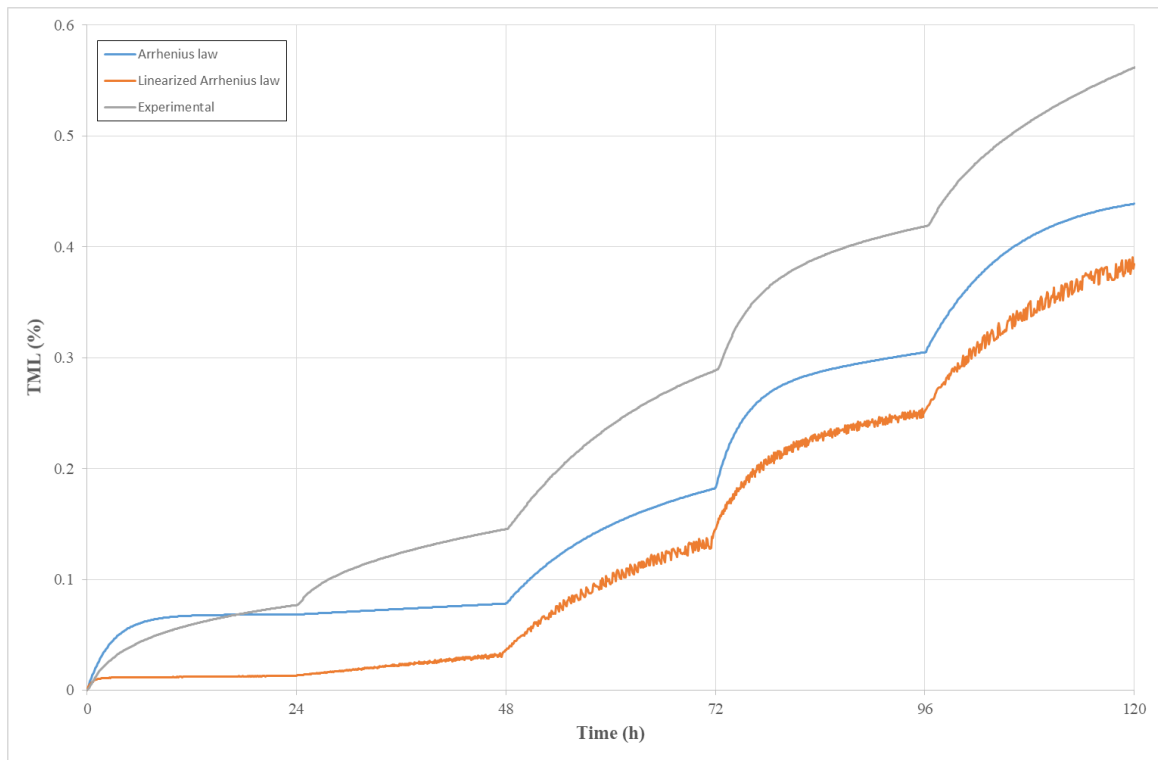


Figure 1. Comparison between simulated and experimental TML by reintroducing the first species

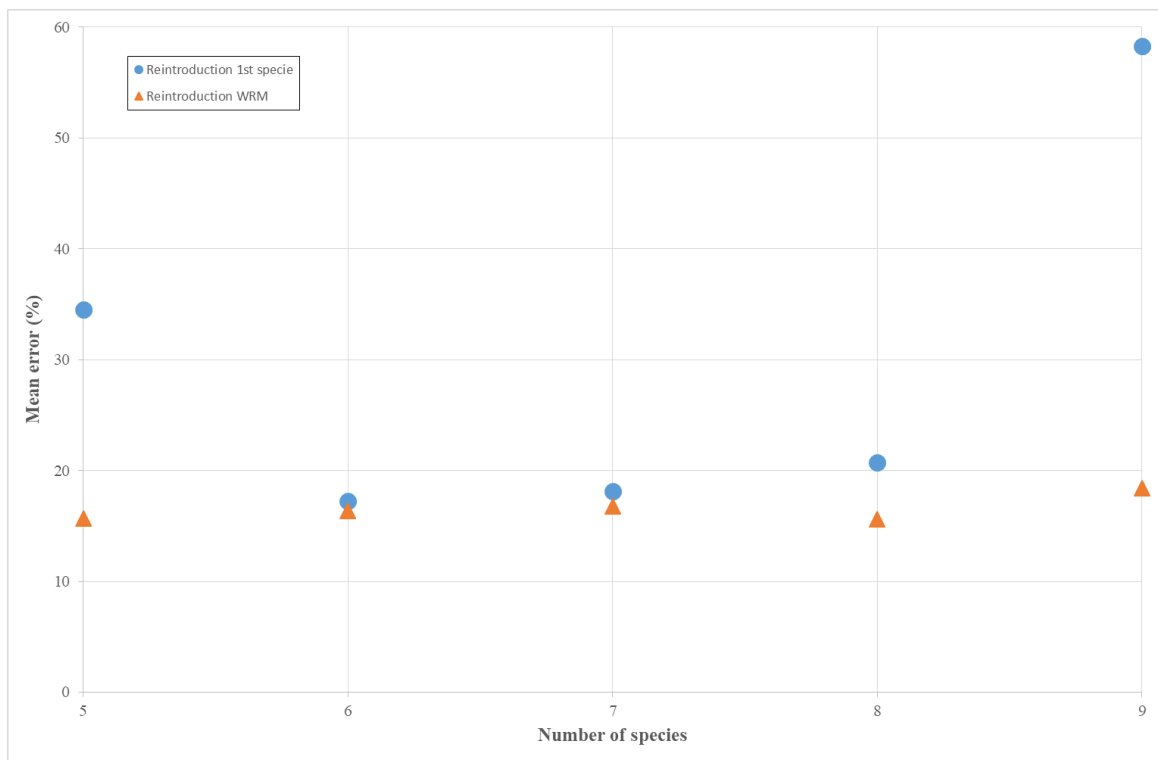


Figure 2. Evolutions of the error between simulated and experimental bake-out by reintroducing the first specie or by gradual reintroduction of WRM

Figure 1 shows a comparison between simulated and experimental deposited masses (TML) on the QCM at -165°C for EC9323-2 material by using this method. Both Arrhenius and linearized Arrhenius laws have been employed. Five and nine mathematical species have been used for Arrhenius and linearized Arrhenius, respectively. The experimental deposits tends to be larger than the simulated ones so the bake-out impact is overestimated. The overestimation is not systematic and depends on the number of mathematical species to perform the fitting before bake-out. Indeed, the number of mathematical species has a strong impact on the simulated bake-out and the induced error (see Figure 2) which is another drawback of this method.

It is interesting to note that the shape of the curves is similar between 48 and 120 hours. This observation leads to think that more than the first species, usually defined as water, must be reintroduced and therefore that the water is contained in more than the first mathematical species. This explanation is corroborated by the physical species separation presented hereinafter (see §3): water, present in near surface as well as in bulk of the material, diffuses toward the material surface before its desorption. In order to fill the gap of the desorption approach, reintroduction according to Water Recovery Mass (WRM) has been studied.

2.3. Reintroduction according to WRM

The basic principle remains the same than those presented before i.e. recalculate the W_0 of each species according to the equation (1). However, instead of reintroducing only the first mathematical species, the reintroduction is based on the WRM. In this study, two different methods have been applied: a reintroduction from the fastest to the slowest species until the sum of reintroduced W_0 becomes equal to the WRM or the reintroduction of the first species and then distribute the remainder of WRM on all the other species.

Figure 3 shows a comparison between simulated and experimental TML for EC9323-2 material by using these two methods named gradual reintroduction and distributed reintroduction, respectively. Linearized Arrhenius law has been employed with nine mathematical species like the previous example (see Figure 1). More accurate predictions are obtained by using WRM instead of reintroducing only the first species. Also, less dependence on the number of species can be underlined as shown by Figure 2.

