ABSTRACT

Thermogravimetric analysis (TGA) of condensed outgassed contaminants is a potential tool for a better characterisation of contaminants evaporation properties. TGA curves were theoretically studied for three ideal deposit configurations: homogeneous pure chemical, homogeneous ideal mixture and clusters of pure chemical.

We extracted general trends on ramp and thickness effect, and on TGA peaks shape.

The three studied configuration lead to very different TGA shapes so that a TGA curve can not be interpreted if the deposit configuration is not known.

These theoretical observations are illustrated with experimental TGA on BisphenolA (model contaminant) performed in the Onera COPHOS set up (COntamination PHOtons Synergies). We show that even a pure contaminant can lead to a two peaks TGA. We also show that a simulated sun irradiation can lead to clusters development, so that the TGA of irradiated BisphenolA strongly differs from the TGA of non irradiated BisphenolA, while the chemical nature of the deposit is only slightly modified.

1. INTRODUCTION

In flight spacecrafts are exposed to the molecular contamination issue. Indeed, some spacecraft materials outgass emitting contaminants that can deposit on other surfaces. Contaminants can also reevaporate from contaminated surfaces, so that even surfaces than are not in direct view of contaminant sources can be contaminated. As far as outgassing and contaminants reevaporation are thermally activated mechanisms, it can be generally considered that warm surfaces contaminate the colder ones. For some mission contamination has to be considered with great care as far as it can lead to drastic optical properties degradations or to thermo-optical properties modifications. For this reason some simulation tools like COMOVA allow to predict spacecrafts dynamic contamination. Materials outgassing properties and contaminants reemission capabilities are among necessary data for such simulations [1-2]. For this purpose space materials are qualified toward contamination and outgassing. Simulation input data are extracted by accelerated TML tests [3]. It is now well known that most outgassing materials are mainly adhesives, cables, paints, polymers and other organic materials. Reemission of contaminants is more poorly known and CVCM test allow indirect estimation. For this reason the idea arose of contaminants reemission study by TGA (thermogravimetric analysis) following CVCM.

In this paper we discuss on contaminants reemission properties extraction by TGA and highlight the difficulty of the interpretation. Experimental work already showed this difficulty [4]. We study three theoretical ideal deposit configurations:

- homogeneous deposit of a pure chemical
- homogeneous deposit of an ideal mixture of contaminants
- heterogeneous deposit (clusters) of a pure chemical.

For these three ideal conditions we predict TGA curve shape or separation capabilities for different temperature rates or total deposit.

As far as these three configurations behave differently, TGA interpretation is impossible if the deposit configuration is not known.

We present some experimental result that illustrate this difficulty in TGA interpretation

2. THEORITICAL TGA STUDY

We consider a contaminant deposit as an homogeneous thin film of thickness $h$ of a pure chemical. We study the evaporation rate ($v$) versus temperature ($T$) curve for a constant heating rate $r$. This curve is called TGA curve. The evaporation rate of the film at temperature $T$ can be approximated by Eq. 1, where $E_a$ is the activation energy (vaporization of sublimation enthalpy) and $A$ a constant preexponential factor.
This simple law lead to dissymmetric TGA curves where evaporation rate increases up to the maximum rate \( v_{max} \) at \( T_{max} \) corresponding to the end of evaporation. Afterward evaporation rate drops immediately to 0. This description is not fully correct as far as contaminant substrate specific affinity should be considered. Furthermore evaporation rate is lower than presented in Eq. 1 as soon as the substrate coverage is lower than unity, thus at least when the medium coverage is lower than a monolayer.

We propose to identify the influence of the initial deposit \( h \) and of the temperature ramp \( r \) on the \(( v_{max}, T_{max})\) point as function of the evaporation parameters \((A, Ea)\). By linearization around \( T_{max} \) one can write that:

\[
h \approx A \cdot e^{-\frac{Ea}{RT}} \cdot 0 \int_{-\infty}^{R_{max}} e^{-\frac{Ea}{RT}} \cdot dt \tag{2}
\]

From this integration results Eq. 3:

\[
v_{max} = \frac{Ea \cdot r \cdot h}{R \cdot T_{max}^2} \tag{3}
\]

One can observe that \( r \) and \( h \) play symmetrical rules so that studying the influence of \( r \) is equivalent to the influence of \( h \). Furthermore, as far as \( v_{max} \) is linked to \( T_{max} \) by Eq. 1, at constant \( r \cdot h \) product, the TGA curve remains the same.

