IN SITU ANALYSIS OF CONTAMINANTS DEPOSIT

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ABSTRACT

An *in situ* analysis of contaminants deposit facility has been developed at CNES. The facility features a Fourier transform infrared spectrophotometer (FTIR), a residual gas analyzer (RGA) in addition to a cryogenic quartz crystal microbalance (CQCM). Contaminants are collected and their chemical nature is determined by RGA and FTIR. Quantitative analysis and species separation are performed with CQCM.

1. INTRODUCTION

Satellites are the spearheads of telecommunication and earth and sky observations. However, the success of space missions could be compromised by molecular contamination, which is composed of all the molecules from materials (paints, varnished, glues…), thrust and human activity [1].

Indeed, because molecular contamination might blind and damage the observation instruments, thermo-optical properties of coatings and solar cells, it is a major risk which must be controlled at every step of the life duration of satellites. Currently, different satellites are designed to perform studies in the infrared domain [2, 3, 4].

To avoid a performance loss in every wavelength domain, some challenges have to be faced:

- Characterization of contaminants properties (outgassing and reemission) specie by specie in order to validate and to improve physical models,
- Study of contamination mechanism determined by UV radiations: photofixation, photolysis and degradation of optical properties,
- Estimation of performance loss.

At the moment, ONERA performed many experiments in order to study the identification of species during reemission [5,6]. This led to the improvement of prediction tools [7].

For these points, CNES has developed an *in situ* and real-time contaminants deposit characterization facility based on FTIR, RGA and CQCM.

A similar facility was developed by the aerospace corporation in the 80's [8]. The interest was to avoid the desorption of contaminants by returning to the standard conditions for temperature and pressure. This paper showed the necessary minimal thickness to obtain an IR signal; some absorption bands increasing with thickness. In this facility, a thickness of 200 Å seemed to be sufficient to characterize methyl and methylsiloxane groups. As expected, substrate temperature where are collected contaminants is also a key factor (order of magnitude is some µg/cm² with cryogenic surfaces).

Another similar facility was constructed by JAXA [9]. The goal of this study was to evaluate the bake-out effectiveness by optical measurement of a contaminated surface. A bake-out of RTVS691 material (72 h at 4 kPa at different temperatures) was performed. Then, RTVS691 material was heated at 125 °C. The IR deposit absorbance was measured during 10 h on a surface cooled at -10 °C in a vacuum chamber (10^{-4} Pa). This study showed that the higher the bake-out temperature, the lower the thickness of contaminants. Moreover, the authors suggest to realize *in situ* optical measurements for tracking the effectiveness of the bake-out temperature.

Finally, the CNES facility is described in this paper and the first very preliminary results are presented.

2. INSTRUMENTATION

The vacuum chamber (**Fig. 1**) is a stainless-steel tank pumped with a Leybold TurboVac 151 turbopump. Joints are made with copper gaskets. Thermocouples are stuck on oven and CQCM / germanium plate support with outgassed adhesives. No background contamination was observed except classic molecules such as water, nitrogen, carbon dioxide and oxygen.
The infrared spectrophotometric system is a ThermoScientific Nicolet 6700 spectrophotometer. Following parameters were used: wavenumber = [600-4000 cm^{-1}], 128 scans, resolution = 4 cm^{-1}, acquisition with the reflection-absorption mode. A MCT detector is outside the vacuum chamber in a chamber electronically linked to the spectrophotometer. This chamber is flushed with GN$_2$.

The sample position is 15 cm from the CQCM / germanium plate. Angle between infrared incident beam and infrared reflected beam is inferior to 15 °.

CQCM is a QCM Research MK18 (15 MHz) QCM.

An Inficon Transpector MPH300M residual gas analyzer is interfaced to the system for mass analysis and detection of outgassed species.
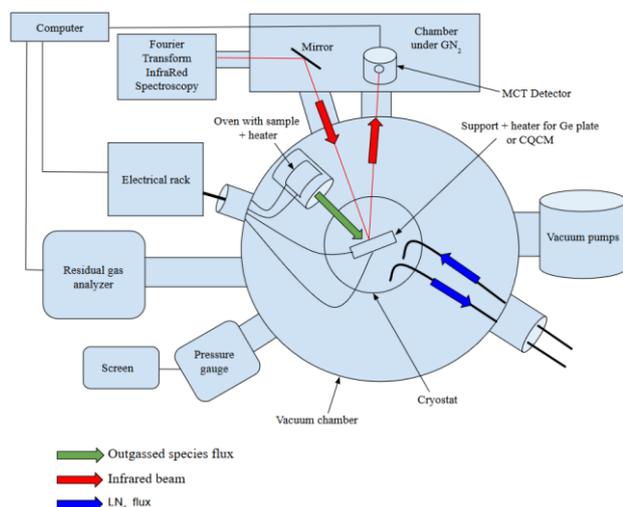
Pressure gauge is a Pfeiffer full range gauge.