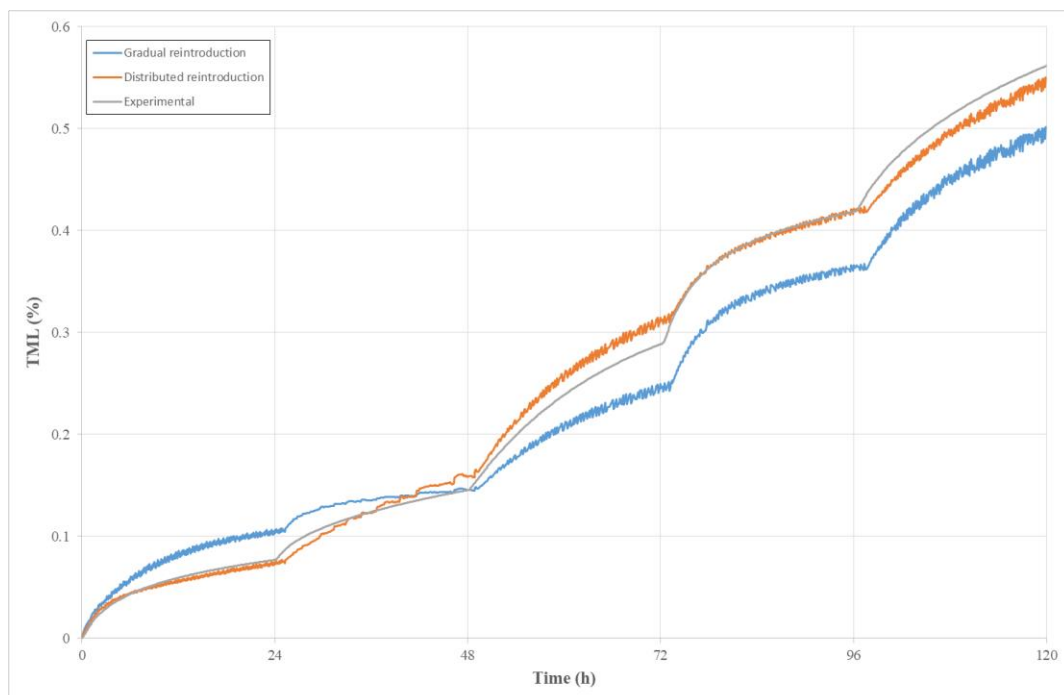


Figure 3. Comparison between simulated and experimental TML by reintroducing according to WRM

3. New approach through physical species separation

This new approach aims at characterizing outgassing at chemical species level to determine more physical and more reliable outgassing laws, and apply them to Bake-Out prediction. This goes in two steps. In a first step, the separation and often the identification of the outgassed chemical species was done through TGA/MS coupling technique as reported in the parallel communication [5], whose results are summarised next (section 3.1). In this communication, we focus on the second step, which is the analysis of the outgassing, equally at chemical species level, by following the m/z fragments specific of each outgassed species during the outgassing phase. This is reported in section 3.2. This allowed us determining the outgassing parameter of these species, namely their diffusion coefficients and activation energies, since their physics was found to obey Fick's law. They were next used to model the quantitative measurements made on QCMs (TML and CVCMM), as reported in section 3.3, and finally how this outgassing is modified by a preliminary Bake-Out (section 3.4).

3.1. Species separation through TGA/MS method

In the parallel communication [5], the study of EC9323-2 material contaminant emission was performed by TGA/MS coupling method at ONERA. It allowed determining m/z fragments, as measured by mass spectrometry, that seem specific to each of the seven identified species. Indeed only six of the seven separated species were found in the set of mass spectra seen in EC9323 material GC-MS at CNES. Here we simply list these seven species and specific fragments in the Table 1 below. They will be tracked during the outgassing pass as reported in the next subsection.

Table 1. m/z values specific of each of the seven separated species (from [5])

Species (TGA peaks):	Single peaks m/z
• Methyl-ethyl-phenyl-ethanone (MEPE) or Methyl-ethyl-benzene (MEB)	147, 162
• Octamethyl-cyclotetrasiloxane (D4)	281, 267
• Butylated Hydroxytoluene	205, 220, 145, 163, 206, 161, 177, 189, 195
• Menthol (indeed 1'-(butyn-3-one-1-yl)-menthol)	165, 180, 193
• Dodecanol	140, 168, 98, 111, 112
• Cyclohexane-dimethanol	95, 93, 202, 264, 108, 67
• Unidentified molecule M (reemitted at 32C in 1 st exper.)	58, 88

3.2. Species outgassing modelling

An important finding of [5] was that among the rich mass spectrum of these species, some fragments seemed to be specific to that species, i.e. only present in the spectrum of that species of EC9323-2 material, and not a (significant) part of the mass spectrum of any other species found in that experiment (i.e. also outgassed by EC9323-2 material or part of the chamber background). While [5] was focussed on the TGA/MS data for species separation, here we focussed on the MS data collected during the outgassing phases of these experiments.

For each chemical species, we studied the MS signal of the best of these m/z fragments, i.e. with the best signal level and specificity. The best two fragments were selected for the plots below. The first objective was to determine the physics ruling this outgassing. We shall see that Fick's diffusion law was always found to match MS data very convincingly. The second objective was then to determine the Fick's law parameter of each species. They are gathered in the Table 2 at the end of this section.

Figure 4 represents the MS signal of the two best specific fragments of menthol, one of the seven species found to be outgassed by EC9323-2, and their fit by the same Fick's law (with a different global factor for each fragment, accounting for their importance in menthol spectrum). The data are quite good: masses 165 and 180 a.m.u. are proportional and significantly above the noise level (around 10^{-14}). Their fit by a solution of Fick's law is also quite good.

