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Contamination Level Prediction: Progress in Species Separation by TGA/MS

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Abstract. Molecular contamination can be detrimental to spacecraft life expectancy as it may induce changes to the properties of the surfaces on which it deposits. In order to control these potential issues, manufacturers need to assess in-flight contamination levels in the quite early design phases, possibly leading to design changes or extra material bake-out to fulfil requirements. The accuracy of model assessments may thus have direct impacts on missions and costs. Prediction of outgassing and deposition at mission timescale is done by extrapolating short-term on-ground experimental results, by fitting the latter with some empirical or physical laws. Common methods are the power law interpolation (in isothermal conditions) or the residence time approach (with thermally activated time constants), which leads to exponential decays in isothermal conditions. Although they allow fitting the measured outgassed flux over few-day-long experiments, their extrapolation to ten or fifteen-year-long missions is more challenging. Validating empirical laws might involve long-term empirical comparisons, while obviously the validation of physical models should start with checking their physics. In spite of many years trying, a basic difficulty was yet found to block significant progress on physical validation. As long as measurements are limited to the total mass on QCMs it looks possible to fit data as a sum of almost any law, such as residence time or diffusion models e.g. for outgassing. Following this observation, a conclusion was drawn that the only way to discriminate between two different physics was to characterize contamination at chemical species level. Such characterizations are a prerequisite to unravel the physics at play during several phenomena: outgassing, deposit films dynamics, photochemistry, environment/ATOX interactions, etc. This innovative approach, presented herein, aims at identifying outgassed contaminants by means of coupled thermogravimetric analysis and mass spectrometry. For this purpose, this paper reports the successful species separation and identification of contaminants outgassed from a material used in space applications: the epoxy adhesive Scotchweld EC-9323-2.

1. Introduction

Upcoming space missions are becoming more and more demanding with their contamination budgets. Simulations of contamination at the satellite scale and their subsequent long-term predictions are of prime importance in order to respect contamination budgets allowed by the missions.

Contamination is the consequence of several phenomena, namely the outgassing of contaminant species from a source material, their transport towards other surfaces, their sticking to the said surfaces, their possible photopolymerization and/or reemission from the target [1]. Though transport in rarefied environment is well known, the other phenomena above-mentioned, especially outgassing and reemission, only remain partially known. So far, contamination predictions rely on several contamination outgassing and reemission models themselves relying on different laws, sometimes



chosen somewhat arbitrarily: first order desorption, zero order evaporation, diffusion, bouncing or sticking on surfaces, etc. [2]–[5]

Though models currently used to fit laboratory week-long contamination experiments and allowing long-term predictions could work well in the hypothetical case where only one chemical species would outgas from a source, their application to real-case materials does not provide satisfactory results. Indeed, it is fairly easy with current methods to fit any data obtained by increasing the number of “virtual species” used to model any of the phenomena already mentioned. Long-term predictions obviously suffer from the lack of knowledge about the actual chemical species responsible for contamination and the physical laws governing their behavior.

For the past 15 years, ONERA, with the help of its partners among which ESA and CNES play an important role, has been convinced that the only way to perform accurate long-term predictions of contamination phenomena is to decipher the data gathered as a total mass in lab experiments into a sum of physical laws for each constituent of the contamination deposit characterized individually [6]. To do so, a technique known as species separation and identification of contaminant species by thermogravimetric analysis coupled to mass spectrometry (TGA/MS) is being developed [7], [8], [9]. Another interesting approach consisted in attempting a species separation based on peaks seen on QCMs during TGAs, and attributing them to different (unidentified) species [10], [11].

The purpose of this study is to strengthen the TGA/MS-technique knowledge that has started to be gathered by ONERA and its partners in the last decade, then mainly on a structural epoxy adhesive, namely Scotchweld EC-2216 [5], [9], and refine the technique leading to the characterization of contaminants. In this context, species separation and identification by TGA/MS was now applied with success to another epoxy glue, Scotchweld EC-9323-2.

2. Experimental section

2.1. Facility

Experiments dedicated to a characterization by Thermogravimetric analysis (TGA) coupled to Mass Spectrometry (MS) were carried out in ONERA’s COPHOS facility (Contamination PHOton Synergy) (figure 1). Transport between the effusion cell, the quartz crystal microbalances (QCMs) and the mass spectrometer follows the “hot shroud” principle. The shroud is maintained at high temperature (< 180 °C) in such a way that the contaminants residence time is very short with regards to every other characteristic time, allowing to talk about instantaneous rebounds.

During outgassing or reemission, contaminants divide between said wells:

- Cold surfaces (QCMs, collection plates)
- Pumping orifices
- Mass spectrometer

During outgassing, both the QCMs and the collection plates are maintained at temperatures below -80 °C. During the reemission phase, QCMs and plates are brought successively to higher temperature of about 150 °C following a heating ramp of 2 °C/min, thus completing TGAs.

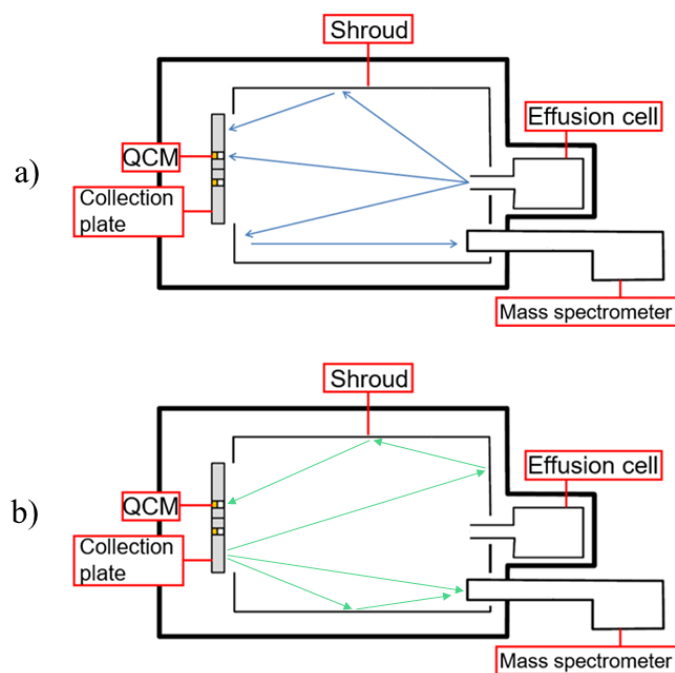


Figure 1. Scheme of COPHOS facility showing the role of the hot shroud principle a) during outgassing, b) during reemission. Contaminants are transported by successive reflections until they reach wells (cold parts, mass spectrometer or pumping orifices).

2.2. Protocol

A piece of Scotchweld EC9323-2 epoxy adhesive is placed in the effusion cell and heated for a few hours, until enough outgassed contaminants are condensed on the plates and the QCMs (typically equivalent to a few thousand $\times 10^{-8}$ g.cm⁻²). Then, the outgassing flux is greatly reduced by letting the effusion cool down passively. After the outgassing flux is lowered sufficiently (undistinguishable with regards to a typical reemission flux during a TGA), series of TGAs are launched according to §2.1.

To perform species separation, 2 distinct phases are necessary:

1) Outgassing phase:

The effusion cell is heated, thus accelerating every thermoactivated processes (diffusion, desorption). Most contaminants deposit on the plates and QCMs but a fraction is also received by the mass spectrometer.

2) Reemission phase (TGAs):

Direct TGA

Direct measurement of the reemission rate by QCM heating (2 °C/min). The vibrating frequency of the QCMs being sensitive to temperature, this effect must be taken into account. Note that the surface of the QCMs is quite small, inducing a weak signal in the mass spectrometer.

Inverse TGA

Heating of the (large) plates. Allows good signal over noise ratio (SNR) in the mass spectrometer. Deposit happens as well on the cold QCMs (direct view to be taken into account), meaning no temperature effect to be corrected.

11 TGA series were performed on four different samples. Sometimes, TGAs were carried out after each outgassing step, except for TGA series n° 7. In the latter case, the mass spectrometer used for species identification had seen its sensitivity decrease strongly. In order to counter the signal loss, a large amount of material was placed in the effusion cell and 4 steps of outgassing were carried out in order to increase the thickness of the contamination deposit on the QCMs and collection plates. Table 1 below sums up the 11 TGA series with their respective outgassing temperatures and the mass of the samples used. Samples were typically of rectangular form, with thickness and width roughly equal respectively to 2 mm and 1 cm. Their length were equal to a few centimeters. The difference in mass observed in series 7 is due to the fact that a larger number of samples were put simultaneously in the effusion cell as discussed later in section 3.5.