Fig. 1: IR-cryostat facility.

Gas chromatography (GC) analysis was performed with a Clarus 500 chromatograph (Perkin Elmer Elite 5-MS column with dimensions of 60 m x 0.25 mm x 0.25 μm) coupled to a TurboxMatrix 300 TD thermal desorber (TD) and a Clarus 500 mass spectrometer (MS).

3. EXPERIMENTAL

3.1. Materials

Samples of Room Temperature Vulcanizing (RTV) S691, which is a silicon-based compound, were polymerized with a mass ratio of 9:1 (compounds A:B).

3.2. Procedure

The vacuum chamber was cleaned with xylene and IPA to remove any contamination from silicon-based compounds and other ones.

After having weighed the sample material, this one was placed on the sample holder in the oven.

MCT detector was filled with LN_2. Pumping system was switched on to reach a pressure of 10^{-7} mbar. LN_2 was then introduced in the system to reach a temperature of -110 °C on the support where CQCM or germanium plate is placed. An IR background was performed.

Sample was then heated at defined temperature and duration. RGA was switched on to record outgassed species from the sample material.

Once the deposit has been performed and RTVS691 sample cooled at 20 °C, reemission started from -110 °C to 30 °C.

The experimented lasted from 5 to 10 days.

Between experiments, ambient pressure was reached with GN_2. The vacuum system was cleaned and baked-out during 24 hours.

4. RESULTS AND DISCUSSION

4.1. Preliminary analysis

Before carrying out any outgassing and reemission experiments, RTVS691 sample was heated at 250 °C during 10 min (ambient pressure) in the TD-GC-MS system where its chromatogram is shown in **Fig. 2**.
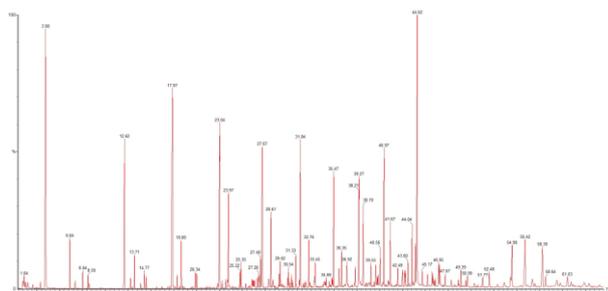

Fig. 2: Chromatogram of RTVS691 sample heated at 250 °C during 10 min.

This analysis was performed to track any interesting fragments of molecules which could be outgassed or reemitted.

Main fragments observed are 57, 78 amu (benzene, $t_r = 4$ min), 73 amu (siloxane, $t_r = 18$ to 35 min) and 135 amu (siloxane / silane, $t_r = 41$ and 50 min) fragments. These fragments will be tracked with RGA.

Peak at $t_r = 44.6$ min is decanoic acid.

4.2. Feasibility

This system was first tested to check if infrared spectrophotometer was fully operational.

A germanium plate was used to collect contaminants at -110 °C. RTVS691 was heated at 125 °C during 24 hours then cooled at 20 °C during reemission.

Fig. 3 shows the IR spectra obtained at different temperatures.

First, IR spectrum was acquired when germanium plate was contamination-free (RTVS691 sample was not heated). Only water absorption band is observed (O-H, 3500-3000 cm^{-1}). When sample is heated, water absorption band is increasing, hydrocarbon absorption band (C-H$_3$, 2960 cm^{-1}) and silicone absorption bands (Si-O-Si, 1260 cm^{-1} / 1150-1000 cm^{-1} / 805 cm^{-1}) appears.

Water, hydrocarbons (solvent...) and fragments of silicon-based compounds are outgassed at 125 °C and

collected on the germanium plate.

Then, reemission was attempted from -110 °C to 60 ° (20 °C step) with a pressure stabilization before starting a new reemission step. Water was desorbed at -50 °C from the germanium plate. Silicone fragments remained, even at 60 °C. This might be explained by a temperature or duration too low to desorb those fragments.
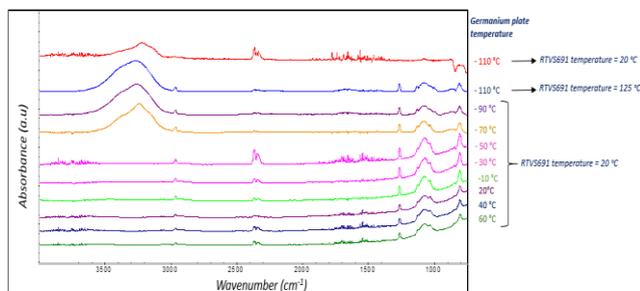

Fig. 3: IR spectra of germanium plate at different temperatures. RTVS691 was heated at 125 °C during 24 hours then cooled at 20 °C to avoid any extra outgassing during reemission.