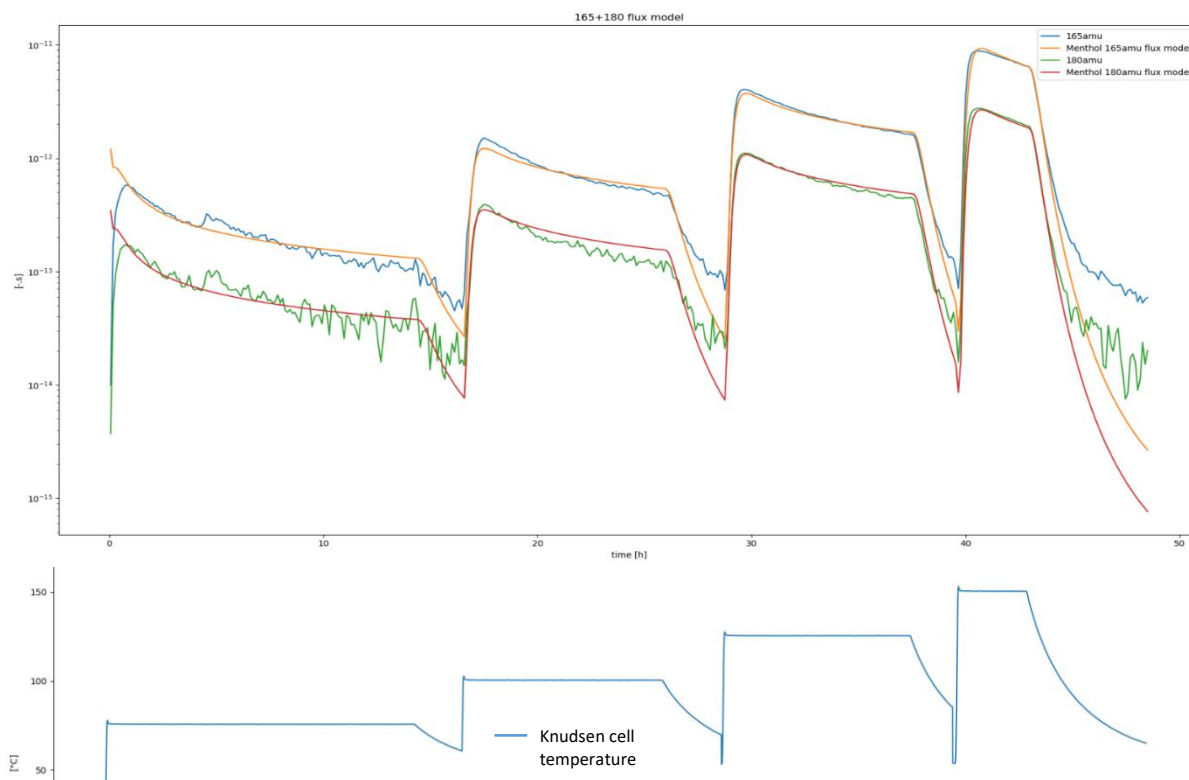


Figure 4. Two fragments representative of menthol (165 and 180 a.m.u.), compared to the same Fick's law (upper panel). The 4 clearly visible steps correspond to 4 outgassing steps at temperatures 75, 100, 125 and 150°C visible on the lower panel (each followed by a passive cooling of the Knudsen cell to stop outgassing and perform TGAs while monitoring them by mass spectrometry). Units of MS data are arbitrary.

Next figure represents the two best fragments specific of Butylated Hydroxytoluene. This time both the flux (direct MS measurement) and its fluence (partial time-integral of the MS signal) are represented. Both are quite well fitted by another solution of Fick's law again. The fit is least convincing when the signal is the smallest, closest to the noise level of the mass spec (around 10^{-14}), which probably artificially increased the measured values.

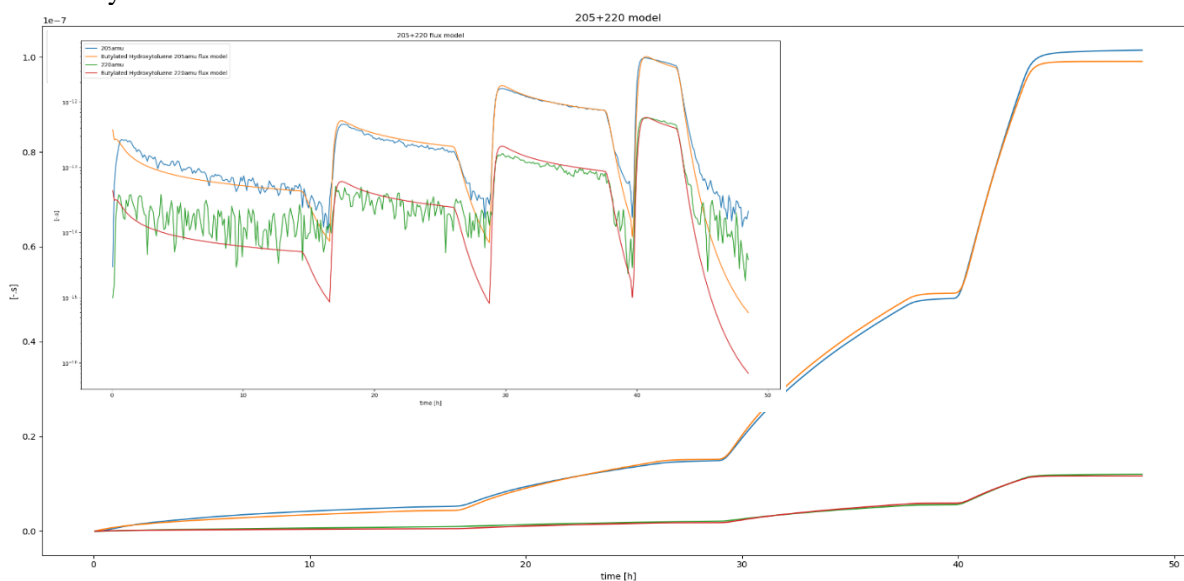


Figure 5. Two fragments representative of butylated hydroxytoluene (205 and 220 a.m.u.), compared to the same Fick's law – flux (upper left) and fluence (lower right)

Similar measurements and fits are given below for the identified molecules that could be either methyl-ethyl-phenyl-ethanone or 1,3-bis(1-methyl-ethyl)-benzene (quite similar molecules, differing only by one functional group). The fit is again quite convincing. The weakest part of the modeling is probably the start of the time interval, where experimental data do not exhibit as sharp a jump as in the model, probably because of the outgassing they experienced before actually heating the Knudsen cell at time = 0 here (kind of pre-outgassing as soon as the sample is put under vacuum).

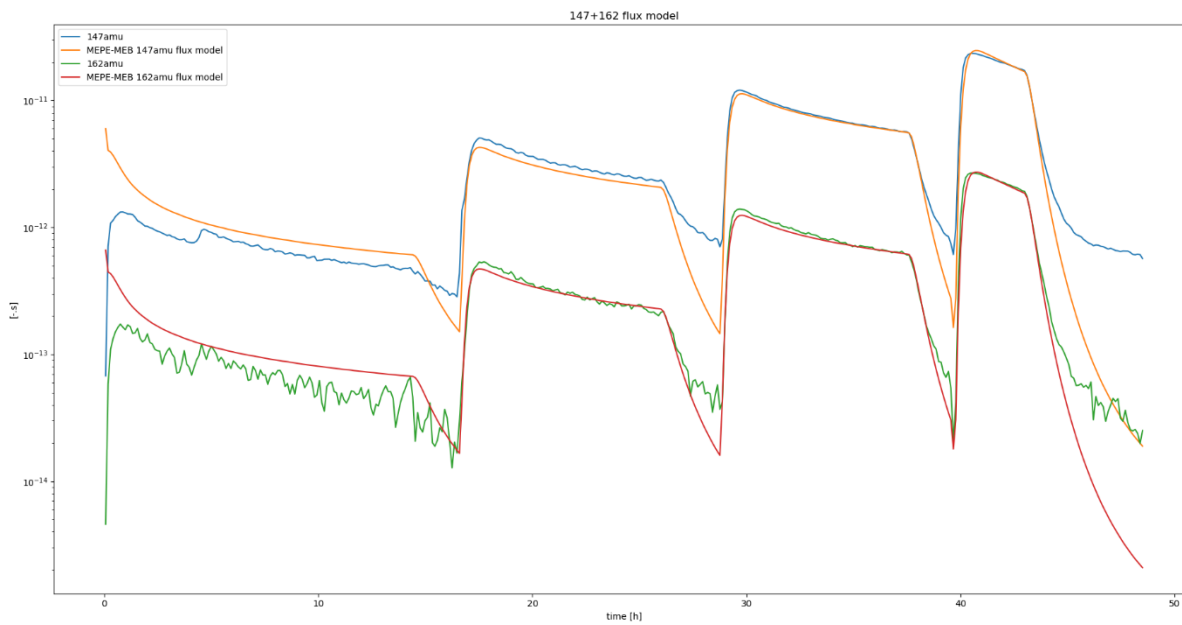


Figure 6. Two fragments representative of methyl-ethyl-phenyl-ethanone (MEPE) or methyl-ethyl-benzene (MEB), very similar molecules (147 and 162 a.m.u.), compared to the same Fick's law

Similar data for dodecanol exhibit a slightly less accurate fit by Fick's law, but still reasonable.