Table 1. Summary of the outgassing temperatures and samples masses of the 11 TGAs series performed.

| TGAs series number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|-----------------------------|------|-----|------|-----|-----|-----|-------------------|------|-----|-----|-----|
| Outgassing temperature (°C) | 125 | 150 | 75 | 100 | 125 | 150 | 75, 100, 125, 150 | 75 | 100 | 125 | 150 |
| Sample mass (g) | 1.38 | | 2.28 | | | | 12.72 | 1.85 | | | |

The amount of data gathered during these 11 TGA series being sizable, only TGA series 1&2 will be used in the following paragraphs. A quick view at series 7 at the end of this paper will also provide interesting data.

In figure 2 can be seen the temperature profile of the elements of interest for these TGAs, namely the effusion cell (or Knudsen cell), the QCMs, the collection plates and the shroud. First, the effusion cell containing the sample was heated at 125 °C for about 2.5 hours. It was then left to cool down passively as mentioned before. After that period, the 4 elements of the sample holder were heated successively from -80 (their temperature during outgassing) to 150 °C at a rate of 2 °C.min⁻¹. Each element underwent a TGA even though one QCM and one collection plate would have been enough: this was done for redundancy purpose. After all the elements that went through a TGA were cooled down again, another outgassing step at higher temperature (150 °C) was performed. Then again, the four TGAs were carried out again.

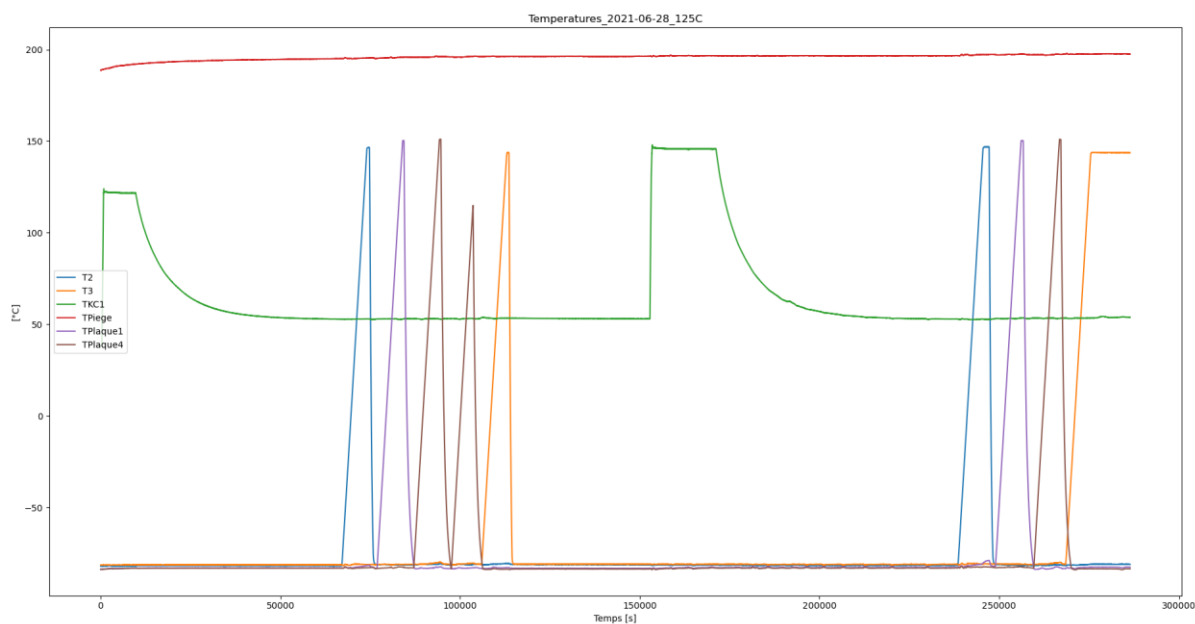


Figure 2. Temperature profiles of the Knudsen cell (TKC1), the QCMs (T2, T3), the Plates (TPlaque1, TPlaque2) and the shroud (TPiege) during tests carried out in June 2021: two outgassing steps, four TGAs after each step. The second TGA of the Plate 4 after the first outgassing step is a mistake.

During the TGAs, the mass spectrometer behaves like a well and is able to detect the reemitted molecules. For this purpose, the TGAs of the plates are very useful as their surface is large and allow good signal over noise ratio in the recorded spectra. For this reason, the MS data presented in the rest of this paper were recorded during the TGAs of one of the plates. The MS ionizes incoming molecules with an electron beam. Following ionization, these molecules are fragmented and the subsequent fragments are separated in function of their mass over charge ratio, noted m/z ratio in the rest of this document. Each molecule follows a pattern of fragmentation where some fragments are more probable than others. A graph bar consisting in the relative abundance of each fragment as a function of their m/z ratio is known as a mass spectrum.

The separation and identification of reemitted contaminants during TGAs are performed following 4 successive steps [12]:

- 1) Finding high m/z fragments that seem to exhibit a single peak during TGA. The combination of these two criteria allows thinking that these fragments are likely to originate from a single molecule.
- 2) Knowing the previous fragments' reemission temperatures, one must find other fragments peaking at the same temperatures and verify that the shape of their peaks in log scale is in accordance with a common molecular origin, that is to say that they must look parallel and thus proportional.
- 3) A stack of parallel fragments peaking at the same temperature is the closest one gets from a mass spectrum at a given temperature. It is then possible to reconstruct a partial spectrum of the outgassed molecule.
- 4) Comparison between the partial mass spectrum and a database and/or previous experiments (typically gas chromatography coupled to mass spectrometry (GC-MS) carried out during the qualification phase of the material) allows relatively reliable identification.

In the following section, species separation and identification of the contaminants outgassed by Scotchweld EC-9323-2 will be presented.

3. Species separation and identification : results

During these series of experiments, seven species were properly separated systematically and among which six were identified confidently. Though it may feel anachronous, the following sections will be named after the identified molecules even if definitive identification only happens at the very end of the process.

3.1. Butylated hydroxytoluene (BHT)

The four steps mentioned in the previous section were applied. For the sake of concision, steps 1 and 2 are presented in a single figure. Peaks with similar shapes and reemission temperatures during a TGA are visible in figure 3. For this first TGA, one can find many fragments exhibiting a single peak, all of them being reemitted with the same shape at around $-28\text{ }^{\circ}\text{C}$. The shape criteria means that their signal is proportional in logarithmic scale. One deduces from this first level analysis that the isolated fragments probably originate from a single chemical species. The relative contribution of each of these fragments corresponds to their contribution in the mass spectrum of the species. It is hoped, once confirmed with several different TGAs, that part of the species' mass spectrum can be determined. That part should be in principle the one constituted of original fragments, that is to say fragments not encountered in spectra of other species.

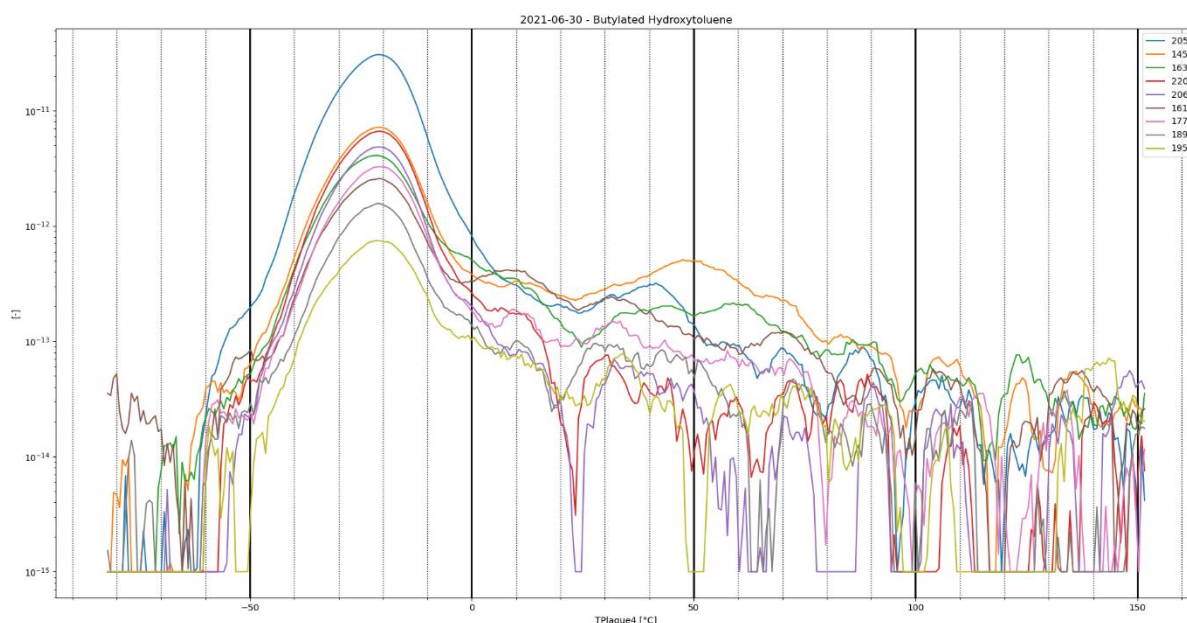


Figure 3. Similar peaks observed during the second TGA series #1 (outgassing step carried out at $125\text{ }^{\circ}\text{C}$) on fragments $m/z = 205, 145, 163, 220$ a.m.u., etc. of the mass spectrometer.

