JOURNAL OF SPACECRAFT AND ROCKETS
Vol. 44, No. 1, January–February 2007

Outgassing Measurements Combined with Vacuum Ultraviolet Illumination of the Deposited Materials

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DOI: 10.2514/1.22375

The "photofixing" of organic molecules to external spacecraft surfaces, by vacuum ultraviolet radiation, has been a long standing concern for the aerospace community. Increased rates of molecular deposition have been observed, quantitatively using quartz crystal microbalances, during several ground based simulations in which vacuum ultraviolet radiation illuminated the deposition surface. However, a common chemical process in which vacuum ultraviolet radiation is used to degrade or photolysis organic molecules suggests that "photofixing" is not a universal occurrence and that some molecules may be broken down into smaller and possibly more volatile molecules. Temperature-controlled quartz crystal microbalance measurements, quantifying the loss of deposited organic materials during vacuum ultraviolet radiation illumination of the deposition surface, suggest that some aerospace materials contribute less to spacecraft surface contamination than common outgassing measurement techniques would imply.

Introduction

The "photofixing" of organic molecules to external spacecraft surfaces, by vacuum ultraviolet radiation (VUV), depends on the chemical composition of the surface contaminant rather than being a universal phenomenon. Typical outgassing deposition measurements do not address VUV interaction with the molecular species being deposited on the condensation surface. Ignoring this important orbital environmental effect, which does not always result in an enhanced deposition of the material, limits the material selection options for spacecraft that can tolerate only minimum amounts of surface contaminants.

The photolysis of three organic materials, by vacuum ultraviolet (VUV) radiation, has been quantified using 15 MHz temperature-controlled quartz microbalances (TQCM's). The rate at which molecular species, released from the individual samples, condensed on two TQCM's was measured for periods of up to 139.9 h. The individual samples were heated in an effusion cell and the emitted molecular species collected on a pair of TQCM's which were maintained at −40°C.

At several points during the deposition measurement, the deposition surface of one TQCM was illuminated by a 30 W deuterium lamp, and the loss of material from that surface was observed. VUV illumination of the TQCM, concurrent with condensation, reduced the rate that material was lost from the deposition surface. These measurements present a contrasting picture of molecular deposition, in the presence of VUV, to that presented by other investigators [1–4], who observed an enhanced rate of molecular deposition when the deposition surface was illuminated by VUV. These measurements do not suggest that photofixing of materials deposited on external spacecraft surfaces can be ignored. Rather, constraints on the selection of materials for aerospace applications could be loosened by including the parameter of VUV illumination of the deposition surface in future outgassing measurement programs.

Received 10 January 2006; revision received 26 April 2006; accepted for publication 28 April 2006.

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Facility Description

The vacuum chamber in which the deposition measurements were made is a glass bell jar that seals against the metal base of the chamber. The chamber can be evacuated to a pressure of to 6.6×10^{-5} Pa (5×10^{-7} torr) or less by a turobomolecular vacuum pump. A liquid nitrogen reservoir in the chamber, that passively cools a large cold wall, provides some additional pumping capacity.

The sample is heated to the desired temperature in an effusion cell that has a direct "line of sight" to both of the chamber's two TQCM's (Fig. 1). The axis of the effusion cell is at an angle of 25 deg to the plane of the deposition surface of TQCM#1 and 41 deg to the deposition surface of TQCM#2. The plane of the deposition surface of TQCM#2 is rotated 12 deg from the line of sight from the effusion cell. The distance from the effusion cell to TQCM#1 was typically 14.2 and 13.8 cm to TQCM#2. A typical view factor for TQCM#1 is 461.7 cm^2 and for TQCM#2, 774.4 cm^2.

A 30 W deuterium lamp is located 36.5 cm from TQCM#1 and the axis of the lamp is aliened with the normal, of the deposition surface, of TQCM#1. There is no direct line of sight from the UV lamp to TQCM#2 but some VUV radiation does reach this TQCM, possibly scattered from hardware surfaces in the chamber. VUV illumination of the deposition surfaces of the TQCM's did not alter the performance of either microbalance. The spectrum of the lamp (Fig. 2) contains a Lyman Alpha band in addition to very Intense peaks at 156, 159, and 161 nm.

Both the effusion cell and the VUV lamp have shutters that block the line of sight between them and the TQCM's. There is a gap, for mechanical clearance, of about 1_cm between the effusion cell shutter and the effusion cell orifice that reduces the effectiveness of that shutter. The effectiveness of the effusion cell shutter varies between 33 and 88%, as measured by TQCM#1, and the effectiveness appears to decrease as the deposition rate decreases. This may be an effect of the deposition rate approaching the chamber background deposition rate.

Both TQCM's are mounted in copper blocks that act as heat sinks for the sensors. Provisions have been made for mounting witness coupons on these blocks, adjacent to the TQCM's, for the collection of samples for ex situ chemical analysis and optical measurements.

