

# MOLECULAR CONTAMINATION FROM SPACE MATERIALS: SPECIES CHARACTERIZATION BY TGA / MS

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## ABSTRACT

The precise determination of the outgassing and reemission properties of each contaminant species is an important matter to carry on reliable predictions of contamination levels. Indeed, one contaminant used on a spacecraft in the space environment outgases several molecular species. Each one of these species has its own outgassing and reemission properties. Deposits are composed by a mixture of those molecules and form on sensitive surfaces. The change of the surface properties that they induce may jeopardize the objectives of a mission. As a consequence, the identification of species and the determination of their contribution to the mixture deposit are required for predictions: no separation of their contribution may entail errors of several orders of magnitude on long-term predictions. As reemission properties are temperature dependent, it is possible to carry on a first separation through thermogravimetric analysis (TGA). However, TGA proves to incompletely separate species since reemission peaks overlap. To get a complete separation, ONERA developed a characterization method by coupling TGA measurements with in-situ and in real time mass spectrometry measurements (MS). A code was also built-up for data treatment. The method allows the determination of the main species contribution, their outgassing and reemission properties, as well as their mass spectrum. The chemical nature of the molecules can thus be determined by comparison to mass spectrum data banks. In this work, an epoxy adhesive EC-2216 has been characterized by this method and results were compared to thermal desorption gas chromatography coupled with mass spectrometry (TD-GC/MS) measurements. This comparison is still in progress and the data treatment is not fully complete because time consuming, but some species have already been identified. TD-GC/MS proved that the coupling of TGA/MS method is not only a numerical fit of data but a clear separation of real chemical species. The full work will be finished in the near future.

## INTRODUCTION

Space materials, particularly polymers, release

molecules in the space environment. Molecular contamination levels results from the competition between the arrival rate and the reemission rate of these molecules. Their accumulation forms deposit thereby composed by a mixture of different molecular species. Each one of these species shows its own outgassing and reemission properties [1]. Those are temperature dependent: cold surfaces tend to foster adsorption while hot surfaces favor reemission. Separating species is essential: no separation may induce errors of several orders of magnitude on long-term predictions. A first form of separation can be obtained through thermogravimetric analysis of deposits made on quartz crystal microbalances (QCM) [2-7]. It is based on the temperature dependence of the activation energy of evaporation that is specific to each species. But the TGA separation is not complete: peaks overlap, making impossible to distinguish two neighboring species. Considering one peak, it is sometimes impossible to detect the small contribution of a second or a third species. Therefore, it is essential to carry on characterization experiments accurate enough to identify and quantify each species coming from one contaminant outgassing. Data treatment must provide assessments of their specific outgassing and reemission kinetics. Some methods already exist to identify species, such as gaseous chromatography coupled with mass spectrometry (GC/MS) or Fourier transform infrared spectroscopy (FTIR) [8]. But GC/MS doesn't give any in-situ and real-time quantitative information and FTIR signals are still representative of a mixture of contaminants. The current work presents an in-situ quantitative and qualitative characterization method for molecular contaminants. It is based on the coupling of thermogravimetric analysis and mass spectrometry analysis (MS). Such new experimental data allow the evaluation of the outgassing and reemission properties of each species with reliability. Experiments were carried out with the COPHOS facility at ONERA and data treatment was executed with COMPEX, a numerical tool also developed at ONERA [9]. The recent efforts were focused on separating and identifying species from the reemission of a mixture of contaminants outgassed from an epoxy adhesive EC-2216. Results obtained from TGA/MS experiments were compared to TD-GC/MS measurements on the same material. This technique confirmed that the

TGA/MS method is not only a mathematical fit but a technique that physically separate species and allows their chemical identification. Full results are expected in the near future.

## EXPERIMENTAL FACILITY AND DATA TREATMENT

### 2.1 TGA/MS experimental setup

Inside the COntamination PHOton Synergy (COPHOS) chamber and under a pressure of  $10^{-7}$  mbar, an effusion cell generates a controlled molecular flux by heating the contaminant to be characterized to a desired temperature (50-250°C). Molecules are transported inside a hot shroud towards a collection plate (steel plate of 10cm<sup>2</sup>) and a QCM (Maxteck 6MHz, 1cm<sup>2</sup>) both thermally controlled from -50°C to 250°C (cooling with liquid nitrogen and heating by resistances). After the last outgassing step, a TGA is performed (collection plate and QCM). The flux emitted by the collection plate is analyzed by a mass spectrometer (Hiden Analytical) and a cold QCM. As the QCM signal is temperature dependent, this dependence has been characterized (without any deposit) before the contaminant test. This contribution inherent of the facility and the protocol has been subtracted to the TGA measurements.

