ADVANCED IN SITU REAL TIME ON GROUND CONTAMINATION MONITORING

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1. INTRODUCTION

Contamination control is a critical aspect of risk mitigation for contamination sensitive surfaces under vacuum conditions. Molecular organic contaminants (MOC) that are deposited on sensitive surfaces like electrical components, tribological contact surfaces or optical parts decrease the performances of instruments, equipment and in some case of entire subsystems. These contaminations are omnipresent in space business, especially at higher temperatures wherever materials are at limit of application range. None of the currently used techniques or their combinations provides a real-time, in situ quantitative and qualitative analysis of surfaces of spacecraft and/or components during thermal vacuum tests. Second, the transferring of surface samples is done generally through ambient atmosphere from the test vacuum chambers to the facility for analysis. During this the MOCs collected on the surface are exposed among others to oxygen and humidity which can cause chemical reactions and/or loss. The goal of this project was to develop a mobile and flexible device for both qualitative and quantitative in situ measurement of MOCs under thermal vacuum conditions and simultaneously get rid of the disadvantage of possible losses during sample decontamination while airing the vacuum chamber or transport.

2. ACKNOWLEDGEMENT

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3. STATE OF THE ART

Find a summary of most frequently used contamination monitoring and analysis methods in space business in the next subsections. Based on this summary a decision for the analysis method and mechanical/optical design was made.

3.1. TQCM

Thermally stabilised quartz crystal microbalances (TQCM) allow measuring the adsorbable amount of molecules contained in the residual gas very precisely and on-line, but do not provide information regarding the chemical structure of the contaminants. The amount of adsorbed material on the crystal surface leads to a frequency change which can be approximately converted to a total sublimated mass of the tested component. The temperature and material – especially the coating – of the quartz crystal surface can influence the amount and type of adsorbed molecules.

3.2. RGA

Residual Gas Analysis (RGA), for example by mass spectrometry, is real-time and in situ. It is important to highlight that this technique represents the residual gas inside the vacuum chamber and not the adsorbed MOC species on an exposed surface. Moreover, RGA is limited to molecules with low molecular weight.

3.3. XPS

X-ray photo spectroscopy (XPS) is a common ex situ analysis method which can be used for example on witness foils. These foils are placed on critical parts of the component to be tested during thermal bake-out under operating parameters. XPS provides a detailed qualitative elemental analysis of the contaminated surface down to a depth of some nanometers.

3.4. IR spectroscopy

Infrared spectroscopy is a common analysis tool in industry and space business, mostly used in the medium infrared range (MIR) of 2.5 µm up to 25 µm. On one hand functional groups can be identified by comparison with reference spectra if the material composition is mostly unknown. In this case the identification of functional groups can be difficult. On the other hand with knowledge of possible material compositions of a contaminated surface a detailed analysis can be made more easily.

4. CONCEPT

A review revealed as most promising concept a combination based on an IR-technique for specifying the functional group and identifying contaminants and on the other hand a TQCM system for quantifying the mass gain. The TQCM crystal is used both as witness
plate and “mirror” for in situ infrared reflection absorption spectroscopy (FT-IRRAS). FT-IRRAS is a variant of IR spectroscopy probing a small layer of IR active substances (adsorbed molecules, surface contamination) on a reflective non IR active “mirror” surface. IRRAS is a combination of transmission and reflection spectroscopy, as the IR beam passes twice through the adsorbate. The sensitivity of the method is strongly dependent upon the angle of incidence and the polarization of the IR beam. High amplitudes of the electric field vector at the surface will result in stronger interactions with adsorbed molecules. The absorbance peaks at an angle of incidence around 88° for unpolarised and especially for p-polarises light, while s-polarised light shows no significant interaction. This is utilized in polarization modulated IRRAS (PM-IRRAS). Furthermore, the absorbance increases – as expected – with film thickness, hence the method can be used for quantitative analysis. However, also the angle of maximum absorbance shifts to lower values with increasing adsorbate film thickness. It has to be noted, that grazing angle IRRAS spectra can differ significantly from bulk transmission because of the influence not only by the absorption coefficient \( k \) but also by the refractive index \( n \).

4.2. Mechanical setup

The core part is a small OEM FT-IRRAS spectrometer. It is a very compact system with dimensions of approximately (21×21×12) cm. The TQCM system and the window flanges are mounted at a small vacuum chamber (“ConMon cube”). The ConMon cube itself is attached to the respective testing vacuum chamber and is designed for a complete bake out up to 200 °C to reach UHV with a pressure of \( 10^{-9} \text{ mbar} \). The ConMon cube is custom-designed by AAC.