Measurement Description

The deposition measurements were based on the American Society for Testing and Materials, Method E-1559 [5], which is commonly used to quantify the rate at which molecular species, emitted from an effusion cell, deposit on the surface of a quartz crystal microbalance. Several times during the deposition measure-

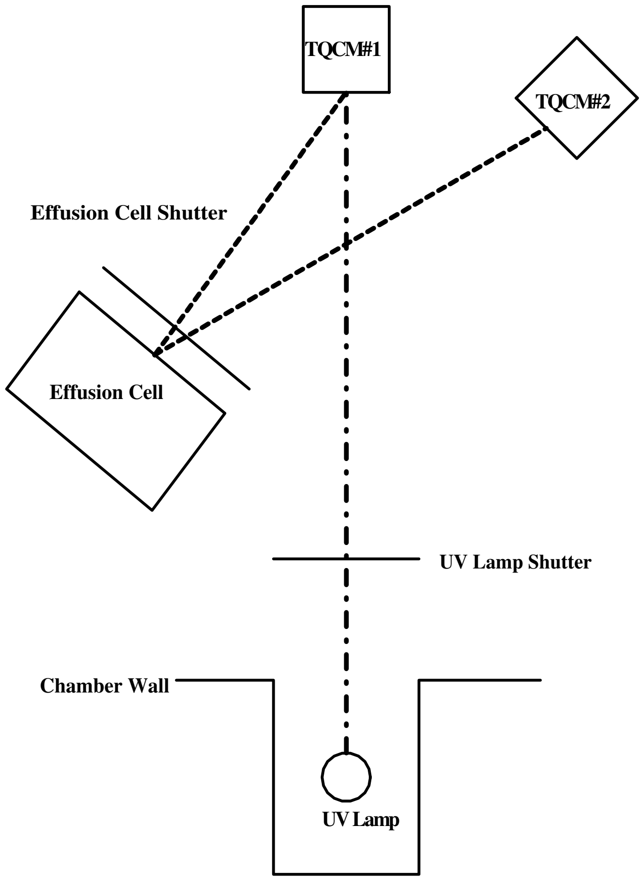

Fig. 1 A sketch of the experimental setup (not to scale).

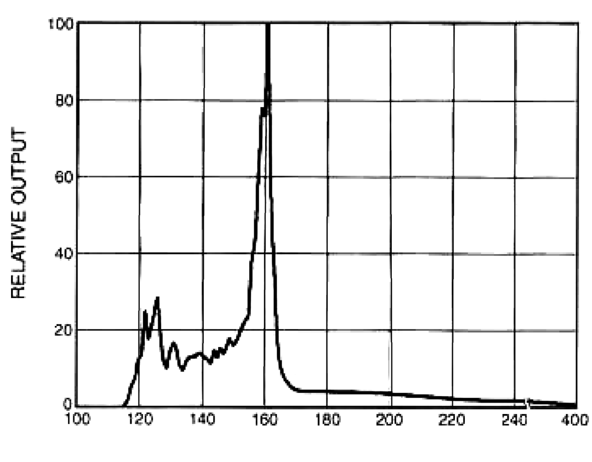

Fig. 2 A vendor provide spectrum for the 30 W deuterium lamp.

ments, the deposition surface of TQCM#1 would be illuminated by the deuterium lamp, changing the rate at which the deposition process progressed. Once the effect of the VUV radiation had been observed, the lamp would be switched off and the "normal" deposition process resumed.

A sequence of operations for the VUV illumination of TQCM#1 was developed that addressed the less than 100% effectiveness of the effusion cell shutter.

Figure 3 illustrates the operation of the effusion cell and UV lamp shutters in support of the measurements presented in this paper.

From point A to point B, in Fig. 3, the effusion cell shutter is open and a clear "line of sight" exists between the effusion cell and the TQCM's. From point B to point C the effusion cell shutter is in the closed position, interrupting the "line of sight" movement of emitted

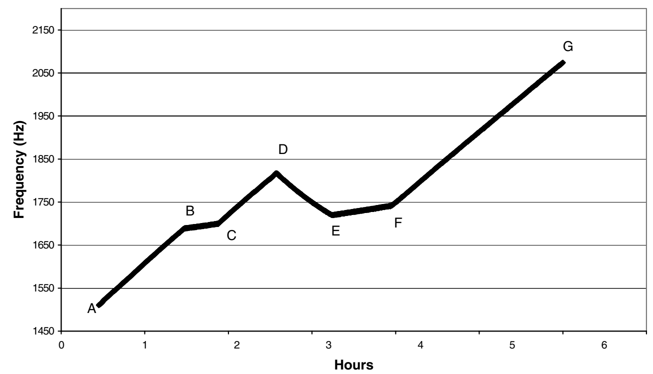

Fig. 3 A typical frequency curve showing the effects of operating the effusion cell shutter, UV lamp shutter, and VUV illumination of the TQCM deposition surface.

species from the effusion cell to the deposition surfaces of the TQCM's. From point C to point D the effusion cell shutter is again in the open position. From point D to point E the effusion cell shutter is in the closed position, the UV lamp is on and the UV lamp shutter is not blocking the UV lamp's illumination of TQCM#1. From point E to point F the effusion cell shutter is again in the open position as is the UV lamp shutter. From point F to point G the effusion cell shutter is in the open position and the UV lamp shutter is closed, blocking the light emitted by the VUV lamp.