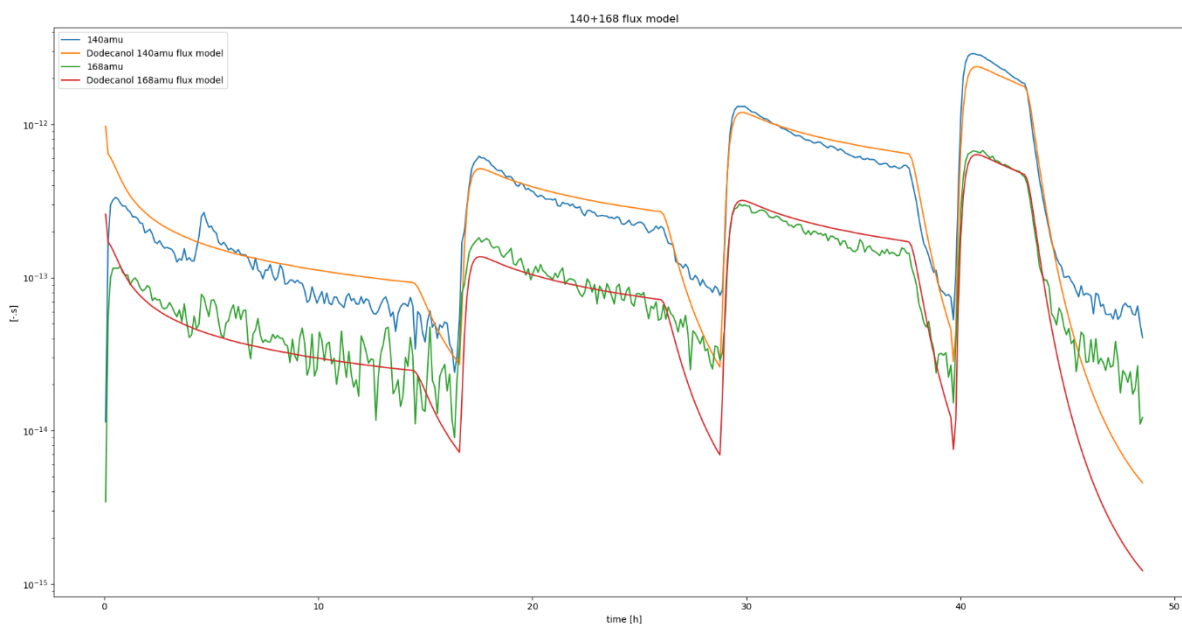


Figure 7. Two fragments representative of dodecanol (140 and 168 a.m.u.), compared to the same Fick's law

Next figure deals with the seventh separated molecule in [5]. We did not manage to make a link with one of the mass spectra of the species identified by GC/MS of the EC9323-2 before these experiments, so, for now we keep naming it as “the molecule whose reemission peaked at 32°C in June 2021 / 125°C experiment”. Fits are still quite satisfactory. The artefact at time = 4 hours, which was already visible in some of the previous graphs, is more obvious here. It is probably due to a small uncontrolled heating of some distant part of the hot shroud or sample holder, leading to the reemission of condensed molecules. It does not seem to have large consequences.

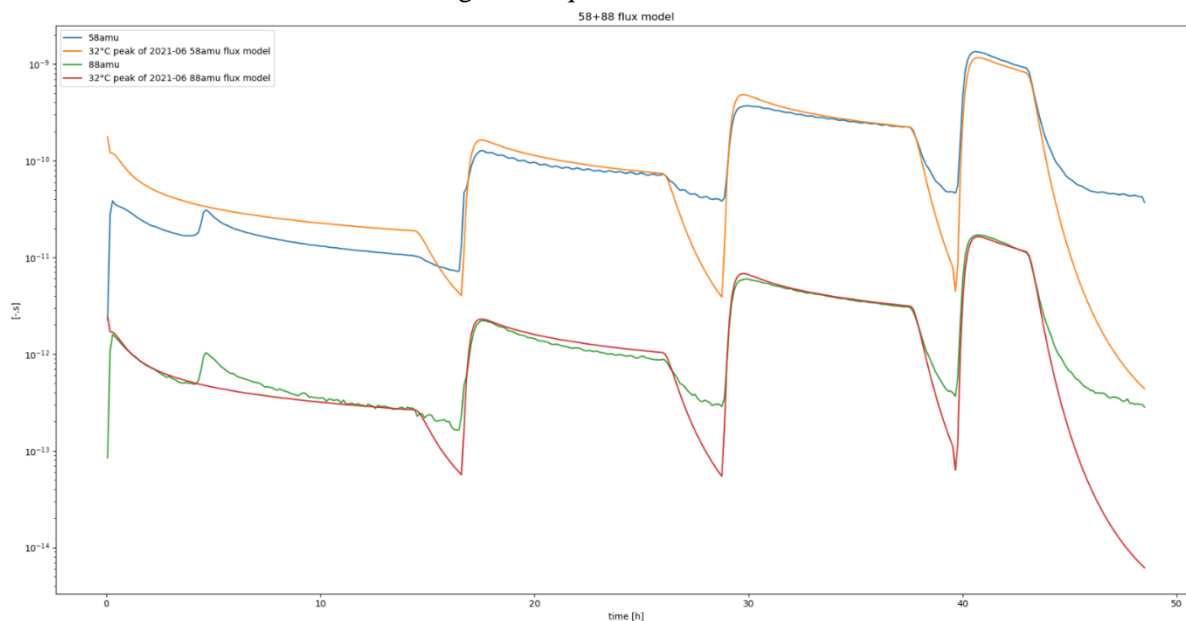


Figure 8. Two fragments representative of an unidentified molecule, the one reemitted at 32°C at 2021/06 TGA (58 and 88 a.m.u.), compared to the same Fick's law

The next graph gives similar data and model for cyclohexanedimethanol. The fit is less convincing than those of the previous separated species. The 95 and 93 a.m.u. fragments, do not have a very high atomic mass, and might be the least specific of studied fragments. It means that they might also be significantly present in the spectra of other outgassed species, contributing to these measurements by a few tens of percents. The artefact at $t = 4$ hours is also significantly present in these data.

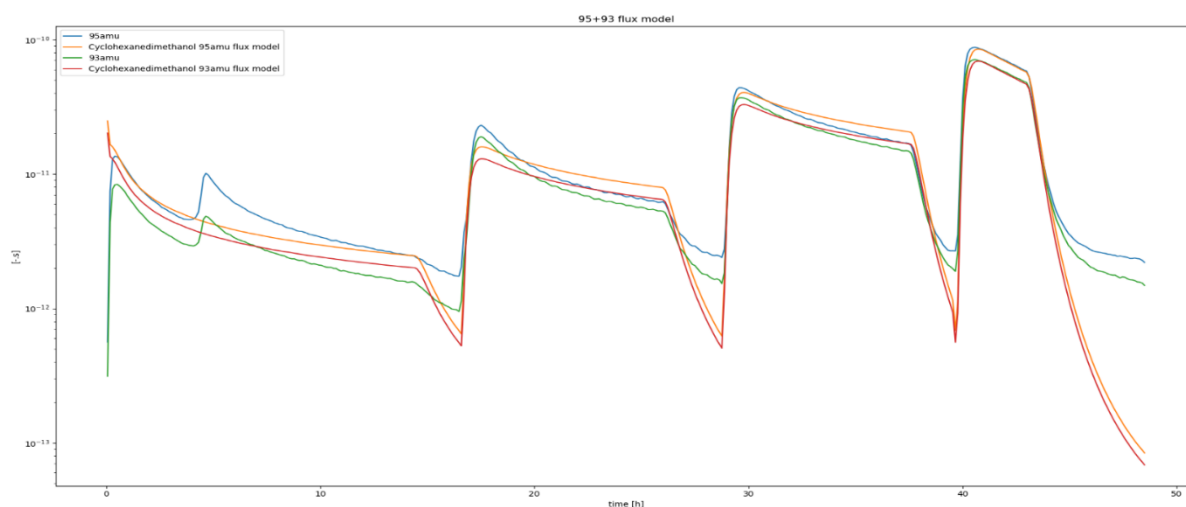


Figure 9. Two fragments representative of cyclohexanedimethanol (95 and 93 a.m.u.), compared to the same Fick's law

Finally, the seventh and last species represented below is octamethyl-cyclotetrasiloxane, or D4. The modeling of lower quality here again, might rather be due to the low signal of these high mass fragments (281 and 267 a.m.u.). Part of the time it is close to the MS baseline, around 10^{-14} (noise level).