This stack of parallel fragments allows the reconstruction of a mass spectrum, visible in figure 4. In this figure, the blue dots represent the background of our chamber, that is to say masses that are detected in the mass spectrometer when no molecule is being reemitted (here, at $100\text{ }^{\circ}\text{C}$). This way, the orange squares are the masses that are peaking around $-28\text{ }^{\circ}\text{C}$, that is to say the temperature at which appears the peak in TGA shown in figure 3.

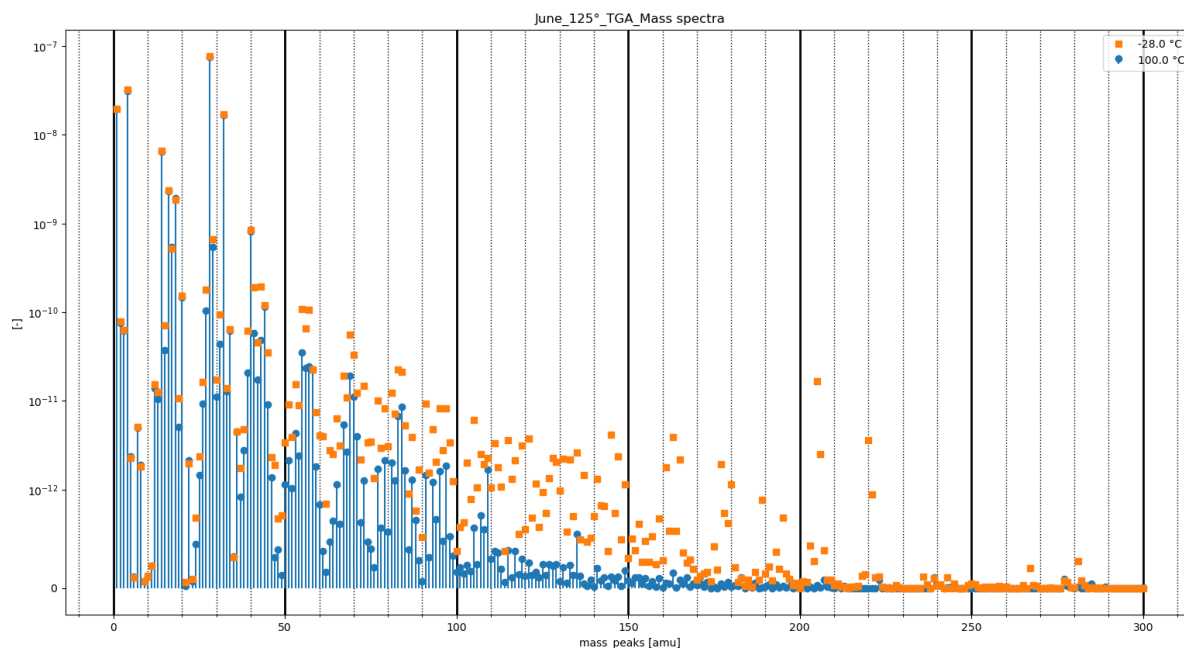


Figure 4. Mass spectrum measured during the TGA peak of the studied (-28 °C, orange squares) and the chamber's background (blue circles).

The figure 4 shown above represents the mass spectrum measured during reemission peak, compared to the facility's background (end of the TGA + 100 °C). As it was seen on the previous figure's temporal signals, this spectrum is very similar, with signal raising well above background level for:

- Fragments already tracked (205, 145, 163, 220, 206, 161, 177, 189 a.m.u.)
- But as well 221, 165, 179, 180 and sometimes 267, 281 a.m.u.

Comparison with NIST spectra [13] of species detected by GC-MS on EC-9323-2 by CNES suggested that the molecule we separated was in fact butylated hydroxytoluene (figure 5). All the tracked fragments exhibiting a single peak with common shape are present, especially the very characteristic 205 and 220 a.m.u. ones. Other fragments appearing in the reconstructed spectra do not appear in BHT's spectrum, probably because they are fragments belonging to other molecules partially reemitted at the same temperature.

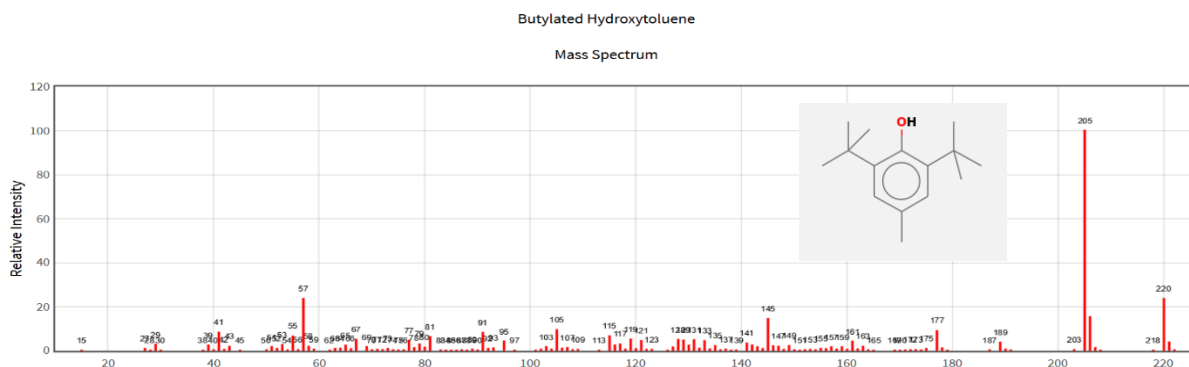


Figure 5. NIST mass spectrum and skeletal formula of butylated hydroxytoluene.

The same work was repeated 10 more times during our study, leading every time to the same conclusion. Table 2 at the end of this section sums up the reemission temperature of each separated molecule for the 11 TGA series carried out.

3.2. 1,4-Cyclohexanedimethanol (CHDM)

The second species separated is especially identifiable thanks to canal $m/z = 95$ a.m.u. The signals for fragment $m/z = 95$, 202 and 264 a.m.u., which are single peaks, as well as a few others, less “pure”, but presenting similar peaks at the same reemission temperature of 8 °C are represented on the MS data presented in figure 6.

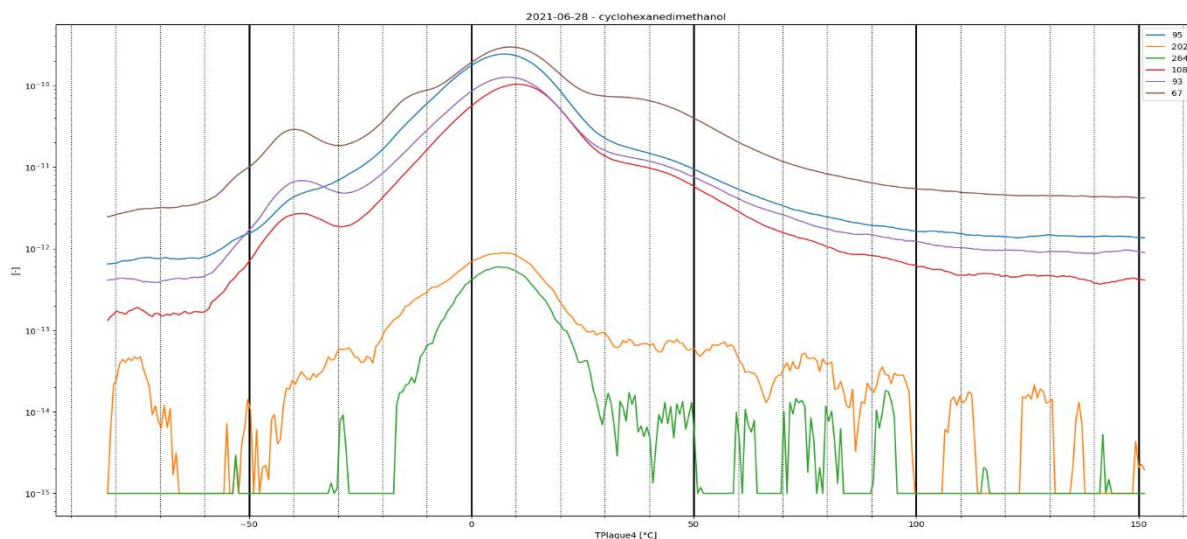


Figure 6. Fragments 95, 202 and 264 a.m.u. as well as some other important ones from the CHDM (non-single ones) reemitted during TGA series #1 (outgassing step carried out at 125 °C).