The effects of solar illumination of TQCM's were previously investigated, for the space shuttle program [6], in support of the post-flight analysis of TQCM measurements that were part of the evaluation of oxygen interaction with materials flight experiment. Two separate effects were observed during the first 100 to 200 s of illumination of the microbalance crystal with a radiance of 135 mW/cm^2.

There was an initial, linear decrease in the beat frequency attributed to expansion of the TQCM's quartz crystals, altering the piezoelectric spring constant of the crystals, during the first 5 to 10 s of the illumination. This is followed by a quickly decaying, asymptotic decrease in the beat frequency that was attributed to radiative heating of the crystal and the material deposited on the crystal.

Six TQCM's were included in the earlier TQCM solar illumination, stability study and in each case the initial, linear mass loss occurred during the first 10 s of illumination; regardless of the temperature of the deposition surface. These six TQCM's were manufactured by the same vendor and were of the same configuration and type as the microbalances used in this study.

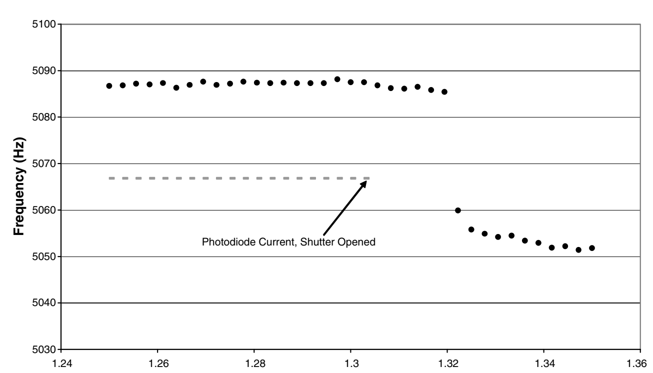

Fig. 4 The delay between the illumination of the TQCM deposition surface (shutter opening) and a decrease in the beat frequency occurred at approximately 1.3 h. The data points were recorded at 10 s intervals. The horizontal line is the output from a photodiode mounted on the lamp side of the shutter. Opening the shutter moves the photodiode from in front of the UV lamp.

During the illumination of TQCM#1 by the deuterium lamp, with the temperature-control circuit of the microbalance disabled, a short duration linear decrease in the beat frequency was observed. However, the decrease was observed 70 s after the illumination of the deposition surface (Fig. 4), suggesting that a thermal stability effect was observed rather than change in the mechanical properties of the quartz crystals.

Continued monitoring of the beat frequency recorded a continued loss of mass from the deposition surface followed by a mass gain (Fig. 5), as the temperature of TQCM#1 drifted from 16°C to 13°C (Fig. 6).

Because VUV illumination of the microbalance did not produce an observable effect on the functional stability of the balance, no adjustments to the following deposition measurements were made.

Adipic Acid Measurements

To confirm the geometric relationship between the effusion cell and the TQCM's, deposition measurements were made with adipic acid (Chemical Abstracts Service Registry No. 124-04-9). The deposition data collected was then used to calculate the enthalpy of sublimation, at several effusion cell temperatures, of the adipic acid. Good agreement of the calculated enthalpy of sublimation with previously published values for this quantity, confirmed that the system was performing as designed and that the relationship of the effusion cell to the TQCM's is understood [7].

Figures 7 and 8 show the adipic acid measurements made over an effusion cell temperature range of 24 to 58°C and condensed on a −40°C surface.

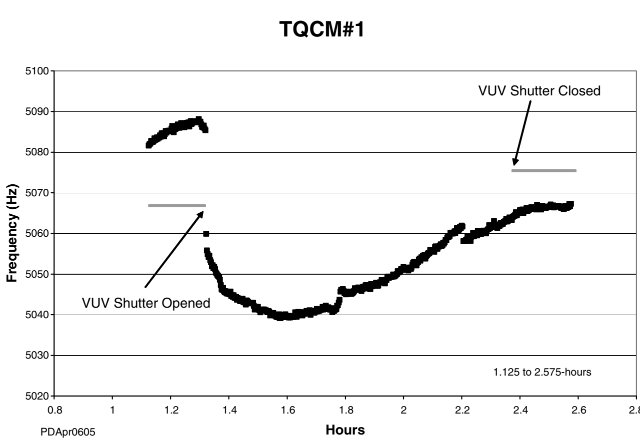

Fig. 5 The effect of VUV illumination of the TQCM#1 during 1.45 h of exposure.