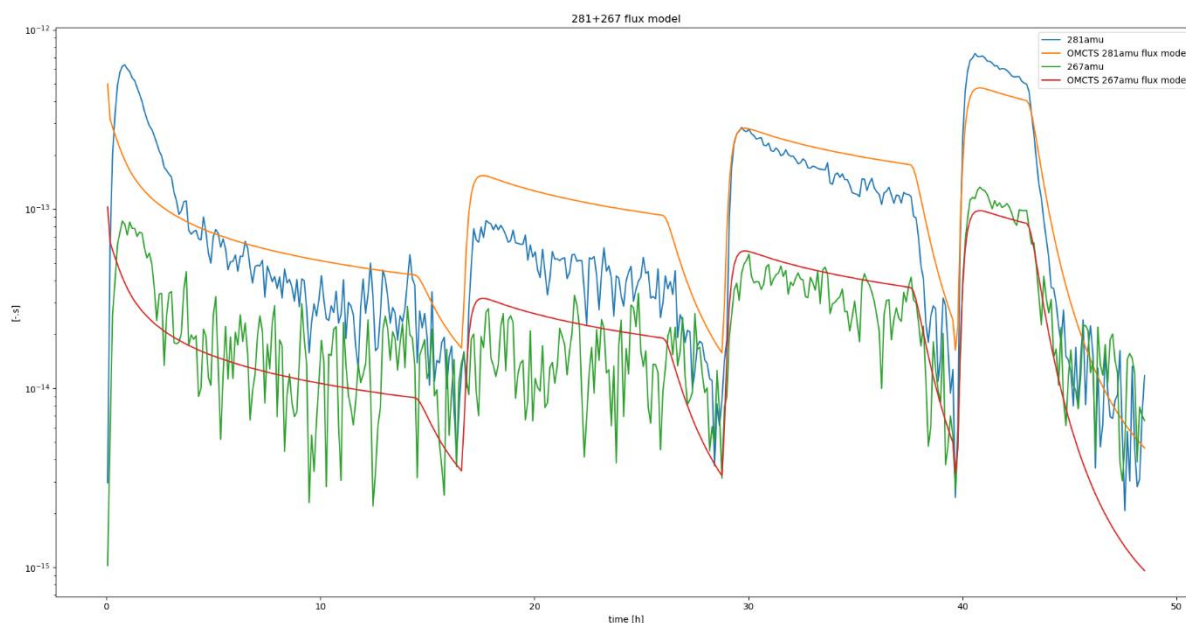


Figure 10. Two fragments representative of D4, octamethyl-cyclotetrasiloxane (281 and 267 a.m.u.), compared to the same Fick's law

The Table 2 below gives the diffusion parameters used in the modeling of the seven species displayed on the seven figures above. It was assumed to follow Fick's law

$$\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2}, \quad (4)$$

which describes the evolution of each contaminant species concentration $c(x,t)$ within a material depth (space coordinate x) over time (t). The diffusion coefficient is thermally activated and should follow an Arrhenius law:

$$D = D_0 e^{-E_a/kT}, \quad (5)$$

whose coefficients D_0 and E_a are compiled in the table. In practice, the model solutions displayed above were computed by using a series development of Fick's law solutions, given e.g. in ref. [7].

Table 2. Diffusion parameters for each of the seven separated species (from the fits above)

Species (TGA peaks):	Specific MS chanel m/z	E_a kJ/mol	D_0 m^2/s	D at 125°C m^2/s
• Methyl-ethyl-phenyl-ethanone (MEPE) or 1,3-bis(1-methylethyl)-benzene (MEB)	147, 162	95	13.5	4.6×10^{-12}
• Octamethyl-cyclotetrasiloxane (D4)	281, 267 205, 220, 145, 163, 206,	63	0.00010	6.2×10^{-13}
• Butylated Hydroxytoluene	161, 177, 189, 195	122	4055	4.1×10^{-13}
• Menthol (indeed 1'-(butyn-3-one-1-yl)-menthol)	165, 180, 193	109	679	3.1×10^{-12}
• Dodecanol	140, 168, 98, 111, 112	83	0.37	4.4×10^{-12}
• Cyclohexane-dimethanol	95, 93, 202, 264, 108, 67	91	4.6	5.3×10^{-12}
• Unidentified molecule M	58, 88	106	232	3.2×10^{-12}

3.3. TML and CVCM modelling

Once the outgassing laws of each of the chemical species were known individually, they were used to model the total quantities measured on the QCMs, i.e. the TML and CVCMs at -75 , -50 and -25°C measured at CNES (with classical outgassing steps at 25, 50, 75, 100 and 125°C). An important question was whether each of these species was condensed at each of these three QCM temperatures, in each of the three CVCMs. Since we did not do a TGA/MS analysis of the deposits obtained at all these temperatures, we simply made assumptions based on the reemission temperatures observed for the seven species during the TGAs experiments coupled to MS performed at ONERA.

We observed in [5] that the reemission temperature of each species could vary depending on the TGA, probably due to different compositions of the deposits. We considered that the main reason of these fluctuations was the trapping of this species in a mixture with heavier species, which could delay the reemission of this species (hence to a higher temperature). So, if something like an “intrinsic reemission temperature” exists for a given species, it must be close to (or somewhat smaller than) the smallest of the reemission temperatures observed in all TGAs. Moreover, these reemission peak temperatures correspond to a large reemission flux. For CVCM deposits cumulated over a few days, a reemission flux quite smaller than that is probably sufficient to evaporate that species (the “start of the peak” is enough for a full reemission over days, no need to go to the peak maximum as seen in TGA/MS).

If we process the reemission temperatures of all seven species during all eleven TGA/MS along this line, we get a kind of “sticking temperature” for each species. In Figure 11 the ranges of observed reemission peak temperatures is displayed on the right (organised as a function of the temperature of the outgassing that led to the reemitted deposit, to show the trend discussed above, where the presence of heavier molecules probably delays the reemission of a given molecule). For each molecule, the minimum of these temperatures, decreased of 15°C , is displayed at their left in the black rectangles. As explained above, they can be considered as approximations of the sticking temperatures of the seven species. On this basis, the presence of each of the seven species in each CVCM was assessed, and summarized in the table on the figure’s left hand side.

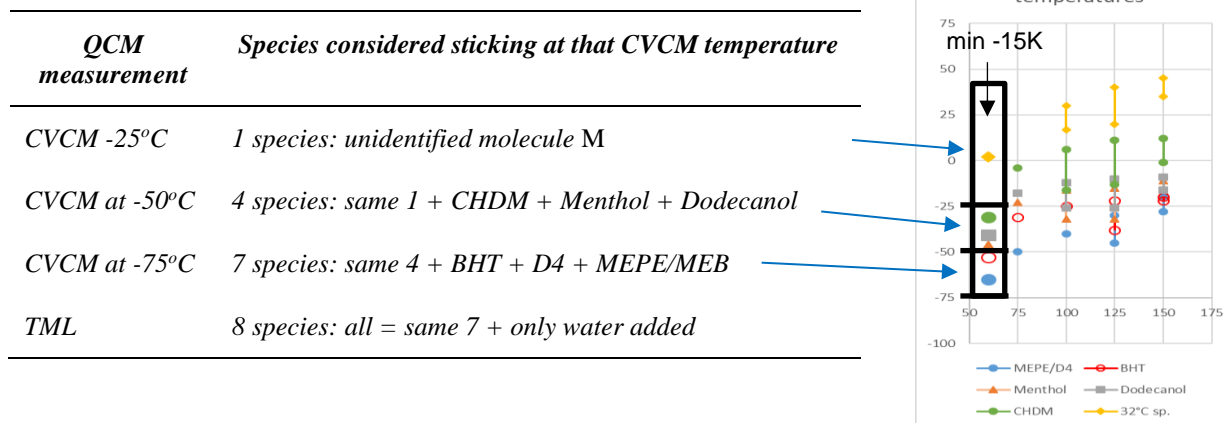


Figure 11. Ranges of observed reemission temperature for the 7 species during 10 TGA/MS from [5] organized in function of the outgassing temperatures (4 columns 75, 100, 125 and 150°C of the r.h.s graph), inferred sticking temperatures (minimum of the previous T° s decreased by 15K for each species, left column of the graph in the black bold rectangles), and assessed presence in each 3 CVCMs at -75 , -50 and -25°C (l.h.s. table)

Since the TGAs of [5] were performed from surfaces at -80°C , the most volatiles species could not be detected (those not condensable at -80°C). They necessarily include water, which was thus added as an eighth species contributing to the TML. There might be some other volatile species. Yet, in the absence of actual data, we did not add another species that would add extra arbitrary fitting parameters, which we wanted to avoid. Moreover, other very volatile species would not be expected to have as big a contribution as water.