With this first experiment, feasibility of this facility is proven: spectra are acquired with correct resolution and intensity.

RGA and CQCM will be now implemented in the next experiments and separation species will be attempted.

4.3. Reemission experiments

5 g of RTVS691 sample was outgassed from 25 °C to 125 with a 25 °C step during 24 hours for each step. CQCM was heated for reemission from -110 °C to 30 °C with a 20 °C step. Only the analysis at 75 °C will be explained in details for more convenience.

RGA fragments tracking and evolution of area density on CQCM are available on **Fig. 4** and mass losses as a function of temperature are summarized in **Tab. 1**.

Small mass losses are observed from -90 °C to -30 °C (0.28 µg, 0.12 µg, 0.17 µg and 0.17 µg). 57 and 73 amu fragments are slightly desorbed at -90 °C and -70 °C.

At -10 °C, the most important mass loss was observed (1.78 µg). This corresponds to the desorption of 57, 73 and 78 amu fragments. Water may be one of the most important contributors to this mass loss. 18 amu fragment will be then tracked in the next experiments.

At 10 °C, 57 and 73 amu fragments are slightly desorbed. No change of the 135 amu fragment was observed during whole experiment. This might be explained by the too low desorption temperature, the view factor between CQCM and RGA or the very low amount of 135 amu fragment on the CQCM.
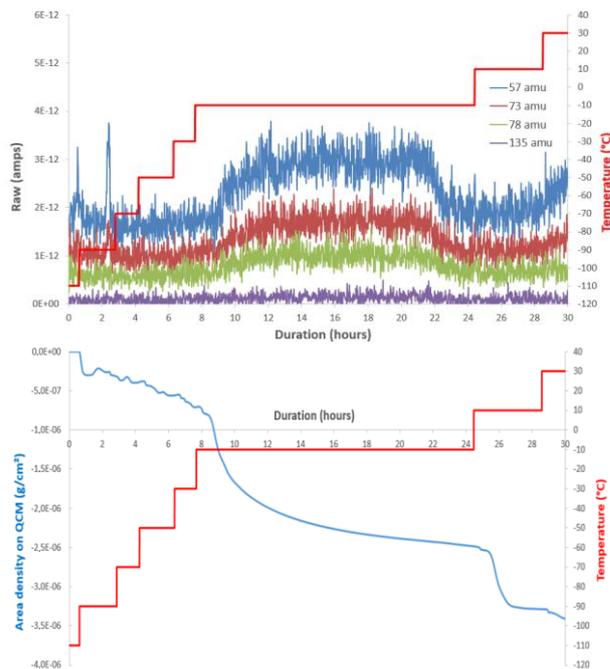

Fig. 4: RGA fragments tracking and evolution of area density on CQCM as a function of time and temperature. RTVS691 sample was previously heated at 75 °C during 24 h.

Tab. 1: Amount of contaminants as a function of CQCM temperatures. RTVS691 was heated at 75 °C during 24 hours.

CQCM temperature (°C)	RTVS691 sample temperature (°C)	Amount of contaminants adsorbed (µg)
-110	75	3.45

CQCM temperature (°C)	RTVS691 sample temperature (°C)	Amount of contaminants desorbed (µg)
-90	20	0.28
-70	20	0.12
-50	20	0.17
-30	20	0.17
-10	20	1.78
10	20	0.79
30	20	0.14

Unfortunately, no IR absorption bands of interest was observed during most of experiments except for 125 °C temperature (**Fig. 5**). This result was not expected since the feasibility has been tested and proven on germanium plate. View factor between oven and CQCM should be improved and the absence of IR absorption bands at other temperatures than 125 °C is currently under investigation.

At 125 °C, the same absorption bands than the previous ones are observed: water (O-H, 3500-3000 cm^{-1}), hydrocarbon (C-H$_3$, 2960 cm^{-1}) and silicone (Si-O-Si, 1260 cm^{-1} / 1150-1000 cm^{-1} / 805 cm^{-1}). Band intensities slightly decrease when temperature increases due to the slow desorption of contaminants. In the next experiments, thickness of contaminants will be calculated.
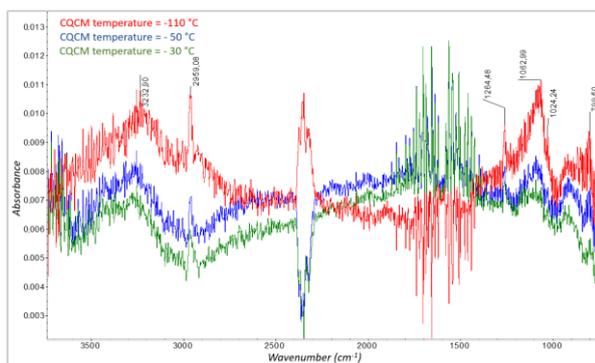

Fig. 5: IR spectra of CQCM at three temperatures: -110 °C, -50 °C and -30 °C. RTVS691 sample was heated at 125 °C during 24 h.