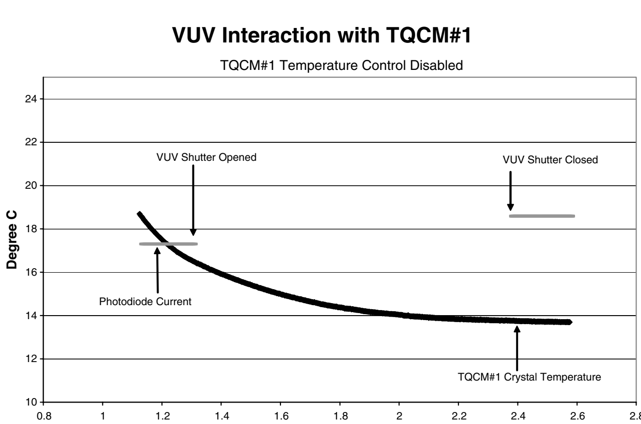

Fig. 6 Illumination of the TQCM deposition surface did not result in a heating of that surface. The TQCM temperature control was disabled for this observation period and the temperature of the TQCM was dropping to the temperature of the copper mounting block, about 7°C.

Closing and opening the effusion cell shutter modified the rate at which material was deposited on the TQCM's. VUV illumination of the deposition surface, while the effusion cell shutter was in the closed position resulted in a loss of material from the TQCM deposition surface. Opening the effusion cell shutter, while the deposition surface was illuminated with VUV, reduced the rate of loss (Figs. 9 and 10).

The loss of material was clearly observed during a total of six VUV exposures or illuminations of the deposited material (Table 1). Interaction of the VUV with material emitted from the effusion cell, but not yet in contact with the deposition surfaces, was also possible but not addressed by these measurements.

Zinc Selenium (ZnSe) Witness Plates

To augment the TQCM deposition measurements, 1 in. diameter ZnSe disks were positioned adjacent to both TQCM's for the collection of samples that would be analyzed by Fourier transform Infrared spectroscopy. The ZnSe disks were attached directly to the TQCM mounts, 0.5 in. thick copper blocks, which are actively cooled by a circulating water/glycol mixture. The temperature of the copper mounting blocks is about 7°C and it was assumed that the ZnSe disks were passively cooled to the same temperature. Figures 11 and 12 are examples of the spectra from ZnSe disks, mounted around TQCM#1, during Scotch weld 3501 epoxy and S-383 silicone rubber deposition measurements.

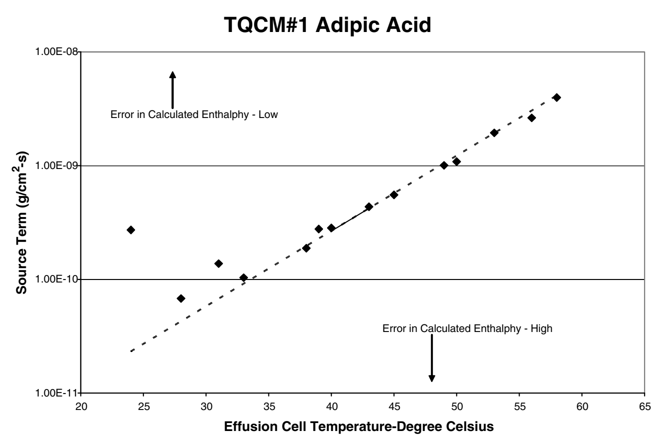

Fig. 7 Adipic acid measurements for TQCM#1. Points falling on the dashed line would have a 100% agreement with the published values for the enthalpy of sublimation. Some percentages are indicated to illustrate the agreement of the calculated heat of enthalpy for these measurements with the published value.

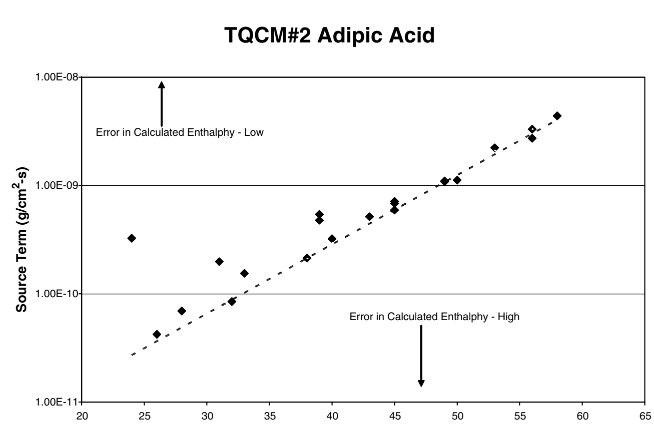

Fig. 8 Adipic acid measurements made with TQCM#2. As in Fig. 7, data points falling on and near the dashed line have a high degree of correlation to the published value for the enthalpy of sublimation for this material.