We now only focus on the ramp effect knowing that initial thickness effect is the same. By derivation of Eq.3 by \( r \), the ramp influence on \( T_{max} \) (Eq.4) and \( v_{max} \) (Eq.5) can be obtained. Fig. 1 presents relative \( T_{max} \) and \( v_{max} \) variations with ramp variations. This effect depends on the considered activation energy. A temperature rate increase of a factor 10 corresponds to a temperature shift of approximately 20°K (reference \( T_{max} \) is 300°K). \( v_{max} \) is almost proportional to \( r \).

\[
\frac{dT_{max}}{dr} = \frac{1}{r} \cdot \frac{R \cdot T_{max}^2}{r \cdot Ea + 2 \cdot R \cdot T_{max}} \approx \frac{R \cdot T_{max}^2}{r \cdot Ea} \tag{4}
\]

\[
\frac{dv_{max}}{dr} = \frac{hEa^2}{RT_0^2 \cdot (Ea + 2RT_0)} \approx \frac{hEa}{RT_0^2} \tag{5}
\]

Half height width can be introduced. \( T_{1/2} \) is the temperature that corresponds to the half of the maximum evaporation rate. \( T_{1/2} \) is given by Eq. 6

\[
A \cdot e^{-\frac{Ea}{RT_{1/2}}} = 1/2 \cdot A \cdot e^{-\frac{Ea}{RT_{max}}} \tag{6}
\]

One simply shows that :

\[
\Delta T_{1/2} = T_{max} - T_{1/2}
\]

\[
\Delta T_{1/2} = \frac{R \cdot T_{max}^2}{Ea + R \cdot T_{max}} \ln 2 \approx \frac{R \cdot T_{max}^2 \cdot \ln 2}{Ea} \tag{7}
\]

\[
\frac{d\Delta T_{1/2}}{dr} \approx 2 \ln 2 \cdot \frac{R}{Ea^2} \cdot T_{max}^3 \frac{R}{r} \tag{8}
\]

Fig. 2 shows that peaks width only slightly depends on temperature ramp.

For TGA optimisations, it is interesting to study how ramp variations influence separation of peaks and the signal/noise ratio. As far as the signal is almost proportional to the temperature ramp, peaks intensity is increased at higher ramp.
Eq. 4 helps to investigate the separation for two different species. Obviously, there is no direct relationship between temperature ramps and separation. Indeed, if two species appear successively at $T_1$ and $T_2$ in a reference conditions, then a ramp increase lead to higher separation only if $(T_2/T_1)^2 > Ea_2/Ea_1$. Else separation decreases.

![Graph showing relative half height width variations with ramp](image)

*Fig. 2: Relative half height width variations with ramp*

The case of a pure contaminant is obviously only theoretical. Especially for deposits characterization by TGA it is interesting to study mixtures of contaminants. If the study is reduced to the case of two contaminants, two main cases can be considered. Contaminants can have a good affinity one for the other and form a ideal solution. Contaminants can have a bad affinity and lead to several phases and probably cluster deposit.

We first treat the case of a homogenous film forming an ideal solution.

We propose to consider that evaporation rate is reduced by a concentration factor as in Eq. 9

$$\frac{dh}{dt} = -\alpha \cdot \frac{h}{h_T} \cdot A \cdot \exp\left(- \frac{Ea}{RT}\right)$$  \hspace{1cm} (9)

We study TGA curve for ideal solutions with two strong assumptions. We consider that $\alpha=1$ and that only one contaminant evaporates.

TGA curves were numerically simulated. Fig. 3 shows simulated modifications of the TGA peak and the temperature shift. Note that the same quantity of the evaporating contaminant is considered in all cases. The normalized evaporation rate in $1/T$ plot shows that the peak shape remains the same whatever the dilution.

![Graph showing diluted contaminant TGA peak for various dilutions (up) and normalised peak shape (down)](image)

*Fig. 3: Diluted contaminant TGA peak for various dilutions (up) and normalised peak shape (down)*

We study the position of the TGA peak. It corresponds to $d^2h/dt^2=0$. We consider a highly diluted contaminant so that $h_T$ remains quasi constant during TGA. This leads to Eq.10

$$T_{\text{max}}^2 = \frac{r \cdot h_T \cdot Ea}{R \cdot A \cdot \exp\left(- \frac{Ea}{R \cdot T_{\text{max}}^2}\right)}$$  \hspace{1cm} (10)

Note that Eq.10 is very similar to Eq.3 for a pure contaminant. In the dilute case $h_T$ has to be considered, while $h$ was considered for pure case. Nevertheless for a pure contaminant $h$ is also $h_T$. Furthermore $T_{\text{max}}$ does not depend on the initial contaminant quantity, but only on $h_T$.