We started this process with the CVCM at -25°C , which had the advantage of involving one species only in this analysis, hence leaving very few degrees of freedom. The fit of that CVCM by that species is displayed below. The diffusion parameters of that species were simply taken from MS data (lower

row of Table 1), and only the global quantity of this species was used as a fitting parameter (since MS data are not quantitative). If compared to what a desorption law would give, the fit can be considered as rather good. The model gives the right order of magnitude all over the experiment (whereas desorption exponentials give a quick exhaustion of the reemission, over a couple of temperature steps). Looking closer at the fit details, it is not so good, in particular concerning the change of deposition rate at temperature steps. The model usually underestimates the accretion rate changes at the steps. This is the sign that a species (or several) with an activation energy larger than in the model (106 kJ/mol) contributes to the CVCM (probably around 150 kJ/mol). This is not a real surprise since in the analysis of the TGA/MS data [5], when looking for specific fragments only, we were aware of probably missing a few species. For some of the observed reemission peaks, no m/z fragment exhibiting a “single peak” (dromedary-like peaks) was found. The reemission peaks showed in all fragments as “double-peaks” (camel-like peaks) or even multiple peaks.

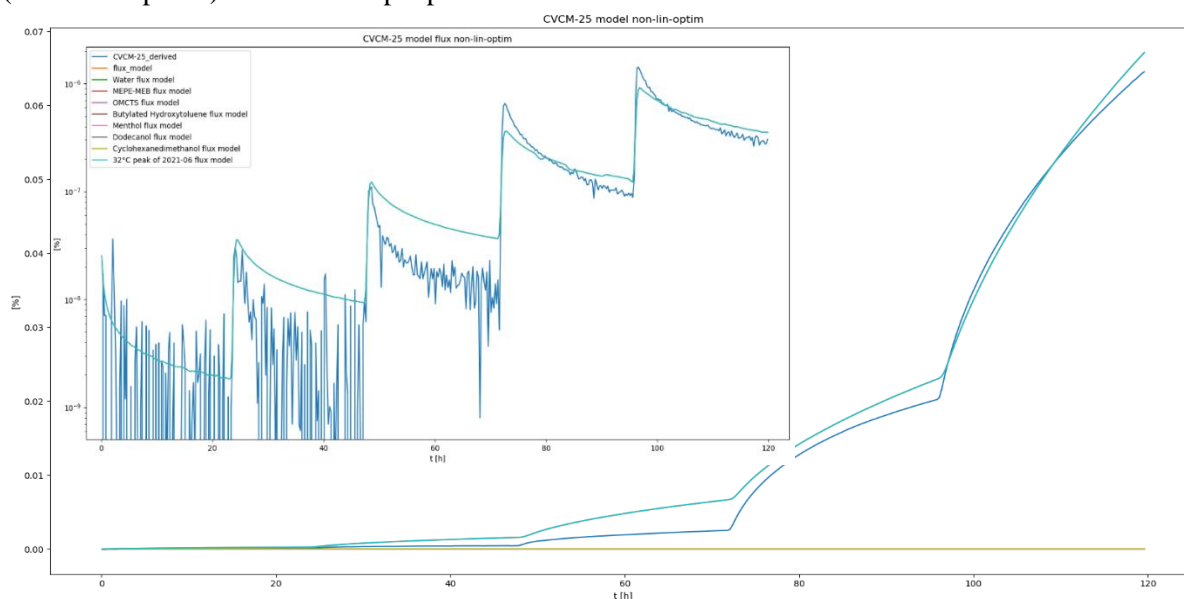


Figure 12. CVCM at -25°C : measurements and modeling (1 single species), deposit in the lower right and desposition rate in the upper left (its derivative)

The -50°C CVCM was next modeled with the four species listed in Figure 11. The fit is quite good again, with rate changes at steps that are not as accurate as one could expect yet.

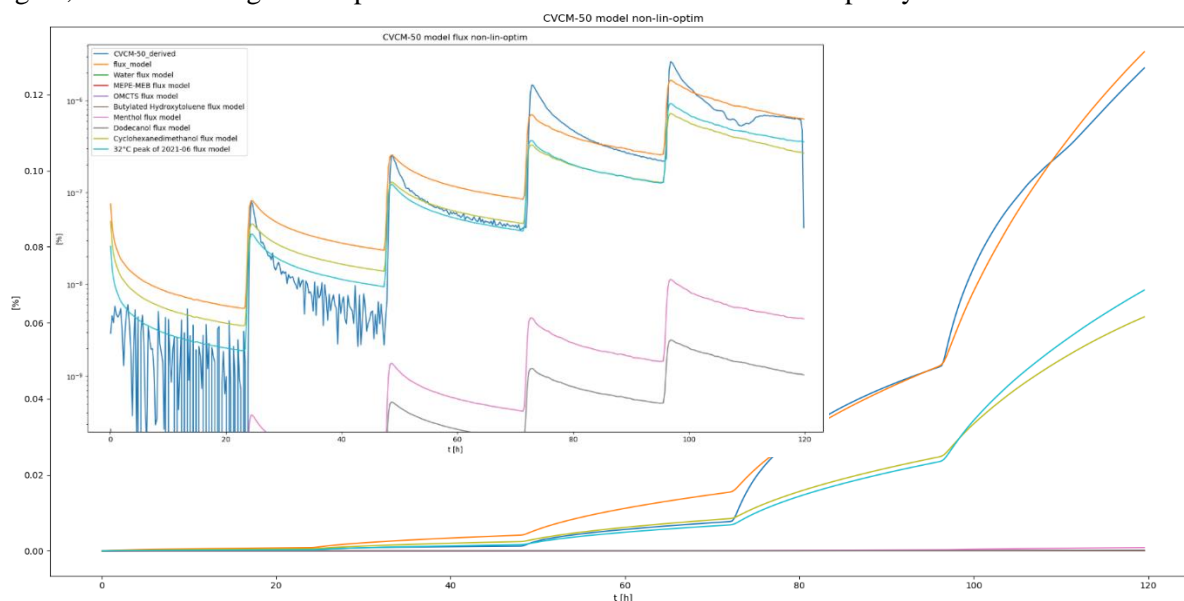


Figure 13. CVCM at -50°C : measurements and modeling (4 species), deposited mass and rate

It is good to see that adding extra species, which condensate on a colder QCM, accounts satisfactorily for the difference between a colder CVCM and a warmer QCM. This difference exists at most of the outgassing temperature steps, and is well described by a diffusion law for the outgassing of these extra species.

The same comments can be done about the -75°C CVCM displayed below.

