

# HIGHLY SENSITIVE MATERIAL EMISSION PROFILING METHOD AT ELEVATED TEMPERATURES BY AUTOMATED TIME SERIES TD-GC/MS

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## ABSTRACT

On major contamination topic is the emission of volatile molecular organic compounds (MOC) from space materials at elevated temperatures. Even traces of these volatiles may condense on optics and other functional parts and subsequent lead to performance loss. Different test methods exist in order to assess this phenomenon. Total mass loss measurement (TML) as a gravimetric approach is well known but does not meet the performance in order to detect ultra-trace emissions over time. For some polymeric materials used as coatings in space applications, outgassing is not only the emission of additives, but a slight breakdown of the material itself at elevated temperatures. This effect can't be detected by TML measurements and single snapshot emission measurements. For the detection of possible material breakdown, the emission over time is assessed using the method described in this article.

Subsequent evaluation of the time dependent MOC emission data will show clearly if the emission is based on thermal degradation of the material itself or release of volatile components present in the material matrix. During the assessment of different materials, degradation was most obvious for one material example at elevated temperature. Based on these results, a contamination of exposed material surfaces during a thermal vacuum bakeout (TVB) in combination with the assessed material was predicted. A cleaned witness sample provided in a suitable transport container was placed into the TVB-chamber together with the component coated with the material of interest. After the TVB process, the witness sample was analysed by thermal desorption GC/MS. On the witness sample, the same MOC contamination could be detected as measured during the automated time series measurement.

## INTRODUCTION

Polymeric materials are already widely used in space applications. It is well known that polymers offgas unwanted volatile compounds as part of their composition such as flame retardants, stabilizers, oligomers from incomplete polymerization or softeners (1). Most of these offgassing products from cured polymers are larger molecules with an extremely low vapour pressure and high boiling point and are therefore classified as semi volatile organic compounds (SVOC).

The SVOC offgassing rate is strongly dependent to the exposure temperature.

Most assembled units or subunits for space applications need a thermal vacuum bake out process for at least 72 hours at elevated temperatures. Emitted SVOCs tend to condense on exposed surfaces leading to unwanted contamination. For that reason, it is important to know the offgassing characteristic for each polymeric material at the selected elevated temperature. Well known screening measurements such as the determination of total mass loss under vacuum and elevated temperature defined by ASTM-E595 only give a sum parameter, mainly the collected volatile condensed matter onto a cooled witness sample (CVCM-value) after 24 hours (2). But what happens exactly by different offgassing compounds during a 72-hour thermal vacuum bake out? For that reason, a novel method for a highly sensitive material outgassing profiling method at elevated temperatures is presented.

## MATERIAL AND METHODS

### Profiling method

A highly sensitive but robust method is established using commercially available standardized automated thermal desorption gas chromatography mass spectroscopy system Clarus 600 series combined with Turbomatrix 650 (PerkinElmer, Waltham). The material sample is placed into a cleaned PTFE liner and an empty thermal desorption tube (Markes International, Llantrissant) that fits directly into an automated thermal desorber (ATD). The tube is heated inline the thermal desorber at the selected temperature, mostly between 80 °C and 125 °C and 20 mL/min Helium flow (primary desorption) in splitless mode. Offgassing products are cryofocused onto the cold trap of the ATD at - 30 °C for two hours. After cryofocussing, the cold trap is heated at 300 °C for 20 min and the collected compounds are injected at 10 mL/min in split mode 9:1 into the gas chromatograph mass spectrometer (GC/MS) equipped with a high performance separation column Elite 5-MS, 60 m, film thickness 0,25 µm, inner diameter 250 µm (PerkinElmer, Waltham). The column temperature program started at 40 °C for 2 min followed by ramp A with 3K/min until 92 °C, then ramp B with 5K/min until 160 °C followed by ramp C with 10K/min until 280 °C and finished with a hold time of 10 min at 280 °C resulting in a total run time

of 54 min. The transfer line to the mass spectrometer and the source are heated to 250 °C. Mass scan was performed after 6 min solvent delay from  $m/z = 33$  until  $m/z = 281$  with a scan duration of 0.2 s and an inter scan delay of 0.1 s. The results for each compound mass were plotted over time.



**Fig. 1.** Material sample inserted into PTFE liner and stainless steel ATD tube

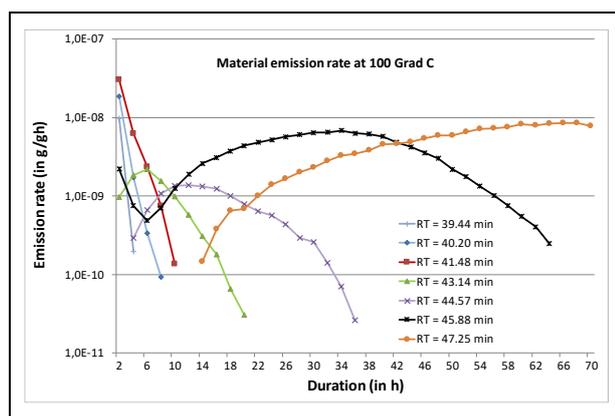
### Witness sample analysis

During a thermal vacuum bake out process, electro polished stainless steel witness samples with a diameter of 100 mm are exposed in the chamber where a unit coated with a silicone based material A. After exposure, the samples were shipped back in a wafer shipping box and analysed according SEMI E 108 (3) at 300 °C. The emissions were collected onto a Tenax TA adsorber tube and desorbed at 280 °C with the same parameters used for the profiling method.