The different experiments are summarized in **Tab. 2**, **3**, **4** and **5**.

Tab. 2: Amount of contaminants as a function of CQCM temperatures. RTVS691 was heated at 25 °C during 24 hours.

CQCM temperature (°C)	RTVS691 sample temperature (°C)	Amount of contaminants adsorbed (µg)	RGA fragments
-110	25	2.24	57, 73, 78
CQCM temperature (°C)	RTVS691 sample temperature (°C)	Amount of contaminants desorbed (µg)	57
-90	20	0.20	none
-70	20	0.11	none
-50	20	0.36	none
-30	20	0.58	none
-10	20	0.35	none
10	20	0.53	57, 73, 78
30	20	0.16	57, 73, 78

Tab. 3: Amount of contaminants as a function of CQCM temperatures. RTVS691 was heated at 50 °C during 24 hours.

CQCM temperature (°C)	RTVS691 sample temperature (°C)	Amount of contaminants adsorbed (µg)	RGA fragments
-110	50	2.17	57, 73, 78
CQCM temperature (°C)	RTVS691 sample temperature (°C)	Amount of contaminants desorbed (µg)	
-90	20	0.20	none
-70	20	0.05	none
-50	20	0.06	none
-30	20	0.50	none
-10	20	0.87	57
10	20	No value taken	57, 73, 78
30	20	0.42	73, 78

Tab. 4: Amount of contaminants as a function of CQCM temperatures. RTVS691 was heated at 100 °C during 24 hours.

CQCM temperature (°C)	RTVS691 sample temperature (°C)	Amount of contaminants adsorbed (µg)	RGA fragments
-110	100	4.74	57, 73, 78
CQCM temperature (°C)	RTVS691 sample temperature (°C)	Amount of contaminants desorbed (µg)	
-90	20	0.22	none
-70	20	0.12	none
-50	20	0.15	none
-30	20	0.07	none
-10	20	0.48	57
10	20	2.86	57, 73, 78
30	20	0.79	57, 73, 78

Tab. 5: Amount of contaminants as a function of CQCM temperatures. RTVS691 was heated at 125 °C during 24 hours.

CQCM temperature (°C)	RTVS691 sample temperature (°C)	Amount of contaminants adsorbed (µg)	RGA fragments
-110	125	7.87	57, 73, 78, 135
CQCM temperature (°C)	RTVS691 sample temperature (°C)	Amount of contaminants desorbed (µg)	
-90	20	0.30	none
-70	20	0.22	none
-50	20	0.08	none
-30	20	0.12	none
-10	20	0.76	57
10	20	2.00	57, 73, 78
30	20	3.90	57, 73, 78

These results show that the most important reemission occurs from -10 °C. The higher the outgassing temperature, the higher the reemission temperature to get an important desorption. For an outgassing temperature of 125 °C for example, total mass loss desorbed from -110 °C to 30 °C does not correspond to the total amount of contaminants: 30 °C is not enough to desorb all contaminants, especially when outgassing temperature is high; 135 amu fragment appearing at 125 °C only and might be still stuck at 30 °C.

During RGA analysis, fragments are not visible at low temperature even if mass loss occurs. View factor should be improved to see what fragments are outgassed at low temperature. Water might be the main compound to be desorbed at low temperature: this will be confirmed by tracking the 18 amu fragment.

Even if a lot improvements have to be made, these first results prove the possibility of following separation species with a quantitative method.

5. CONCLUSION

The conclusions from these first experiments are:

- Feasibility is proven and separation of species is possible. Repeatability needs to be done to completely validate this facility.
- Protocol of analysis should start with TD-GC-MS analysis to specify what fragments to track. Then, outgassing and reemission at a specific temperature should be performed with duration depending on CQCM stabilization. CQCM, RGA and FTIR will allow us to get a quantitative analysis of deposit and reemission.

This facility has the potential to be useful for identification and quantification of outgassed species. However, a lot of work is still ongoing:

- Improvement of the view factor between CQCM and sample,
- Improvement of the control and concentration of contaminants flux,
- Potential implementations of ellipsometry and UV source.
- Different supports to be contaminated (IR compatibility) and materials to be tested.

The main information which could be soon obtained is the thickness of deposit as a function of temperature / substrates / materials, nature of outgassed and reemitted molecules, the effectiveness of bake-out...

Results will allow us to improve the design of CNES getters, prediction and mitigation.

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