From these signals, the reconstruction of a mass spectrum was made possible. The result is shown in figure 7 below.

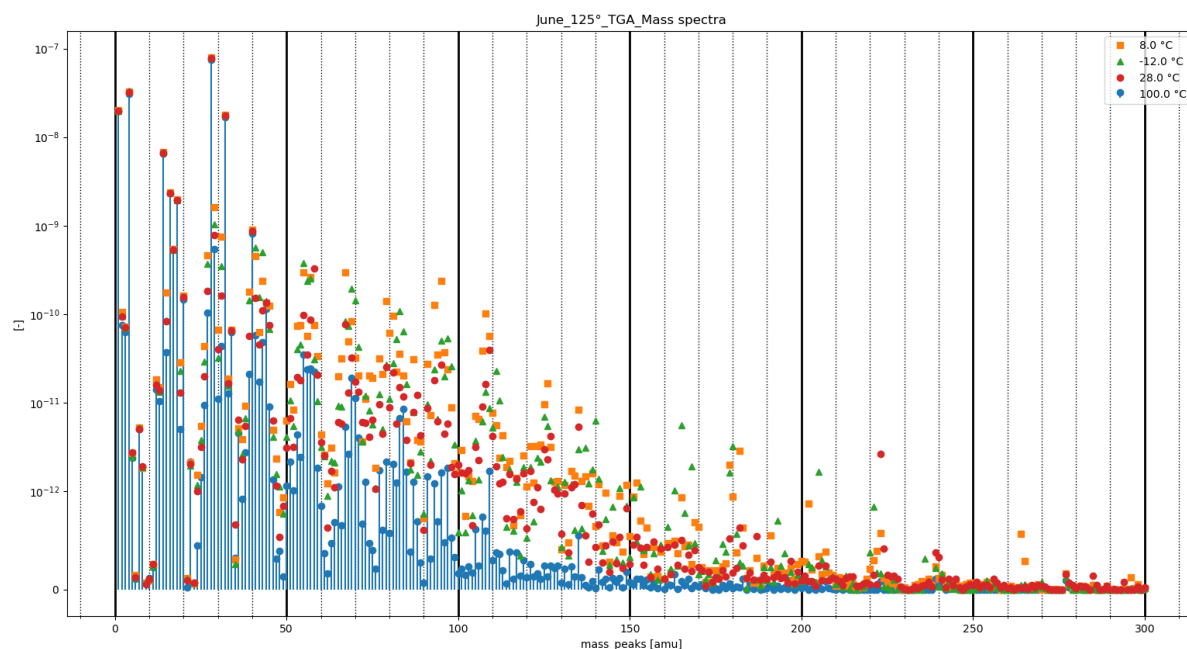


Figure 7. Mass spectrum reconstructed during the discussed peak in TGA (8 °C, orange squares), compared to the chamber's background (blue squares) and some other peaks

Similarly to what was done for BHT, the background of the chamber is represented by blue circles, while the signals detected at 8 °C is represented with orange squares. This mass spectrum exhibits on the one hand the fragments already discussed (264, 202, 108, 95, 93, 67 a.m.u.) but as well other masses present in the CHDM mass spectrum [14] (figure 8): 126, 107, 109, 81, 91, 55 and 41 a.m.u. It seems that the predominance of CHDM in the TGA peaks is almost certain especially since this molecule was observed by CNES in GC-MS experiments performed on the same material.

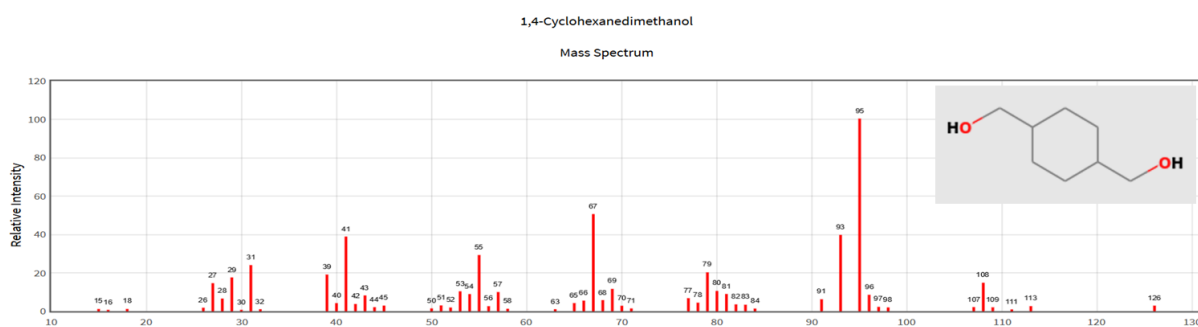


Figure 8. NIST mass spectrum and skeletal formula of 1,4-cyclohexanedimethanol.

3.3. 1-Dodecanol and Menthol derivative

The TGA peak seen at -13 °C on the June 2021 TGA carried out after an outgassing step at 125 °C is arduous to treat. Indeed, from this first TGA (figure 9), it seems that two different shapes of reemission peak are present: some being narrow (98, 111, 112, 140, 168 a.m.u.), the others wider (165, 180, 193 a.m.u.).

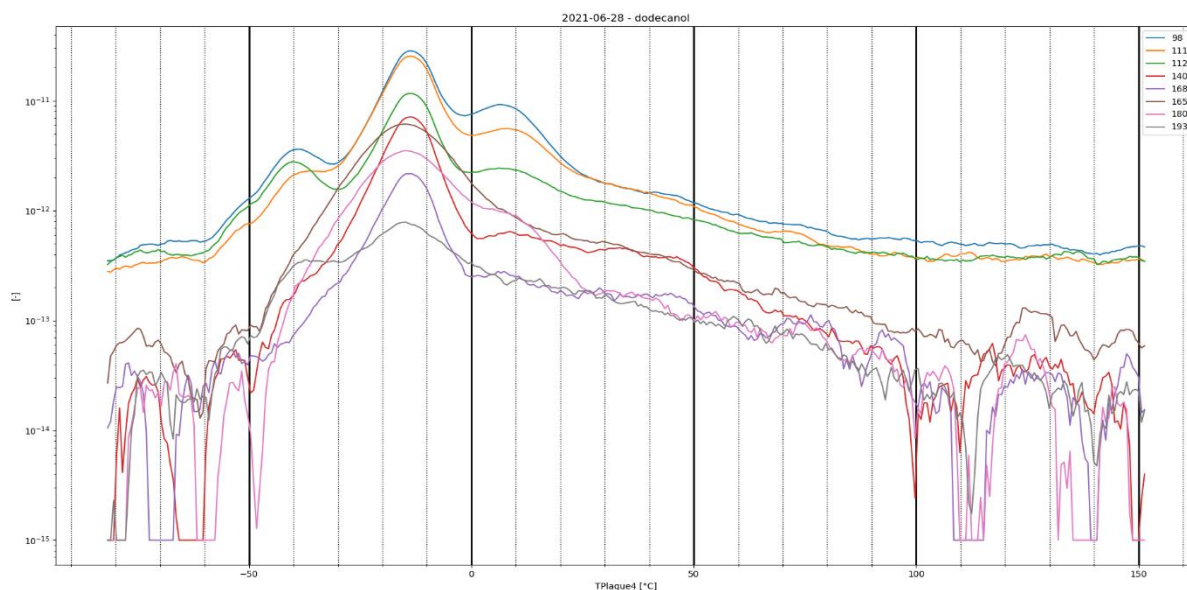


Figure 9. Several fragments reemitted around -13 °C during TGA series #1. (outgassing step carried out at 125 °C).

These results being sufficient to separate and identify two distinctive species, a typical mass spectrum as seen in MS during the reemission peak (figure 10) followed by two mass spectra from database (figures 11 and 12) are presented. As often, these species were selected among the ones seen in GC-MS by CNES. Using these data allows on the one hand to narrow the research of species to those actually outgassed by the source material EC-9323-2 (representability) and on the other hand to limit ourselves to research smaller database (practical numerical efficiency).