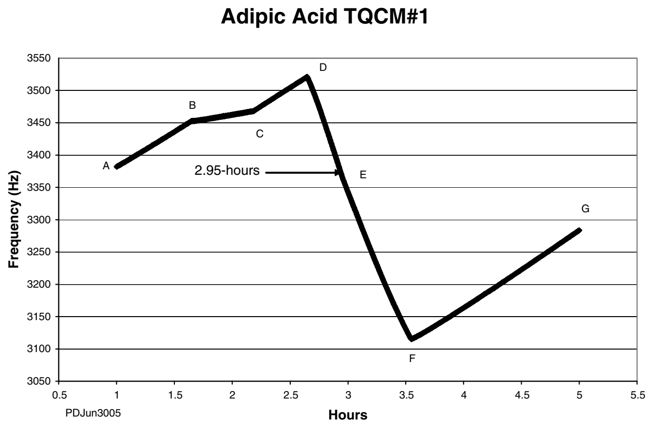

Fig. 9 A typical frequency curve observed during shutter operations and VUV illumination of TQCM#1. The effect of opening the effusion cell shutter (2.95 h) is not apparent in this figure.

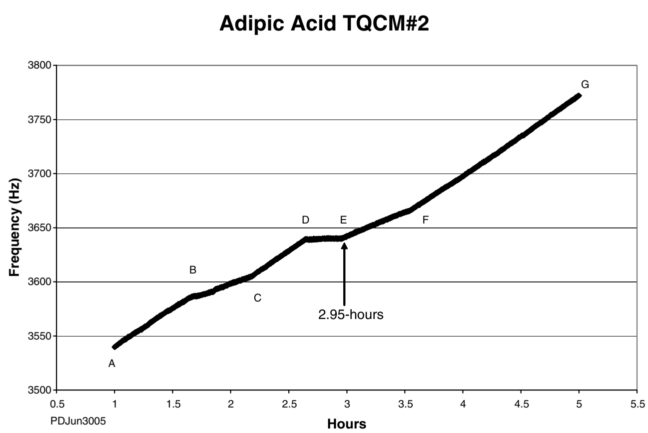

Fig. 10 Shutter operation and VUV illumination of TQCM#2. The effect of opening the effusion cell shutter (2.95 h) had a clearly discernible effect.

To ensure that material emitted by the samples would condense on the ZnSe disks, the outgassings from samples of Scotch weld 3501 and S-383 silicone rubber were individually measured in the Marshall Space Flight Center, E-1559 Outgassing Facility. Deposition measurements are made in this facility using four cryogenic, quartz crystal microbalances that view an effusion cell. The temperature of one of the balances was maintained at 10°C to mimic the ZnSe disk temperature and the temperature of another microbalance would be maintained at −40°C to mimic the TQCM temperatures used for the Photodeposition Facility measurements. Based on the deposition rates for the 10°C microbalance, the effusion cell temperatures for the Scotch weld 3501 and S-383 measurements, to be made in the Photodeposition Facility, were selected.

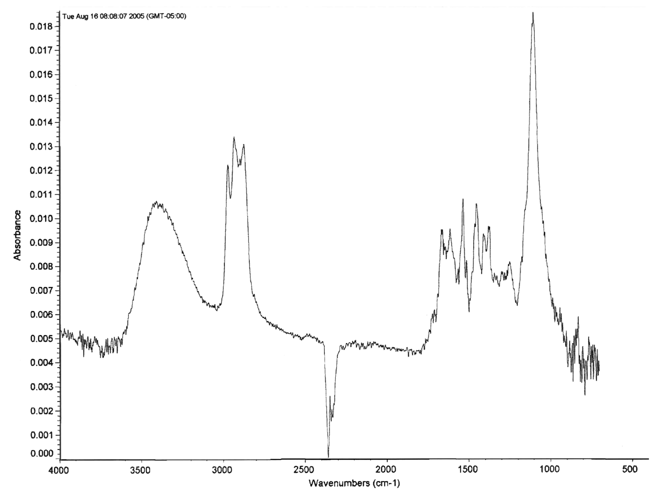

Fig. 11 An infrared spectrum of materials deposited on ZnSe disks during the Scotch weld 3501 epoxy, outgassing measurement. The absorbance bands at 2970, 2937, and 2868 cm^{-1} are typical hydrocarbon absorbance bands.