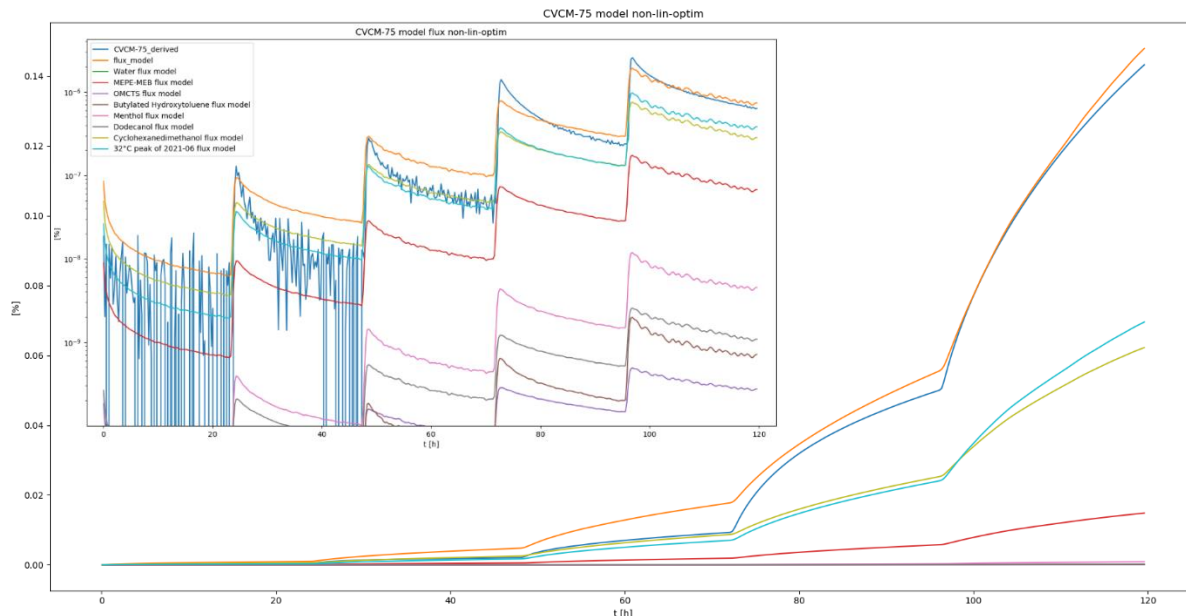


Figure 14. CVCM at -75°C: measurements and modeling (7 species), total deposited mass and rate

As explained above, we only added one extra species, water, to model the TML. So, the large difference between the TML and largest CVCM (-75°C), needed to be modeled as the contribution of one single species, water. And the figure below shows that the diffusion law used for water does a very decent job in modeling this difference, which extends over the first 4 temperatures steps and represents about 80% of the TML. Even though this was not confirmed by direct measurements of water, it is interesting to see how the model predicts the end of water outgassing before the last outgassing step (125°C). This is why the difference of deposit between the TML and the -75°C CVCM is small during that last step (almost no more water outgassed) and large difference during the first four steps (mostly due to water).

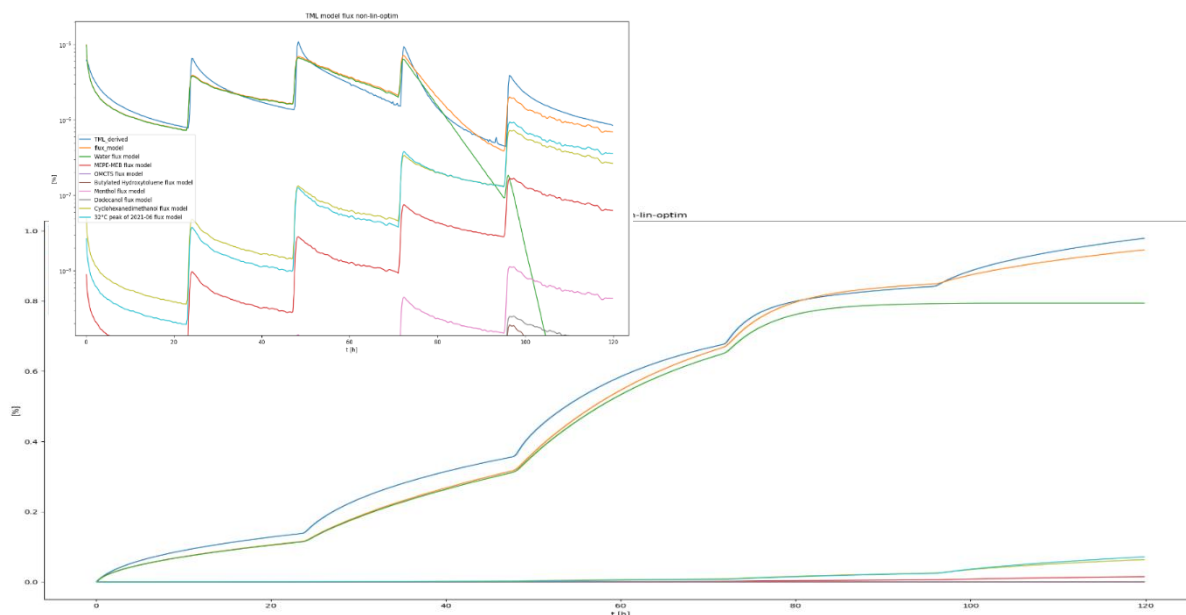


Figure 15. TML: measurements and modeling (4 species), total deposited mass and rate

3.4. Bake-Out modelling

With a physical model of outgassing that looks to capture its physics satisfactorily, modelling under-vacuum Bake-Out simply amounted to modelling the modified temperature history. The key points to obtain a predictive modelling of Bake-Out this way are having the right physics of outgassing, and a realistic species separation. The first point is of course needed for a good modelling with a modified temperature (+72h at 60°C before the start of the outgassing test) and the second point is needed to cope with the issue of water regain after the Bake-Out, as we shall see.

Next figure compares the post Bake-Out TML measurements with various modelling approaches. Graph (a) compares the experimental TML of a baked-out EC9323 sample to an unchanged model. Clearly, Bake-Out reduced the material TML, and the model needs to be modified to take BO into account. If the announced model change, consisting in simply modelling the BO as a pre-test temperature evolution ruled by the same Fick's law, is applied (b), the model now underestimated measurements. The cause of this discrepancy has been known for long. It is due to water regain, from the atmosphere, in the interval between the BO and the outgassing test. If we assume that water, which we now believe to be the first species, is fully regained during these few weeks (c), the model comes back to an overestimation of the measurements. It is not surprising since the Bake-Out's main effect was on water. It is also known that water regain in lab conditions in the short term is only partial. Assessing water regain is no easy. We wanted yet to keep to a simple and reasonable hypothesis, so we tried assuming that 50% of water was regained. This simple modelling approach yielded results reasonably close to data (d), within 10% of the maximum TML.