The study of the influence of the ramp $r$ on the peak position leads to Eq. 11 and Eq 12.

$$\frac{dT_{\text{max}}}{dr} = \frac{R \cdot T_{\text{max}}^2}{r \cdot Ea}$$  \hspace{1cm} (11)
\[
\frac{dv_{\text{max}}}{dr} \approx -\frac{Ea}{R \cdot T_{\text{max}}^2} \cdot h(T_{\text{max}}) \tag{12}
\]

It was numerically verified like on Fig. 3 that \(h(T_{\text{max}})\) is approximately 60% of the initial deposit for the studied contaminant for a concentration lower than 10%. This proportion increases to approximately 70% for a concentration of 75%. As far as Eq. 11 and Eq. 12 are very similar to Eq. 4 and Eq. 5, trends presented on Fig. 1 for a pure contaminant remain true for a diluted contaminant.

It was discussed for a pure contaminant that for a \(r.h\) constant product the TGA remains the same. We also showed that it is true for the \(r.h.T\) product for high dilution and separated evaporation temperatures. It was numerically verified that this is true for any dilution and even if evaporation of the two contaminants is not separated. As an illustration Fig. 4 presents three TGA simulations with a constant \(r.h.T\) product. This can have a great consequence for exploitation of TGA. Indeed it could be proposed that the best way to compare two deposits by TGA is to adapt the temperature ramp for analysis to the total deposit on each QCM.

\[
k = \left(\pi \cdot h \cdot N\right)^{-1} \tag{13}
\]

\[
\frac{v}{v_0} = 5.24 \cdot \gamma \cdot k^{-2/3} \tag{14}
\]

One can observe on Fig. 5 the influence of the \(k\) parameter on a TGA. Actually \(k\) evolves during evaporation. For this reason the initial \(k_0\) value is considered. A normalized representation is also presented, and shows that in a \(1/T\) plot all curves have the same shape. For half spheres the peak corresponds approximately to 70% of evaporation.

Nevertheless for this it is necessary to know that the deposit is an homogeneous thin film. Indeed in some cases the deposit can evolve to clusters. The formation of clusters modifies the surface access to vacuum thus the global evaporation rate. The bigger the clusters, the lower the evaporation rate. It is important to note that because of evaporation, clusters tend to become smaller so that evaporation rate would decrease continuously at constant temperature.

We propose to characterise the clusters by a dimensionless parameter \(k\), function of the medium contaminant thickness \(h\) and of the cluster density (number per surface unit) as in Eq.13. It is considered that a cluster corresponds to matter accumulation from an area of deposit of thickness \(h\). This area is assimilated to a disk. Then \(k\) is the ratio of the disk radius divided by \(h\). The normalized evaporation rate \(v/v_0\), where \(v_0\) is the evaporation rate for an uniform film is given by Eq. 14. A hypothesis has to be considered for drops shape. \(\gamma\) is a dimensionless form factor that is 1 for spheres and 0.84 for half spheres.

![Fig. 4: Three TGA curves for a mixture of two contaminants (50% -50%) and a constant \(r.h.T\) product](image1)

![Fig. 5: TGA curves for a same medium deposit with different initial deposits \(k_0\) values(half spheres)](image2)
3. EXPERIMENTAL EVIDENCE

We now present some experimental observation of TGA interpretation difficulties. Experiments were performed in the ONERA set up COPHOS dedicated to contamination and VUV irradiation – contamination synergies. COPHOS is mainly a vacuum chamber equipped with an effusion cell that generates a molecular beam for contamination on 4 temperature regulated QCMs and on four passive samples for ex-situ characterizations. In COPHOS two QCMs and two passive samples can be irradiated by VUV light.

It is obviously expected that the TGA of a pure molecular deposit leads to a unique TGA peak. Nevertheless we observed the contrary with Bisphenol A. Indeed, as presented on Fig. 6 we observed 2 peaks for pure Bisphenol A. Fig. 6 shows different TGA performed at various temperature ramps (0.5, 1, 2 and 5°C/min) for various initial deposit thicknesses (800Å to 5500Å). It appears that low temperature ramps favour the second peak as well as high initial deposits. It was also observed that the first peak slope can be fitted by a 120kJ/mol activation energy Arrhenius law while the second can be fitted by a 150kJ/mol.

It was checked during evaporation that the deposit is a thin film. Indeed evaporation was followed during successive stepped temperature increases. It was observed that evaporation in this case is constant at constant temperature. Fig. 7 presents such an experiment. It can be observed that during the first temperature steps the evaporation rate is constant. At constant temperature, during the transition steps, evaporation rate decreases with time. During the later steps evaporation rate remains constant and is coherent with the Fig. 6 second TGA peak evaporation rates. The final constant evaporation rate indicates that the deposit is an uniform film or at least that the surface exposed to vacuum remains stable.