### 2.2 Experimental protocol

The outgassing phase is defined by eight temperature steps of 20 minutes, at 75, 100, 125, 150, 175, 200, 225 and 250°C. A TGA is performed at the end of the last step at 250°C with a heating rate of 2°C/min. For both outgassing and reemission phases, the contaminants flux is analyzed by mass spectrometry.

### 2.3 TGA/MS measurements

QCM measurements are recorded every 10 seconds. The mass spectrometer executes a scan of 120 masses, from 105 to 225 mass-to-charge ratio, every 35 seconds. Mass spectra are often represented as a function of time. However, a representation in function of the TGA temperature is more interesting: it allows a much better comparison between TGA signal cf. Fig. 1 and m/z ratios cf. Fig. 2.

### 2.4 COMPEX analysis

Although some of the m/z signals are representatives of single species, most m/z signals are representatives of a mixture of species. Effective separation of species can be obtained by numerical optimization of MS data. To reach this goal, the numerical tool COMPEX is used. This code is described by E. Vanhove and al. [9]. It allows the numerical decomposition of the TGA signal, of the m/z signals, but also determines the mass

spectrum of each species. Some m/z signals had a non-physical behavior and have been deleted from the set of signals used with the code.

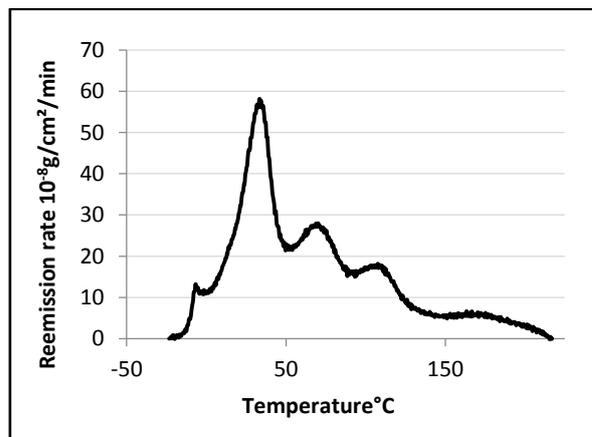


Fig. 1. TGA measurement after the last outgassing step at 250°C

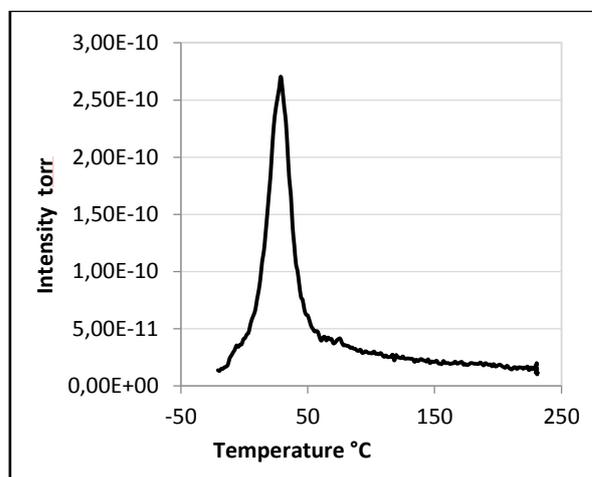
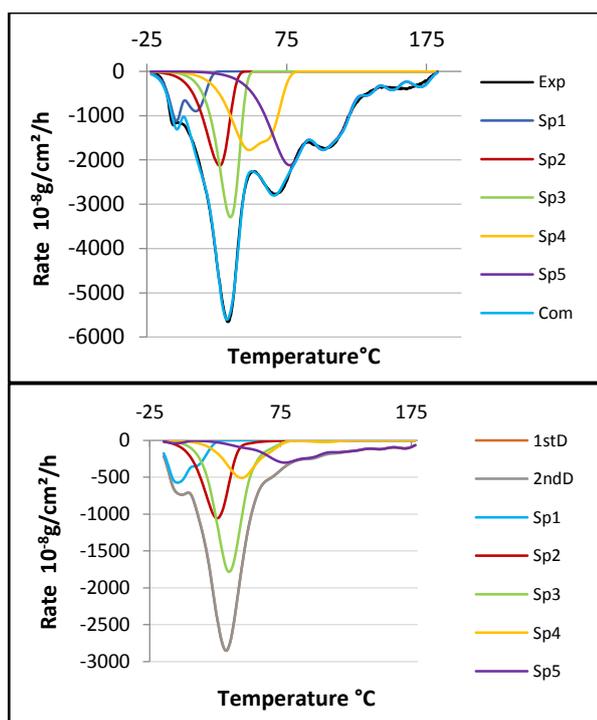