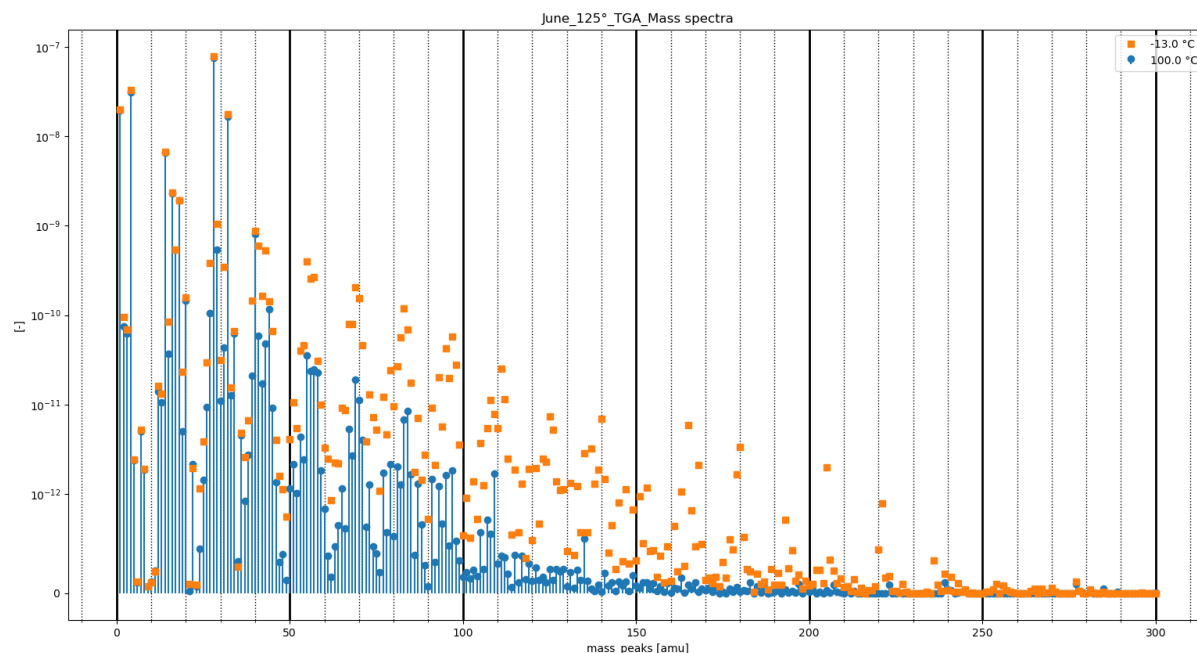


Figure 10. Typical mass spectrum measured during the reemission peaks at $-13\text{ }^{\circ}\text{C}$ during TGA series #2 after an outgassing step carried out at $125\text{ }^{\circ}\text{C}$ (orange squares). The background of the chamber is represented with blue circles.

This slightly more complicated case is great to recap the process leading to the identification of a chemical species:

- 1) Among temporal measurements in TGA/MS, one can look for and find several fragments exhibiting peaks at the same temperature and being proportional with one another. Out of these canals, the most useful are the ones exhibiting single peaks (a single peak for a given m/z signal as a function of time, with a shape close to what is expected during reemission). This indicates that this fragment probably exists in the spectrum of only one molecule.
- 2) In order to validate this hypothesis, the selected fragments must all be found in the mass spectra of the candidate molecules from which they are thought to originate. Warning: the signals observed in mass spectrometry are often shown in log scale to demonstrate proportionality over time whereas mass spectra found in databases are often shown in linear scale.
- 3) Other peaks found in the mass spectra of the candidate molecules [15], [16] (figures 11 and 12) must as well be present in the measurements (figure 10), even though they may not be detected as single peaks.

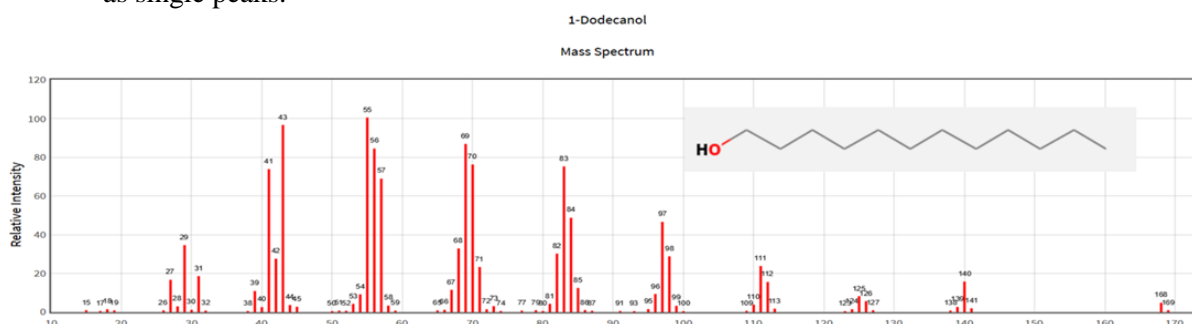


Figure 11. NIST mass spectrum and skeletal formula of 1-Dodecanol. Note that the spectrum includes fragments from the first group: 98, 111, 112, 140 and 168 a.m.u.

For 1-Dodecanol, the three steps above-mentioned give:

- 1) Fragments $m/z = 98, 111, 112, 140, 168$ all exhibit simple, proportional peaks (see TGAs above)
- 2) These fragments can all be found in the NIST mass spectrum of 1-Dodecanol (figure 11)
- 3) Other important peaks from the database spectrum can all be found in the actual measurements (figure 10) even though they were not selected as they were not detected as single peaks (they appear in other species' spectra).

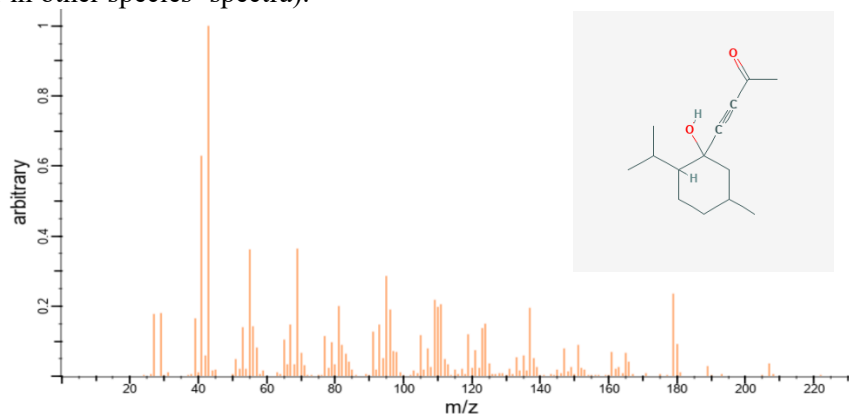


Figure 12. SpectraBase mass spectrum and skeletal formula of (1R,2S,5R),1'-(butyn-3-one-1-yl)-menthol. Note that the spectrum includes fragments from the second group: 165, 180 and 193 a.m.u.

The same thing is observed for (1R,2S,5R),1'-(butyn-3-one-1-yl)-menthol:

- 1) Fragments $m/z = 165, 180$ and 193 present proportional single peaks (see TGAs above)
- 2) These fragments can all be found in the database spectrum above (even $m/z = 193$ a.m.u., with very small signal, compatible with what was measured, represented in log-scale...)
- 3) Other important peaks from the database spectrum (figure 12) can all be found in the actual measurements (figure 10) even though they were not selected as they were not detected as single peaks (they appear in other species' spectra).

It must be noted that even if in the case presented here these two molecules were reemitted at the same temperature, it has not been the case in every TGA series. The actual reemission temperatures of these two molecules for each TGA series can be seen in Table 2.

The 4 species presented so far are the ones that were identified with most certainty. 3 more were detected and possibly identified and will be presented in the next section.

3.4. Other identified species: octamethyltetrasiloxane (D4), methyl-ethyl-phenyl-ethanone (MEPE)/ 1,3-bis(1-methyl-ethyl)-benzene (MEB)

Before summarizing these results, let us mention a few other species that were only characterized partially. Four new fragments seemed to show single similar reemission peaks. Measurements carried out afterwards allowed the distinction between two pairs: masses 147 and 162 a.m.u. in the one hand and masses 281 and 267 a.m.u. on the other hand. Exploitable TGAs are represented in the following figure 13.