5. FUNCTIONAL TESTING

This chapter shall give an overview of the timeline and functional tests done for validation.

5.1. Long-time stability of QCM system

The long-time stability of the QCM system is shown in Table 1. Meanwhile a cooling temperature of -20 °C is possible due to a better isolation. Lower temperatures would require an upgrade of the cooling system to liquid nitrogen. The reference frequency represents the covered reference quartz which represents the baseline for the measuring quartz. Considering a typical frequency change of the measuring quartz in a range of several 1000 Hz a peak-to-peak value of 4 Hz due to noise and a slight temperature drift is negligible.
Table 1: Long time statistics of QCM

<table>
<thead>
<tr>
<th></th>
<th>Quartz crystal temp. / °C</th>
<th>Reference frequency / Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>-13.47</td>
<td>5989396</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.04</td>
<td>0.6</td>
</tr>
<tr>
<td>Peak-to-peak</td>
<td>0.3</td>
<td>4.0</td>
</tr>
</tbody>
</table>

5.2. Manual Contamination of QCM surface

For validation of detection of contaminants on the surface of the QCM, a small amount (0.07 mg) of Fomblin Z25 was applied to the surface of the QCM manually. The IRRAS spectrum was compared to the ATR reference of Fomblin Z25 and ATR measurements on the QCM crystal that was used beforehand in the IRRAS setup. The contaminant could be identified using the ConMon IRRAS method. Find a plot in Annex A, 7.1.

6. VALIDATION TESTING

6.1. ConMon module TQCM data

During this project a lot of validation tests were done to show the functionality of the setup. The long-time stability of the IRRAS baseline was shown and an outgassing test with an electrical plug for vacuum applications was done successfully.

![Figure 3: Cut-out of vacuum plug](image)

Figure 4 and Figure 5 are showing the sample temperature, the mass loss of the sample measured with a high precision balance in the sublimation chamber and change (decrease) of frequency of the TQCM which is already temperature compensated during the measurement. This is realized with a covered reference quartz. The frequency curve shown in Figure 5 is the difference of frequency on the measuring quartz and the frequency of the covered reference frequency.

Figure 4: Sample temperature

![Figure 4: Sample temperature](image)

Figure 5: Mass loss and frequency change

The process of resublimation on the QCM surface is starting about 7 h after test start when constant test temperature is reached and a sufficient outgassing rate is exceeded. The noise pattern which can be seen in the mass loss curve between hour 11 and 23 is no measurement error or signal noise. This behaviour is well known at AAC and indicates a spontaneous outgassing of whole surface areas – outgassing of pores – from the sample. Each of these processes causes a reaction force to the sublimation sample holder and subsequently the high precision balance. This effect does also influence the vacuum pressure. The same noise pattern can be found there because the spontaneous outgassing of pores leads to slight vacuum pressure fluctuations.

At around hour 25 of the test, the active heating of the sample is stopped and the passive cooling process of the sample starts. Figure 6 shows a detailed plot of this process. The sample temperature decreases and the mass loss of the sample stops at this point. The detected mass gain on the QCM surface – the delta frequency measured due to re-sublimated MOCs on the QCM surface – decreases slowly up to approximately hour 26.7. This indicates minimal mass loss rate at the QCM surface.
After 26.7 hours the active cooling of the QCM was turned off which led to a passive heat up phase of the quartz crystals to room temperature. Simultaneously, an increase of the vacuum pressure and a nearly total loss of the collected mass on the QCM surface can be observed. This is shown in Figure 7. It has to be stated here that the exact temperature of the quartz crystal surface is unknown since the thermocouple is located in the quartz crystal holder.

Compared to the highest measured delta frequency of 4700 Hz the remaining delta frequency of 330 Hz indicates that around 93% of the collected mass on the QCM surface sublimated during the heat up phase. Additionally a mass loss occurs while venting the vacuum chamber. This mass loss cannot be quantified online because both systems – the QCM and the high precision balance of the sublimation chamber – are affected in a chaotic way during venting process.

6.2. ConMon module IRRAS data

For better visualisation find larger plots of the IRRAS spectra during validation testing in Annex A, 7.3. Due to missing information on the customer’s vacuum plug material and composition a literature research (NIST database) was done. No exact correlation with a specific material could be found. Find a summary table in Annex A, 7.2.

6.3. Comparative measurement with RGA

During validation test additionally a RGA was done using a quadrupole mass spectrometer. During the sublimation test the spectra acquisition interval was set to 30 min. At the end of the test and before the start of the QCM heat up period back to room temperature the acquisition period was set to 5 min to allow a better observation of the sublimation process during this phase from the QCM surface. Find larger plots for better visualisation in Annex A, 7.3.