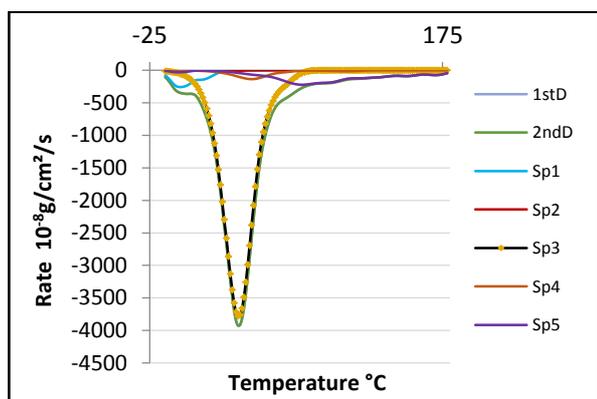
Fig. 2. Intensity of the m/z 165 during the TGA

## DATA TREATMENT RESULTS

The data treatment is not fully complete yet but nevertheless shows a five species separation cf. Fig. 3. They are respectively reemitted at -5, 25, 35, 50 and 75°C. The TGA and all mass signals have been reconstituted by linear combination of the five species found cf. Fig. 3. As an illustration, Figure 4 shows that the 155 mass signal can be attributed to the reemission of one unique species (number 3) whereas 122 mass signal is attributed to several species cf. Fig. 3.



**Fig. 3.** Deconvolution of the TGA signal by COMPEX on the top and deconvolution of the  $m/z$  122 as an illustration on the bottom



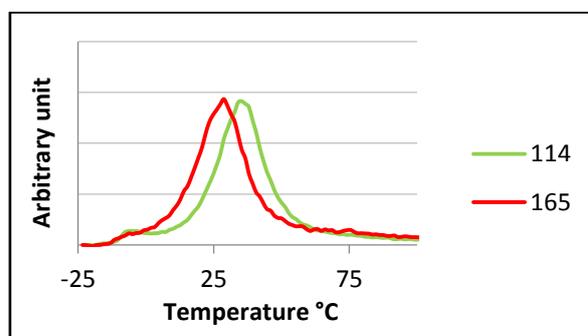
**Fig. 4.** Deconvolution of the 155 mass signal by COMPEX

These results are consistent with previous campaign carried on 2016 [9]. As shown Fig. 5, unlikely to TGA data, MS data allow a clear separation between two neighboring peaks with only an interval of 8°C.

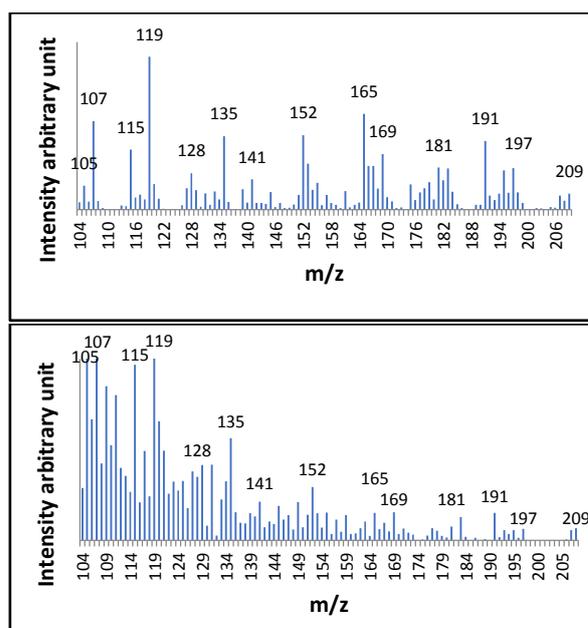
Data cannot be exploited after 75°C because of the too low reemission rate and an artefact of molecule transport towards the mass spectrometer.

The biggest concern was to establish whether the method is able to give a physical species separation rather than a numerical fit. This motivated the comparison with GCMS measurements. So far, two of the five species found were identified thanks to the

confrontation of MS data from COPHOS and TD-GCMS measurements. The mass spectrum of the species 2 shown Figure 6 is very similar to the one of Benzene,1,3-dimethoxy-5-[(1E)-2-phenylethenyl]-, taken from the NIST chemical data bank. Same method has been applied to identify the species 5 as Oxirane cf. Fig. 6.



**Fig. 5.** Distinction between species 2 and 3 from MS data



**Fig. 6.** Mass spectrum of Oxirane on the top and experimental mass spectrum of the species 5 on the bottom

## CONCLUSION

No separation of contaminant species may induce errors of several orders of magnitude on long-term contamination levels predictions. One way to obtain a clear separation is to couple thermogravimetric analysis measurements with in situ and in real-time qualitative

measurements like mass spectrometry. These new experimental data give information about the main species, their contribution, their outgassing and reemission kinetics and their mass spectrum. It is thus possible to clearly identify those molecules by simile with mass spectrum data banks. Comparison with other qualitative characterization techniques demonstrated that such method is not only a numerical fit of data but a real separation of chemical species. As the ONERA's facility and the numerical tool are always in progress, more results are expected in the future.

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