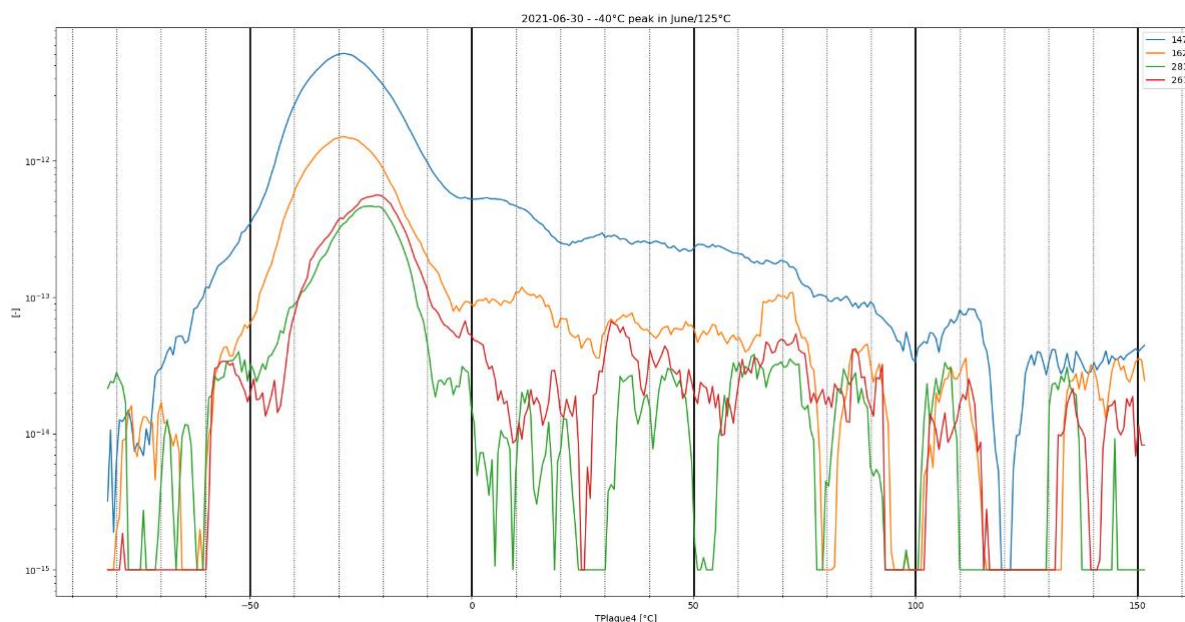


Figure 13. Fragments 147 and 162 a.m.u. as well as 281 and 267 a.m.u. detected during TGA series #3 after an outgassing step carried out at 150 °C.

In figure 13, it is clear that the two pairs of fragments mentioned earlier have their own behavior, suggesting each pair represents a single molecule. Concerning the first pair mentioned, masses 147 and 162 a.m.u., candidate species seen in GC-MS at CNES are two look-alike molecules, namely methyl-ethyl-phenyl-ethanone (MEPE) and 1,3-bis(1-methyl-ethyl)-benzene (MEB). Due to their almost identical molecular weight and structures, it was difficult to distinguish these two molecules, especially since both these molecules were found in GC-MS experiments. The measured ratio of 162 amu to 147 amu signals, is close to 0.25, quite to similar to that of MEB, while MEPE has 0.38 ratio. It is an argument in favor of the former.

The reconstructed spectra of these two molecules are represented in figure 14 below. One can see on their NIST database mass spectra [17], [18] that these two molecules share most of their main peaks (figure 15). The peaks that could have allowed better discrimination are small masses that are most of the time drowned in the facility's background.

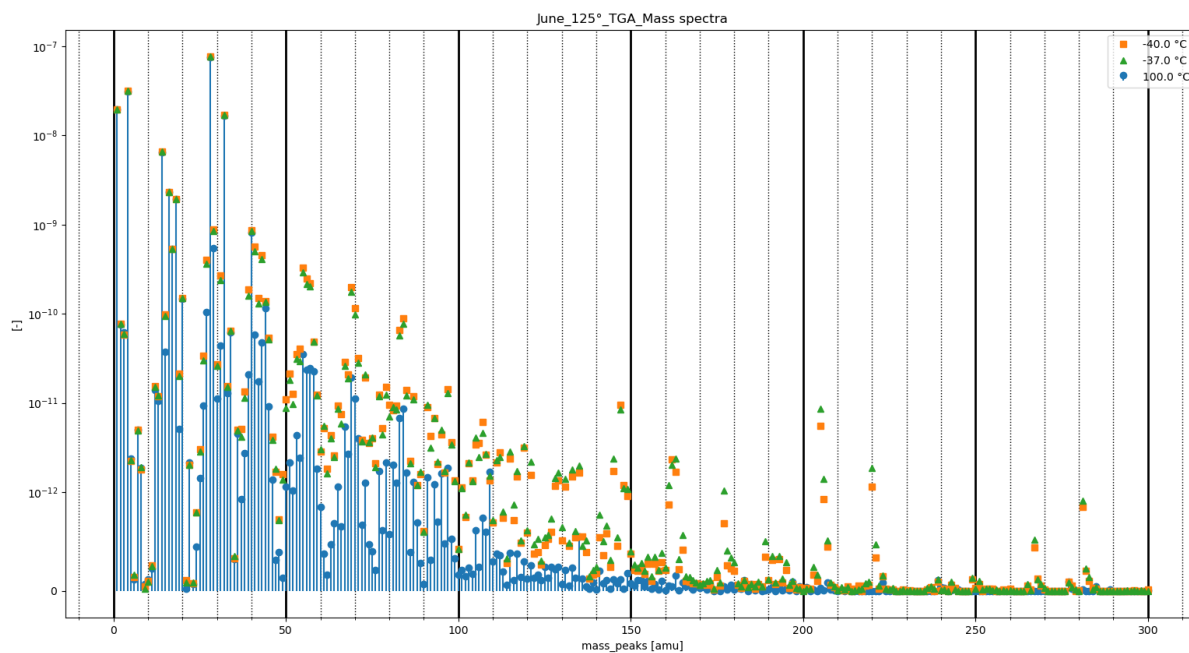
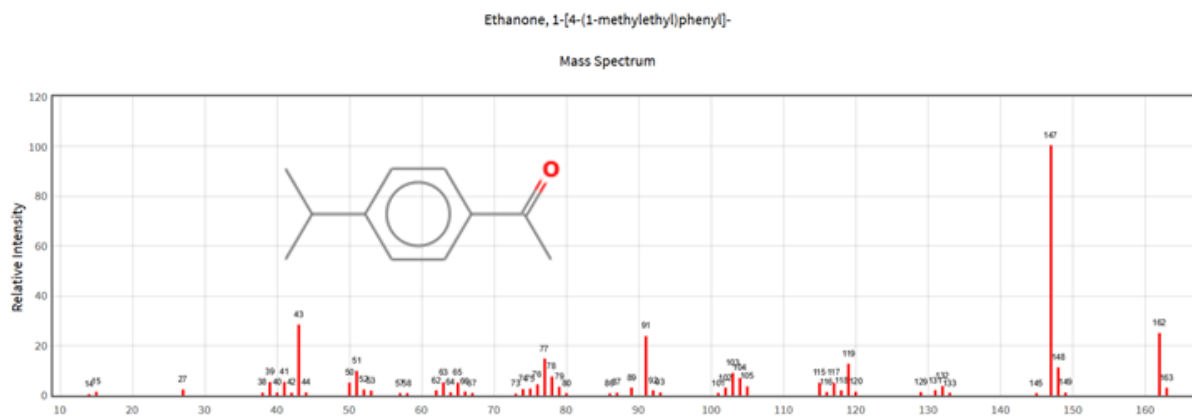


Figure 14. Spectra measured during the peaking of fragments 147, 162, 267 and 281 a.m.u. They were reemitted at two different but close temperatures of $-40\text{ }^{\circ}\text{C}$ for $m/z = 147$ and 162 a.m.u. and $-37\text{ }^{\circ}\text{C}$ for $m/z = 267$ and 281 a.m.u., represented respectively with orange squares and green triangles.

As both were seen in GC-MS, it is also quite probable that both these species are reemitted concomitantly.



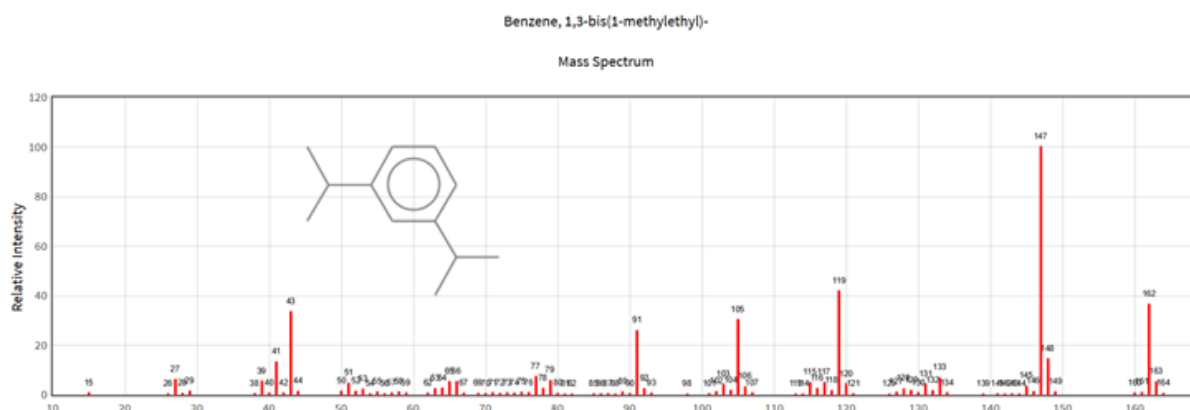


Figure 15. NIST spectra and skeletal formulas of the two candidate species seen in GC-MS having large contributions of fragments 147 and 162 a.m.u., namely methyl-ethyl-phenyl-ethanone and 1,3-bis(1-methyl-ethyl)-benzene.