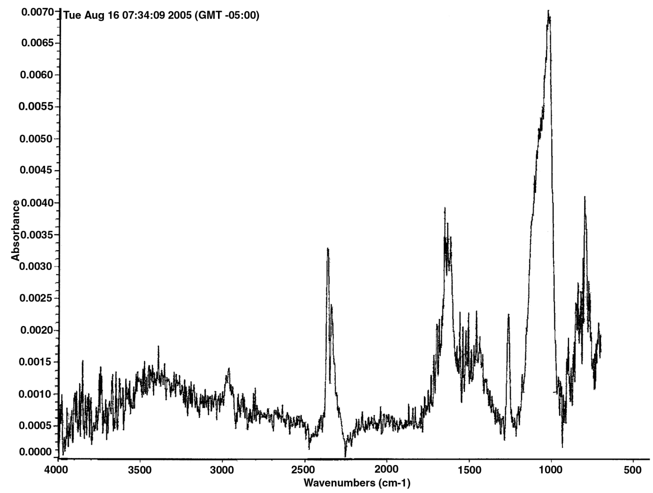

Fig. 12 An infrared spectrum of material deposited on a ZnSe disk during the S-383 silicone rubber, outgassing measurement. The absorbance band at 1266 cm^{-1} is typical of a silicone atom bonded to a CH_2 group.

Scotch Weld 3501 and S-383 Silicone Rubber Deposition Measurements

The adipic acid measurements were typically made over a period of 24 h, at a single effusion cell temperature, and then effusion cell temperature would be increased for the next measurement. The Scotch weld 3501 epoxy and the S-383 silicone rubber measurements were isothermal and much longer in duration than the individual adipic acid measurements.

Table 1 Adipic acid: frequency measurements during shutter operations

TQCM#1					
Effusion cell temperature	No Illumination	No Illumination	No Illumination	VUV illumination	VUV illumination
Degree Celsius	Shutter open Hz/hour	Shutter closed Hz/hour	Shutter open Hz/hour	Shutter closed Hz/hour	Shutter open Hz/hour
32	49.123	25.538	28.121	−193.3	−79.228
39	26.443	13.857	28.216	−384.48	−91.757
40	31.578	16.414	30.738	−465.92	−163.63
45	43.93	20.945	58.032	−253.63	−88.899
50	105.78	29.681	114.32	−520.48	−427.64
56	180.97	37.082	254.87	−782.96	−81.764
Shutter operation segment	(A–B)	(B–C)	(C–D)	(D–E)	(E–F)

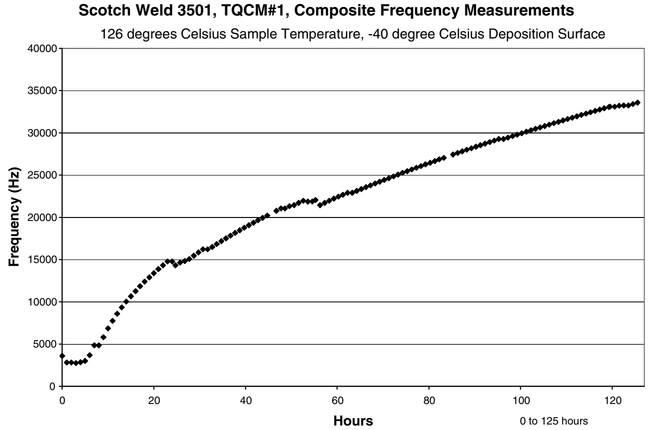

Fig. 13 The overall, TQCM#1, deposition measurement for Scotch weld 3501 epoxy.

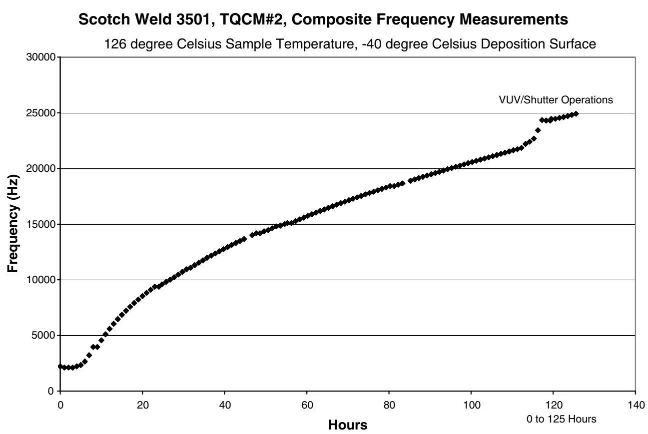

Fig. 14 The overall, TQCM#2, deposition measurement for Scotch weld 3501 epoxy.

Typically the Scotch weld 3501 epoxy and S-383 silicone rubber data files were about 24 h in length and when all of the measurements were completed, the data files were appended together to create an overall picture of the outgassing measurement. The following frequency curves were constructed from multiple data files and some

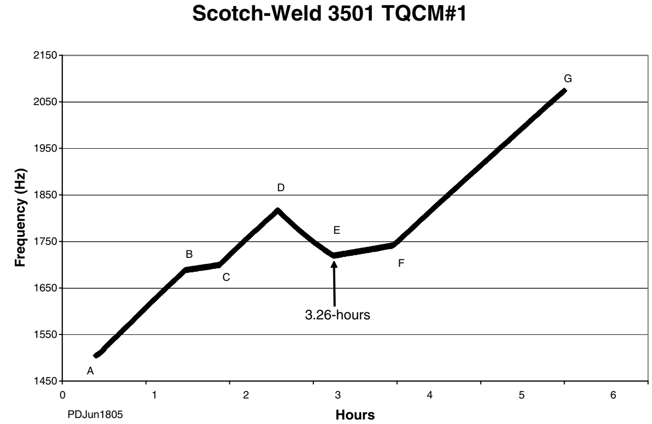

Fig. 15 The effects of effusion cell shutter operations and VUV exposure can be clearly seen at 3.26 h.

irregularities from the data file, appending process can be seen in the frequency plots for the overall measurement.