Complementary Gas Chromatography analysis indicated that the deposit is only composed of Bisphenol A.

On the basis of all these observations the two TGA peaks are interpreted as a two Bisphenol A phases. The transition from one peak to the other is interpreted as a phase change transition. Note that fusion temperature for Bisphenol A is 150°C so that for thermodynamic reasons Bisphenol A is expected to be solid (crystallized) during TGA. Nevertheless Bisphenol A is deposited by molecular beam deposition on cold QCMs (-20 to -100°C). We propose that molecular beam deposition at low temperature lead to an amorphous Bisphenol A thin film. During TGA, because of temperature increase molecular mobility can be activated. We attribute the transition to crystallization. It is interesting to note that Bisphenol A fusion enthalpy is 30kJ/mol. This corresponds to the difference of activation energy corresponding to the two peaks.

Note that for characterization of condensed outgassed contaminants, by nature test procedures are close to those observed with Bisphenol A. Nevertheless it is also known that impurities tend to favour crystallization, so that for a contaminants mixture the amorphous peak
could not exist. We also indicate that we tested other pure molecular contaminants that did not present this two peaks TGA shape.

Experimental morphology effect were observed on VUV irradiated Bisphenol A. Fig. 8 presents the TGA curves for two Bisphenol A deposits, one being irradiated and one not. One can observe that the non irradiated deposit TGA curve is characteristic for thin film TGA (to compare with 100% on Fig. 3). Note that this experiment corresponds to an initial deposit of 1000Å with 2°C/min ramp. In these conditions only the amorphous Bisphenol A evaporation is observed, so that there is only one TGA peak for the non irradiated deposit. In opposition, for the irradiated deposit two peaks are observed and both appear at much higher temperature than for non irradiated deposit.

Obviously, a too rapid interpretation of this TGA would have been that all Bisphenol A evolved to a new contaminant under VUV irradiation. Nevertheless complementary GC/MS analysis showed that the deposit is mainly bisphenol A. Thus the main peak shift can be explained by a phase change, a dilution effect or a morphology effect.

A stepped temperature elevation experiment was performed with irradiated deposit. Fig. 9 presents the evaporation rate for successive temperature plateau. The evaporation rate decreases with time for each plateau. This excludes the phase effect possibility (see phase transitions). Thanks to the complementary GC/MS measurement we exclude the dilution effect as far as the deposit is known to be mainly Bisphenol A. We conclude that some morphology (clusters) developed on the irradiated deposit. Furthermore, SEM characterizations showed the presence of clusters on the irradiated deposit while the non irradiated deposit seems more homogeneous (see Fig. 10). The $k$ factor is estimated to be a fraction of hundred to few hundreds. This is coherent with the 20°C shift observed on Fig. 8. Note that these SEM measurements are ex situ so that passive samples had to be heated up and exposed to air before SEM measurement. This transfer could induce a modification of the deposit. The stepped temperature characterization in opposition is in situ. Thus it is clear that clusters existed at least when the deposit was heated up to 20°C.

The clusters TGA peak shape is not similar to that predicted. This can simply be explained by the cluster size dispersion and by the specific clusters shape. Furthermore it is suspected that clusters evolve during the TGA.

Fig. 9: Stepped temperature evaporation experiment of irradiated Bisphenol A

Note that the second TGA peak observed near 120°C was attributed to evaporation of product formed during irradiation. The peak shape lets suppose that those newly formed contaminants form clusters.

4. CONCLUSIONS

In this paper we showed theoretically and experimentally that the TGA characterization of a thin molecular film is not sufficient for species characterization. Indeed the TGA curve is strongly influences by dilution effects, morphology effects and phase change effects. We especially showed that one pure contaminant can lead to two TGA peaks. Obviously if the contaminant source was unknown these two peaks would have been interpreted as two molecular species of different evaporation energy. For outgassed contaminants characterization by TGA great care must be taken in the interpretation. One should be conscious that for a mixture of contaminants, because of lack of solubility of contaminants one with
the other, clusters of different composition and different sizes are expected. Furthermore we showed that the initial deposit and the temperature rate influence the TGA curve so that it can be difficult to compare two TGA performed in different conditions.

Fig. 10: SEM characterization of passive samples. Upper picture: irradiated (up) and non irradiated Bisphenol A (down). Lower picture: detail of irradiated deposit

5. REFERENCES


3. ASTM E 1559 - 93