Concerning fragments 267 and 281 a.m.u., the candidate species is octamethylcyclotetrasiloxane (D4), also observed in GC-MS (figure 16) [15]. This identification may not seem as convincing that the previous ones for several reasons. First of all, one would expect a little bit more signal for fragment 265 a.m.u. than for fragment 267 a.m.u. Besides, the relative amplitudes of fragments 281 and 267 (or 265, 266) a.m.u. would be expected to be in the order of 10 times, whereas they appear similar. Though one should be conscious that a mass spectrometer is not a quantitative tool, such discrepancy with databases has to be noted. Other fragments expected to be found with such molecules are present in the recorded spectra even though their signal is very weak (205, 249, 282 a.m.u.).

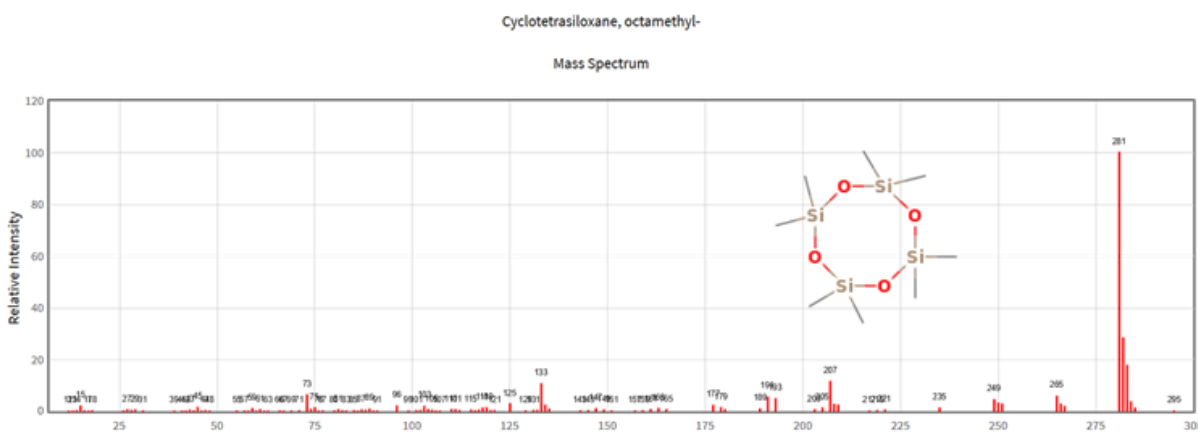


Figure 16. NIST spectrum of the candidate species seen in GC-MS showing contributions for fragments 267 and 281 a.m.u., namely octamethylcyclotetrasiloxane (D4).

Finally, one can mention fragments 58, 88, 223 and 224 a.m.u. that were judged as simple peaks in TGA series 1&2, with reemission peaks at 32 °C. No candidate molecules were identified neither for these four fragments nor for two pairs (their shapes and sizes might have suggested two different pairs: 58 and 88 a.m.u. on one side and 223 and 224 a.m.u. on another side), see figure 17 below.

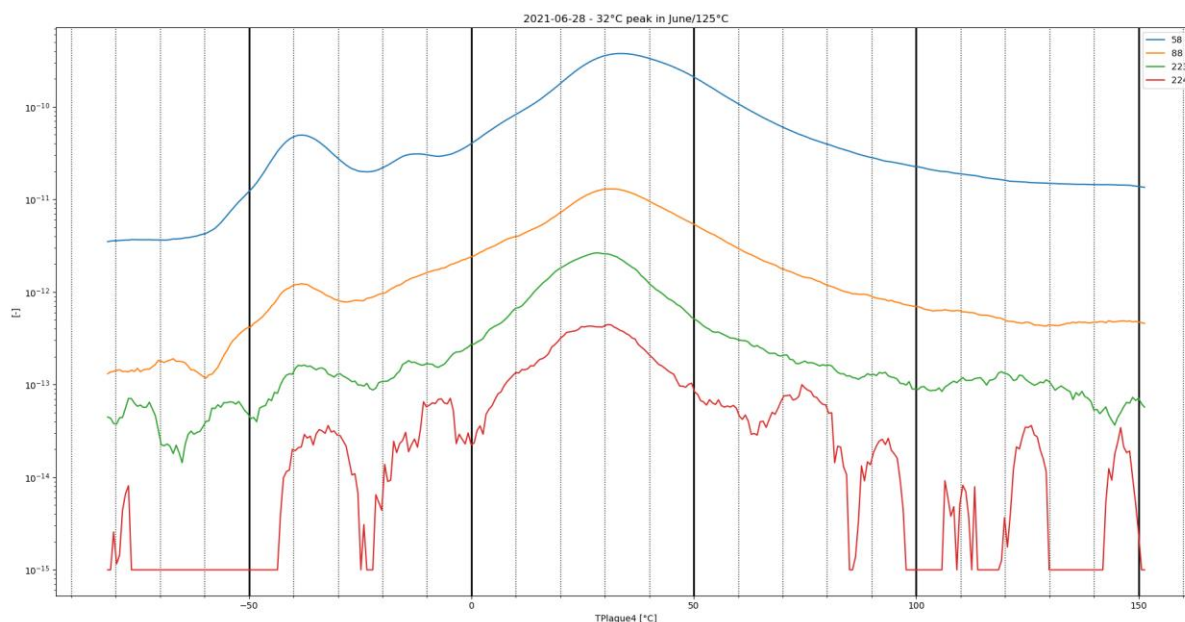


Figure 17. Fragments 58, 88, 223 and 224 a.m.u. seen as “single peaks” in TGA series 1&2.

3.5. The special case of TGAs series #7

Following a drop in sensitivity (about two decades) of the mass spectrometer used for this study, a series of TGAs were carried out trying different parameters to overcome the issue. First of all, a lot more material was put in the effusion cell: 12.72 g compared to 1.38 to 2.28 g in the other experiments presented here. Secondly, the temperature of the effusion cell containing the source material was progressively raised from 75 to 150 °C by steps of 25 °C, without any intermediary reemission (TGA) with sole purpose to increase the amount of matter deposited, thus the signal in the mass spectrometer. The outcome of these new parameters was that the deposit at the surface of the QCMs and the collection plates was huge when compared to other experiments. Whereas the deposits usually present thicknesses of about a few thousands of Angstrom, the one created in such conditions was estimated by the QCM at about 5 μm .

The consequence of such a thick deposit was that almost every contaminant previously separated was reemitted concomitantly (they shared almost the same higher reemission temperature somewhere around -6 °C) (See Table 2 and figure 18). This experiment will prove itself to be very interesting to understand reemission temperature shifts observed along the 11 TGAs series carried out for this study.

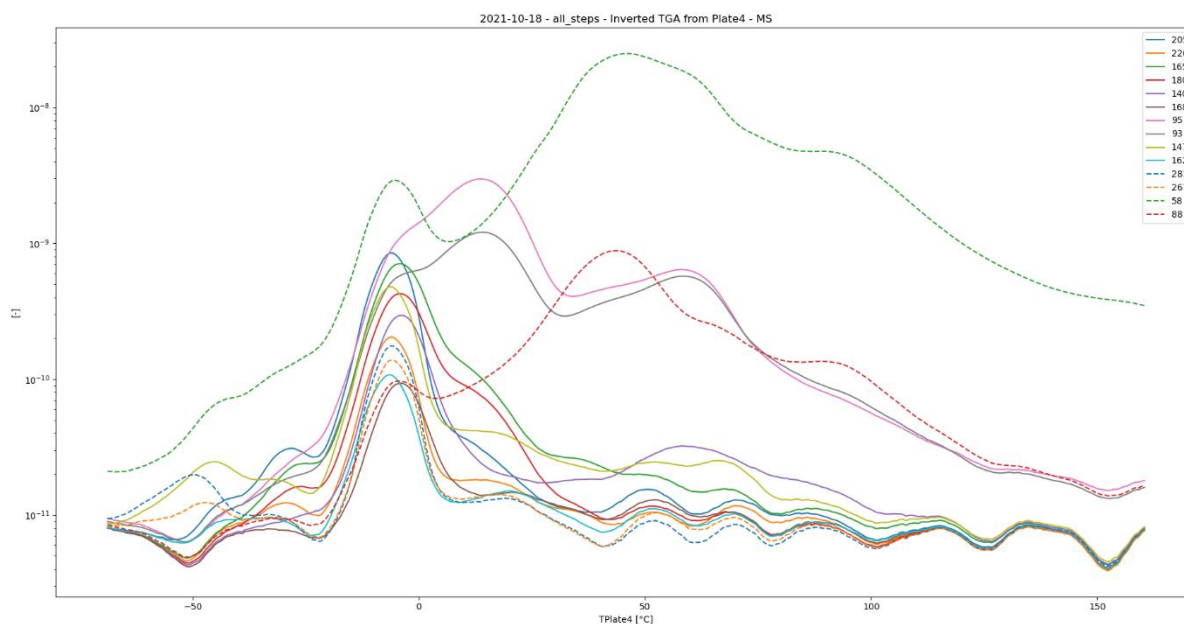


Figure 18. Several fragments representative of the seven separated species outgassed by EC-9323-2. This figure shows that during TGAs series #7, the very large deposit caused almost every species to be reemitted altogether at a higher temperature of about -6 °C.