During these measurements the TQCM's were "baked out" when the amount of deposited material reaches the capacity of the microbalance which also contributed to the irregularities of the appended files. The deposited material is thermally driven from the deposition surface by raising the temperature of the TQCM's to 90°C, causing the deposited material to evaporate from the deposition surface. The deposition surface was then cooled to −40°C and the deposition measurement resumed.

Scotch Weld 3501 Measurements

Unlike the adipic acid measurements, the Scotch weld 3501 outgassing measurement was an isothermal measurement. The effusion cell temperature was 126°C and the TQCM deposition surfaces were held at −40°C during the measurement. The duration of the measurement was 118.52 h, which started when the sample reached the desire temperature for the measurement and includes any periods when the TQCM's were "baked out."

The frequency curves for the overall deposition measurements are presented in Figs. 13 and 14. The frequency curve for a typical VUV exposure of the material deposited on the TQCM's are presented in Fig. 15. The deposited material was exposed to VUV 4 times (Table 2) during the overall outgassing measurement of the Scotch

Table 2 Scotch weld 3501 epoxy: frequency measurements during shutter operations

TQCM#1					
No illumination Shutter open (A–B) Hz/hour	No illumination Shutter closed (B–C) Hz/hour	No illumination Shutter open (C–D) Hz/hour	VUV illumination Shutter closed (D–E) Hz/hour	VUV illumination Shutter open (E–F) Hz/hour	Onset of B–C Elapsed test hours
430.02	51.962	426.73	−174.36	252.14	25.4
——	[a]51.962	378.17	−336.61	56.29	[a]25.4
277.78	40.234	264.47	−192.31	112.67	49.6
173.83	27.634	167.8	−147.68	30.918	121.0

[a]The deposition rate with the effusion cell shutter closed, and no VUV illumination, was not repeated before the next reported measurement set with UV illumination was made, 3.5 h later.

Table 3 S-383 silicone rubber: frequency measurements during shutter operations

TQCM#1					
No illumination Shutter open (A–B) Hz/hour	No illumination Shutter closed (B–C) Hz/hour	No illumination Shutter open (C–D) Hz/hour	VUV illumination Shutter closed (D–E) Hz/hour	VUV illumination Shutter open (E–F) Hz/hour	Onset of B–C Elapsed test hours
56.227	12.657	52.078	−407.64	−99.823	21.9
37.106	13.518	43.018	[a]	4.6267	48.8
19.412	6.478	20.038	−68.914	−13.267	124.1

[a]The rate of change was not linear but the overall change in frequency was −36.598 Hz in 1.041 h or a −35.156 Hz/h loss.

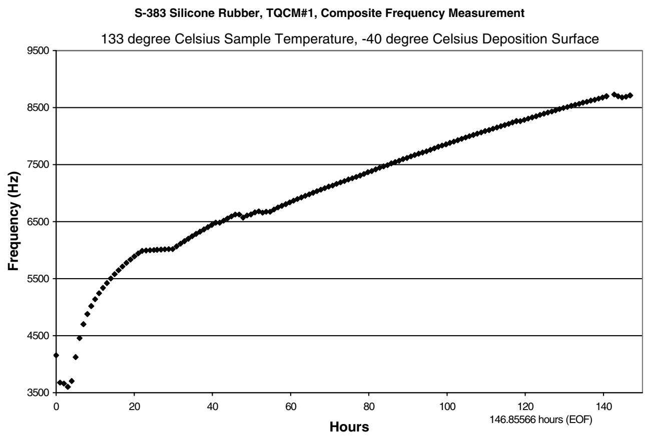

Fig. 16 The overall frequency curve for TQCM#1.

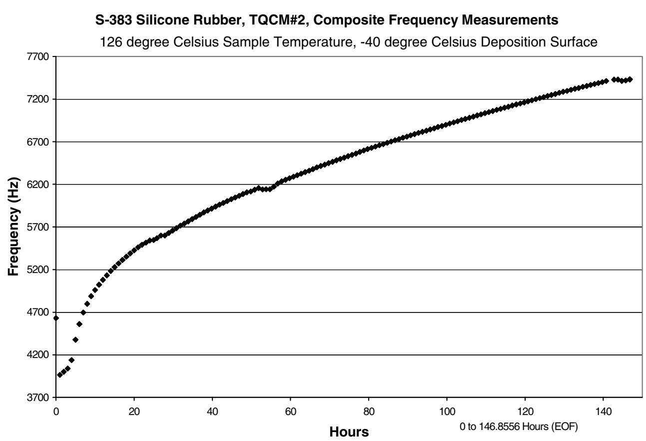

Fig. 17 The overall frequency curve for TQCM#2.