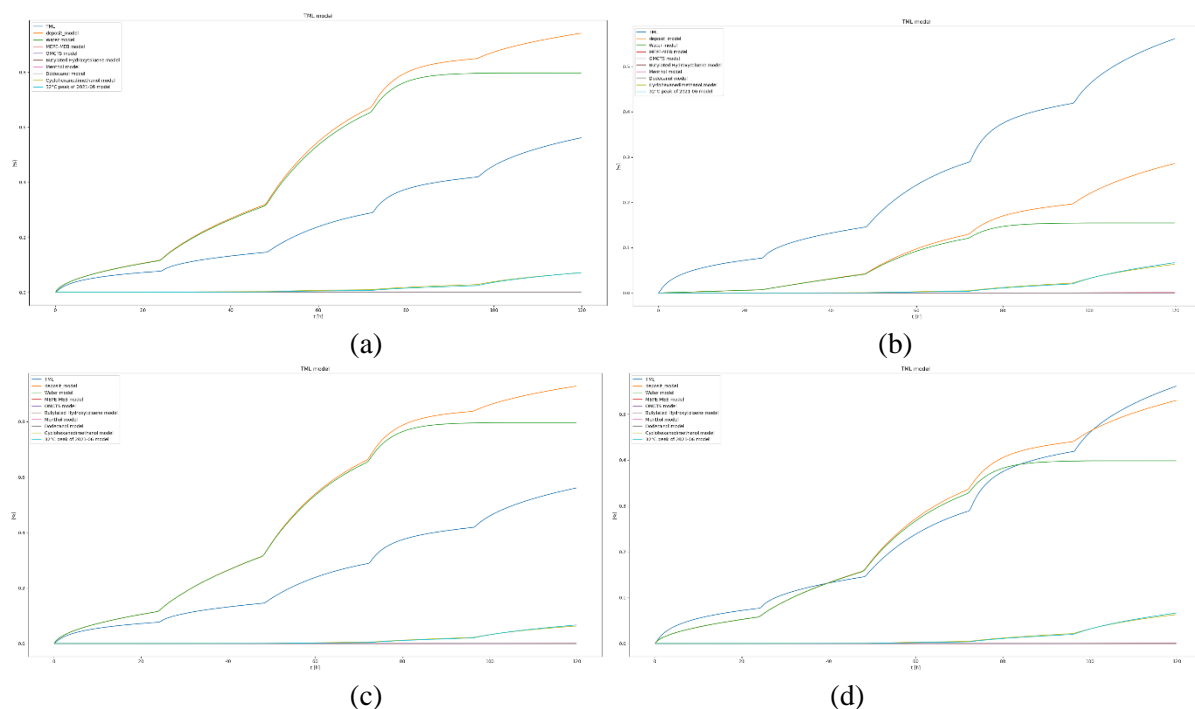


Figure 16. Comparison of post Bake-Out TML measurements (blue line) and model results (orange), decomposed in eight species (green = water, etc.): (a) unchanged model (no BO), (b) direct modeling of BO as 72 h at 60°C, (c) ditto with full water regain (1st species), (d) ditto with 50% water regain

It is interesting to compare this approach to that of section 2, the traditional one, based on mathematical species. There, since most mathematical species could in reality be partly composed of water, a partial regain needed to be assumed for all species (of variable amplitude) in order to fit the data. Here, the fact that a partial regain of only the lightest species allowed a rather good fit of the data is a very good argument in favour of the validity of our species separation.

If one (cautiously) tries to further interpret the (small) residual model-data discrepancy of graph (d), we see that the model underestimates the initial outgassing (first temperature step) and overestimates it later (third step). In the diffusion model, water regain is assumed to be uniform throughout the whole

material depth. The initial water concentration in EC9323 is simply reduced by 50%, uniformly from the surface to the bottom of the material. Since water regain happens from the surface, by diffusion through the material of the molecules condensed at its surface, water concentration could eventually be larger close to the surface. This would lead to a larger outgassing at test beginning, exactly as it was seen in experimental data. It seemed to us too early to dig into this direction now, since we first wanted to verify the quality of the results of the diffusion modelling based on species separation, and no extra assumption on BO. But of course, a better modelling of water regain might be worth trying in the future.

Next figure also displays the CVCMS of EC9323-2 after BO, comparing the measurements and the models with 50% water regain. Indeed the water regain does not impact the CVCMS. These graphs can be compared to the unbaked cases of Figure 12 (-25°C CVCMS), Figure 13 (-50°C) and Figure 14 (-75°C).

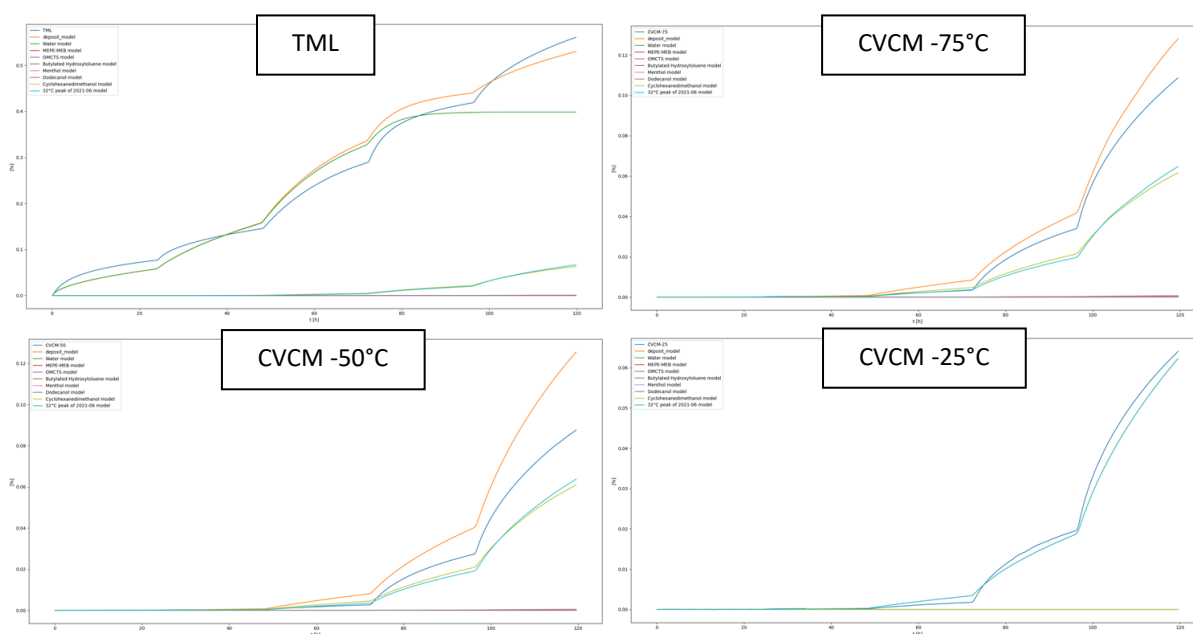


Figure 17. Comparison of post BO measurements and post BO model with 50% water regain: TML and CVCMS

The species condensed at -25°C have a small volatility, and the BO has little effect on them, both in the measurements and the model. The more volatile species condensed at -50 and -75°C are more affected by the BO and the comparison is more interesting there. In both cases the model (orange lines) underestimates the data (blue lines). We think that these small discrepancies could be due again to some species missed in the species separation of [5], rather volatile species in this case. From these graphs, we can estimate these missing species as representing a total of around 0.04% of the outgassing material (versus 0.15% for the -75°C CVCMS). As already suggested, improving species separation completeness is another direction of progress to pursue.

4. Conclusion and perspectives

Two different approaches were used to model post Bake-Out outgassing, and compared to experimental data. The first is the usual method which uses mathematical species and desorption laws. This study has highlighted that reintroducing only the first species after bake-out to take into consideration water reabsorption generally leads to a significant error on the simulated bake-out. Moreover, the error depends on the number of species. Methods based on the reintroduction according to WRM have been presented and have shown better results than reintroducing only the first species. The main drawback is the requirement to have the WRM value. Also, more investigations will be carried out to consolidate the reliability of these methods and their ability to predict CVCMS after a bake-out.

The second is a new method based on a realistic species separation through TGA/MS technique [5] allowed modelling outgassing of actual chemical species, through Fick's diffusion laws. A reasonable

reproduction of the post-BO data was obtained by the simple assumption of a 50% water regain, water simply being the first species. To our knowledge, this is the first time this program, separating species at molecular level and modelling outgassing and BO on this basis, was implemented.

In the new approach, even though the models of the outgassing of the seven individually-separated species are quite good (comparison to MS data), the modelling of the global data (total masses and deposits, TML and CVCMS) is somewhat less accurate. It could be due to the fact that a couple of significant chemical species might still need to be found, and that water modelling might be somewhat less accurate since it could not be directly measured, due to chamber water background. In the future, these points will need to be improved. Other progress directions will be the testing of other materials, to gain more experience and understanding of these limitations, and the improvement of data processing automation.

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