4. Summary and discussion

The following Table 2 summarizes species identified or simply separated by MS. For each TGA, the temperature at which the reemission peak is reached is indicated. The darker the grey in the table, the better are the separation and identification of the considered species.

Table 2. Reemission temperatures of each species seen in each TGAs series

| TGAs series number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|--|-----|-----|-------------|---------|-----|-----|------------------|--------|----------|-----|-----------|
| Effusion cell outgassing temperature (°C) | 125 | 150 | 75 | 100 | 125 | 150 | 75 to 150 | 75 | 100 | 125 | 150 |
| Species (TGA peaks): | | | | | | | | | | | |
| 1) MEPE/MEB | -40 | -28 | -30 to | -45 to | -45 | -20 | -7 | -50 | -40 | -30 | -28 |
| 2) D4 | -37 | -22 | 0 | -38 | | | | ? | ? | | |
| 3) BHT | -28 | -21 | -30 to -10 | -3 to 5 | -38 | -20 | -7 | -31 | -25 | -22 | -22 |
| 4) 1-Dodecanol | | | -40 to -13 | -26 | -26 | -16 | -4 | -18 | -12 | -10 | -9 |
| 5) Menthol derivative | -13 | -11 | 13 | -32 | -32 | | | -23 | -16 | -15 | -11 |
| 6) CHDM | 8 | 6 | -3 | -16 | -13 | -1 | -5 (et 13 et 60) | -4 | 6 (mult) | 11 | 12 (mult) |
| 7) "32 °C peak" | 32 | 35 | 55 (et -46) | 17 | 20 | 35 | 45 (et -5) | divers | 30 | 40 | 45 |

Sets of fragments exhibiting unique and proportional reemission peaks were found. Each of these sets constitutes part of the mass spectrum of a chemical species. Seven species were separated (numbered in table 2), among which six were identified with a relatively good certainty. To our knowledge, this is the first time outgassed products from a material are characterized in that much details with such techniques.

As it will be outlined in the following section, the number of outgassed species as well as their amount do not allow qualifying this experiment as exhaustive. An important result from these series of experiment, on which emphasis was not yet put in spite of its omnipresence, is the fact that reemission peaks' temperatures vary and shift very often from one TGA to the other. Here, considering the important number of TGAs (11 for the record), the pervasiveness of the phenomenon, the metrological progresses on both the calibration and the thermodynamics of the system used, it is now believed that the shifts observed in the reemission peaks temperatures are absolutely linked to physics.

Table 2 summarizes all the reemission peaks temperatures, species by species and for every TGA. Most variations are in the order of 10 K, though they can reach more than 20 K in some cases. The very thick deposit obtained during TGA series #7 (5 μm thick) is a special one in the matter. In this case, every reemission peaks temperatures increase and pile around $-6\text{ }^\circ\text{C}$, being the sign of a brutal and global reemission of a large part of the deposit. The interpretation that can be made is the one of a very thick layer of (almost entirely) mixed contaminants, among which the less volatile ones disable the migration and reemission of the more volatile ones.

If one overlooks that special case, a trend can be identified in these reemission temperatures. The higher the outgassing temperature leading a deposit, the higher the reemission temperature peak. This trend seems to be general enough, despite being sometimes a little fluctuating if one considers every data available, some of it barely standing out of the noise. If one limits itself to data gathered in TGAs series #8 to 11 (with a brand new mass spectrometer) and to the four species best identified, the trend appears very clearly (figure 19).

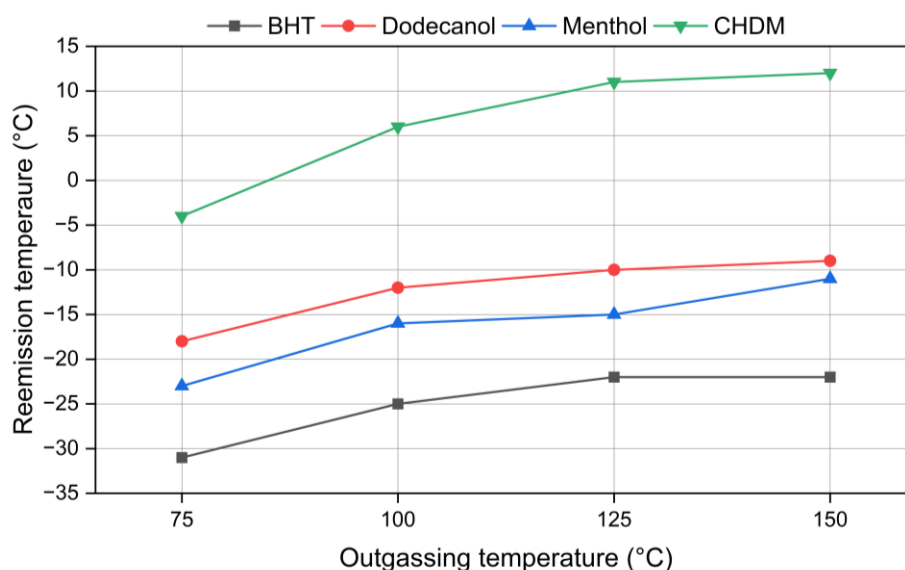


Figure 19. Recorded temperatures of the four main identified species reemission peaks as a function of the outgassing step temperature that leads to their deposition.

If one tries to determine what would a molecule's reemission temperature out of any "mixture effects", it would logically be closer from the left column (outgassing at $75\text{ }^\circ\text{C}$), and probably a little bit lower, since even at that "low" temperature of outgassing a small mixture effect can happen in the deposit made primarily of quite volatile species. That "ideal reemission temperature" that many people have in mind in an idealized or simplified vision could actually be the reemission temperature of the pure substance, unmixed. One could think that this temperature could be reached for very thin (sub-monolayer) deposits, where inter-species interactions stop being prevalent. Unfortunately, in this very case, reemission could be governed essentially by the interactions with the substrate, which could become very strong in this sub-monolayer hypothesis.

Though this stays true, in the scope of the very applicative researches presented here, one should stick to the fact that:

- Reemission peaks temperatures fluctuate and those fluctuations range from 10 to 20 K
- The presence of less volatile species in the deposit seems to drag those reemission temperatures higher
- Very thick deposits exacerbate those shifting effects that tend to pile most species' reemissions together at higher temperature
- Despite these shape and temperature fluctuations, mass spectra are very reproducible from one TGA to the other and are the species' signatures.

5. Conclusion

The work presented in this paper aimed at improving species separation and identification of contaminants outgassed from a space material, namely the epoxy glue Scotchweld EC-9323-2. The knowledge of these species, associated with a marker allowing to follow them individually (m/z fragments specific of each species), will also permit in other works to follow them during the outgassing phase of the source material. This is of prime importance in order to be able to predict and model the behavior of the said material once in space.

Thanks to the TGA/MS method further developed during this study, 7 species were systematically separated (that is to say they were "seen" in every TGA). Out of these 7 species, 4 were identified with a high degree of certainty, namely butylated hydroxytoluene, 1-dodecanol, (1R,2S,5R),1'-(butyn-3-one-1-yl)-menthol and 1,4-cyclohexanedimethanol. Two more were quite well identified, though only a couple of fragments were really characteristic, leaving some room to doubt concerning the actual molecules. These molecules were methyl-ethyl-phenyl-ethanone (or methyl-ethyl-benzene) and octamethylcyclotetrasiloxane. Finally, one species was always separated but could not be identified.

These separation and identification showed that the reemission temperatures of the identified species shifted from one TGA to another. This had been seen in previous studies, especially on Scotchweld EC-2216, and was then thought to be metrological artefacts. In this study, it was systematic and happened for each of the 11 TGAs carried out, allowing to think it is really a physical phenomenon. These shifts usually happened in a 10 to 20 K range. It is believed they originate from mixture effects, in which lesser volatile species trap the more volatile ones. On a very specific case, where the contaminant deposit was very large, (a few microns), the shift in temperature could be several dozens of Kelvin as almost every species were reemitted concomitantly. Despite these shifts, mass spectra reconstructed from the gathered data were very repeatable and were the signature of species. This constitutes a large progress in the separation and identification of outgassed species under vacuum and paves the way to new contamination control standards in the space industry, especially when hurdles of data processing automation will be overcome.

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