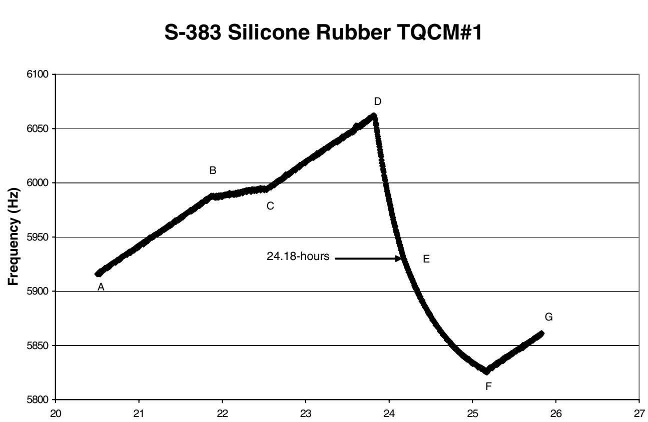

Fig. 18 During the VUV illumination of TQCM#1 the effusion cell shutter was opened at 24.18 h.

weld 3501 epoxy. The order of shutter operations, used during the VUV exposure of the adipic acid, was also used for these exposures and was presented in Fig. 2.

S-383 Silicone Rubber

Like the Scotch weld 3501 outgassing measurement, this 139.9 h measurement was an isothermal measurement. The effusion cell temperature was 133°C and both TQCM's were maintained at −40°C, excluding TQCM baked out periods. Figures 16 and 17 show the overall frequency curves for the S-383 measurements. Typical frequency curves for the VUV exposure periods are presented in

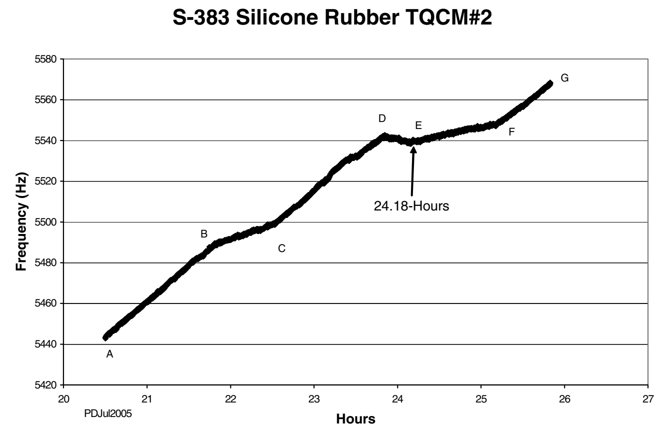

Fig. 19 The opening of the effusion cell shutter at 24.8 h had a more pronounced effect on TQCM#2.

Figs. 18 and 19 and the VUV exposures followed the order of operations previously used for the previous samples. There were a total of three VUV exposure periods (Table 3) during the overall S-383 measurement.

Conclusions

Outgassing measurements for samples of adipic acid, Scotch weld 3501 epoxy, and S-383 silicone rubber, made in the NASA Marshall Space Flight Center Photodeposition Facility, produced results similar to outgassing measurements made in other facilities that are operated according to the ASTM E-1559 methodology. The effectiveness of the effusion cell shutter, in blocking the emission of materials from the effusion cell, was less than 100% and an order of shutter operations was adopted to address this ineffectiveness. Samples suitable for Fourier transform infrared analysis were successfully collected on passively cooled witness plates during the epoxy and silicone rubber outgassing measurements.

VUV illumination of material on the TQCM deposition surface resulted in the loss of material from that surface. The process involved is believed to be photolysis and due to the ineffectiveness of the effusion cell shutter, at completely halting the emission of material from the effusion cell, the photolysis may occur to a greater extent than recorded by these measurements. These measurements did not address the possibility that materials in transit, from the effusion cell to the TQCM, may have been altered by VUV illumination. Reactive molecular species, ions or free radicals, could have played a role in the observed loss, by a mechanism other than or in concert with photolysis of the deposited materials.

Direct illumination of the deposition surface, while the effusion cell shutter was not in the "line of sight path" between the effusion cell and the deposition surface, reduced the rate at which material was lost from the TQCM. During the adipic acid, Scotch weld 3501 epoxy, and S-383 silicone rubber deposition measurements, the measured rate was less than the deposition rate measured when the deposition surface was not illumination.

The deposition measurements reported here document that VUV illumination of material condensing on a surface will not always occur at a rate greater than deposition rates measured without VUV illumination.

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Associate Editor