The data shows a decrease of nearly all significant peaks during heat up phase of the TQCM surface which confirms that nearly all collected mass on the surface sublates during this phase.

CONCLUSION

The validation tests were done successfully on a limited number of samples. In the final validation test the remained mass gain on the QCM surface after the passive heat up phase from -20 °C up to room temperature is only 7% of the total mass gain. This indicates a great mass loss – the collected mass sublimates. Taking this into account some species may be not visible on the TQCM surface at room temperature when analysed using ex-situ methods for identifying the MOCs. This behaviour was confirmed in several ex-situ analysis using XPS and ATR devices. This new findings qualifies the ConMon IRRAS module as additional instrument used while bake-outs and can be used – maybe additional to the currently used ex-situ analysis on QCM surfaces – to characterise MOCs for different components or space materials.

REFERENCES

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2. Outgassing, ECSS Q-ST-70-02C
3. Kinetic outgassing, ECSS-Q-TM-70-52A
4. Detection of organic contamination of surfaces by infrared spectroscopy, ECSS-Q-ST-70-05C
6. Recent advances in QCM-based sensors, DOI: 10.1155/2011/571405
7. **ANNEX A**
For reasons of better visualisation find here a compilation of more detailed plots and images.

7.1. **Manual contamination of TQCM surface**

The band at 1400 cm\(^{-1}\) is strongly pronounced in IRRAS compared to the ATR reference. In this region a weak CF\(_3\) band could be found. As already stated in section 4 the grazing angle IRRAS spectra can differ significantly from bulk transmission because of the influence not only by the absorption coefficient \(k\) but also by the refractive index \(n\). The lower fingerprint regions from 600 up to 1000 cm\(^{-1}\) are comparable in all 3 tests. Compared to the ATR measurements of Z25 (liquid reference and thin layer on QCM) the bands in the IRRAS measurement (thin layer on QCM) using the ConMon setup are pronounced different. The IR bands in the range of 1800 up to 2800 cm\(^{-1}\) couldn’t be identified until now.

![Figure 8: Spectra composition for Fomblin Z25, sorted from highest to lowest peak at 1100 cm\(^{-1}\): liquid ATR, residue ATR, liquid IRRAS](image-url)
7.2. ConMon module IRRAS data (validation testing)

Figure 9 shows different IR spectra during validation testing. The spectra are sorted in chronological order beginning with the baseline at test start. The last spectrum on the top is taken after the heat up phase of the TQCM system. As already observed in TQCM frequency data the condensed mass on the quartz crystal surface sublimated here. The spectrum below was taken right before the start of the TQCM heat up phase and represents the maximum amplitude. Peaks of H$_2$O and CO$_2$ due to a slight baseline drift are visible and slightly drifting over test duration. This is caused by a leakage in the ConMon module housing.

![Figure 9: IRRAS spectra composition during validation test with vacuum plug](image)

As stated in section 6.2 no material data from customer’s side was available. A literature research (NIST database) was done. No exact correlation with a specific material could be found.

<table>
<thead>
<tr>
<th>Wavenumber / cm$^{-1}$</th>
<th>Range</th>
<th>Description (material suggestions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>766, 814, 840 (760 – 850)</td>
<td>Fingerprint region</td>
<td>-</td>
</tr>
<tr>
<td>901 (890 – 920)</td>
<td>Fingerprint region</td>
<td>1,4-Dioxane</td>
</tr>
<tr>
<td>1031, 1107, 1134 (1000 – 1160)</td>
<td>Alkoxy C-O</td>
<td>1,4-Dioxane (1107)</td>
</tr>
<tr>
<td>1214</td>
<td>C-O</td>
<td>-</td>
</tr>
<tr>
<td>1272</td>
<td>C-O</td>
<td>1,4-Dioxane</td>
</tr>
<tr>
<td>2912, 2963 (2900 – 2990)</td>
<td>Aliphatic C-H stretch</td>
<td>1,4-Dioxane (2900-2990)</td>
</tr>
</tbody>
</table>
7.3. Comparative measurement with RGA

Figure 10 shows the plot of the RGA for the whole test duration including the cool down phase of the sample to nearly room temperature. This results in a decrease of the significant peaks due to a stop of outgassing.

Figure 10: RGA plot, full test duration

Figure 11 shows the plot after sample cool down was already finished, but before starting the TQCM system heat up phase. The peaks starting with measurement cycle 3 show the sublimation of condensed mass on the quartz crystal surface and therefore the mass loss which also can be observed in the IR data.

Figure 11: RGA plot, heat up phase of TQCM system