## RESULTS

### 2.2 Material A

A silicone based material was screened with the above described method at 100 °C for 72 hours. The material was analysed in the form of chips. Therefore, a mass specific emission rate was calculated.

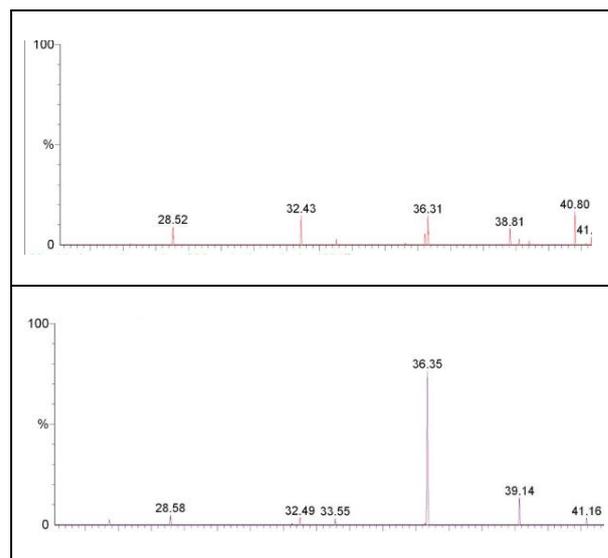


**Fig. 1.** Material A

All major detected emissions were siloxanes and are plotted in Fig. 1. The high boiling Siloxane at the chromatographic retention time  $RT = 47.25$  min started to show up earliest after 14 hours but increased permanently leading into a stable emission rate. This compound would not be detected during snap shot

emission analysis at elevated temperature such as defined in ASTM D 7706 (4). This leads to the assumption about thermal degradation. In order to prove this thesis, a sample was placed into a thermogravimetric analysis (TGA) at 125 °C which showed a permanent mass loss of material A at the selected elevated temperature.

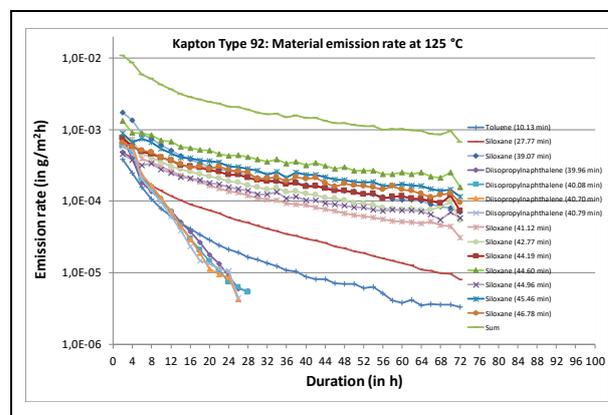
During a TVB-process with components coated with material A, the detected siloxane emissions from the material A at 125 °C could be found condensed onto a stainless steel witness sample analyzed after exposure, see identical retention times in the  $m/z = 281$  extracts from the two chromatograms in Fig. 2.



**Fig. 2.** Top: condensed siloxanes onto stainless steel witness plate. Bottom: material emission at 125 °C

### 2.2 Material B

A Kapton tape with a silicone based adhesive (Type 92) was screened with the above described method at 125 °C for 72 hours. The material was analysed in the form of an applied tape onto aluminium foil. Therefore, a surface specific emission rate was calculated.



**Fig. 3.** Material B: Kapton tape Type 92

All major detected emissions were siloxanes and naphthalene based compounds shown in Fig. 3. The naphthalene based compounds decline rapidly and were all not detectable any more after 28 hours. All detected siloxanes also decline permanently but in a slower rate. All detected emissions are most probably from non-bound compounds and not due to thermal degradation of the tested material.

*Screening of VOC Emissions from Products Using Micro-Scale Chambers.* ASTM International, West Conshohocken.

## DISCUSSION AND CONCLUSION

The presented method is a valuable tool in describing the offgassing behaviour of selected materials at elevated temperatures in detail. Each detected compound can be tracked and plotted as a time series. This supports strongly the later discussion about the criticality of outgassing compounds as GC/MS analysis will not only summarize offgassing products but also define the chemical nature, vapour pressure and boiling point. This enables to estimate a possible condensation of these volatile compounds during TVB-processes onto exposed surfaces leading to unwanted organic-chemical surface contamination.

The sensitivity of the method with 1 ng total mass for each compound outstands the ASTM-E 595 by orders of magnitude and gives a boost in information content. Nevertheless, the method is performed at ambient pressure and not in vacuum. Further research is planned in order to describe similarities and discrepancies in material offgassing under vacuum and ambient conditions.

The described time series screening method is robust, cost effective, easily established and has a high potential for a fast and effective screening of polymeric materials used in space applications.

## REFERENCES

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