QTGA ANALYSIS WITH CONCURRENT DEPOSITION

David W. Hughes
NASA Goddard Space Flight Center

ABSTRACT

Analysis of outgassed species behavior is often performed using QCM thermogravimetric analysis (QTGA). Prior methods are suited to laboratory testing of materials samples where the source of contaminant can be removed from the system. An approach suitable presented for use during hardware bakeout and outgassing certification is presented. An iterative process is shown to fit surface activation energies and the arrival flux for multiple species.

INTRODUCTION

In the analysis of molecular contamination transport, the behavior of molecules condensed on a surface is important. Different parameters may be used to characterize the desorption behavior, depending on the quantity of contaminant and nature of the surface. One of the test methods to determine these parameters is QTGA. To perform a QTGA, a QCM with a molecular deposit on the exposed crystal is heated at a constant rate. The rate of mass loss is then analyzed using a model of the physical behavior of the molecules.

Prior QTGA analysis methods used either a Langmuir gas model to fit vapor pressure constants, as was described in reference 1, or a residence time model using an Ahrrenius temperature dependence, such as was published in reference 2.

Both of the aforementioned models do not contain a term for arriving molecules; they can only be used when the source of contamination may be isolated from the QCM prior to performing the QTGA. This is not a serious limitation when testing materials in the laboratory; when trying to extract contaminant properties during a flight hardware bakeout, however, neither method will prove satisfactory.

In this paper, a contamination model that accounts for continuing influx of contaminant molecules is defined and shown to fit artificially generated QTGA curves with good accuracy.

SYMBOLS

Values are given in SI Units.

Ea	Activation energy for desorption of a molecule, J/(mole K)
T	Temperature, Kelvin
R	Gas constant
τ_0	Pre-exponential constant, seconds
τ	time constant for desorption
dm/dt	rate of change of mass on the QCM
m	mass
m_i	mass of species i
τ_i	time constant for desorption of species I
Φ_i	arriving mass flux of species i

PROPOSED MODEL

Contaminant molecules are assumed to be arriving at the QCM surface at a constant, species dependent rate. Once on the surface, the residence time model is employed. The time constant for an individual molecule to desorb is

$$\tau = \tau_0 e^{\frac{Ea}{RT}} \tag{1}$$

A first order mass loss equation is employed because depletion of a species in the presence of others results in a changing stoichiometry on the QCM surface. The Langmuir evaporation equations, which are zeroth order in mass, are only appropriate for single species calculations. The first order mass loss equation may be written as

$$\frac{dm}{dt} = -\frac{m}{\tau} \tag{2}$$

The pre-exponential constant τ_0 is sometimes correlated to the vibrational period of a molecule. Experimentation with this value has shown that the rate of desorption curve produced by equation 2 has a broader, shorter peak that occurs at a higher temperature as the vibrational period is increased. The slower desorption results in a mass curve that is less steep during the desorption period. Figures 1 and 2 show this tendency. Unfortunately, a less steep desorption curve is also obtained by having several species with similar activation energies. For purposes of species identification, this distinction is important; it is not, however, necessary to identify contaminants for modeling if their cumulative behavior can be reproduced. Because this author's work will be used to model spacecraft outgassing, and to reduce the number of parameters to be solved, τ_0 is fixed at 10^{-13} seconds.

Combining desorption with a constant arrival flux phi for each species, the equation that will be fit to the rate of change of mass on the QCM is given by

$$\frac{dm}{dt} = -\sum_i \frac{m_i}{\tau_i} + \phi_i \tag{3}$$

METHOD OF FITTING

Overview

The author has observed that QTGA curves exhibit segments of high slope interspersed with segments of low slope. By detecting inflections in the curve, the data for the temperature ramp is divided into sections, some of which are dominated by a rapidly desorbing species. The final instants of the QTGA are desorbing only one species – that with the highest activation energy. If one considers the last segment to be dominated by one species, a simple logarithmic transform can be used to extract the activation energy. The sections dominated by one species are curve fit individually, beginning with the species that desorbs at the highest temperature. As each species is solved for, a guess at the deposition rate is made based on the time of collection and the quantity collected. These terms are used to back out the effect of the solved species throughout the QTGA period before solving for the next segment.

Separation of Species

The division of the QTGA curve into segments is based on sign changes in derivatives. The rate of desorption is the first derivative of the QTGA mass curve. The maximum rates may be found where the second derivative is equal to zero. Inflections in the rate curve may be found where the third derivative is equal to zero. The author has chosen to fit sections of the curve following depletion of the previous species,

but before depletion of the current species causes a significant drop in desorption rate. As shown in figure 3, this section falls between a local minimum in rate and the inflection before the next local maximum in rate. Automatic detection of these segments is accomplished by finding data for which the following relation is true

$$\left(\frac{dm}{dt}\right)\left(\frac{d^2m}{dt^2}\right) < 0$$
$$\left(\frac{d^2m}{dt^2}\right)\left(\frac{d^3m}{dt^3}\right) < 0 \qquad (4)$$

Linearizing the Equation

Having identified the segments to be curve fit, each is fit according to the following procedure. Equations 1 and 3 are combined and linearized (with the assumption that only one species is being fit) to form

$$\ln\left(\frac{m}{\phi - \frac{dm}{dt}}\right) = \ln(\tau_0) - \frac{E_a}{RT} \qquad (5)$$

Being of the form Y=mX+b, equation 5 is easily fit with a least squares routine, using 1/T as X and the left hand side as Y, to find the slope Ea/R. The initial guess for arriving flux phi is zero.

Subtracting the Effect

The desorption equation is run in reverse using a simple time steping sequence. The sequence starts at the temperature and mass on the QCM at the beginning of the recently fit segment. After calculating what the mass must have been at each time point during the QTGA, the calculated mass is subtracted from the original QTGA curve. The new curve is checked again for segments in case the location of inflections has changed, and the next species parameters are determined.

Refining the Guess

Having calculated the initial masses at the beginning of the QTGA, the time of collection prior to the start is used to guess deposition rates. In the current work, a constant rate of deposition was assumed to be an adequate fit for a collection time of several hours. On the next iteration of the solution, these values of flux are used in equation 5. For the contrived data set, where the answer is known, four iterations produced good convergence, but the fifth iteration overshot the actual values. In practice, a damping scheme that prevents over correction of the guess on each iteration would be advisable.

RESULTS

The test data set was composed of three species with the parameters shown in table 1. The QTGA mass curve, and the curves of the individual species are shown in figure 4. The QTGA rate curve is shown in figure 5. Superimposed on figure 5 are the regions identified for curve fitting by the automated procedure in each iteration. Note that the species which desorbs at the lowest temperature is fit last, and that segment underwent the most modification during the subtraction of the other species. In the case of the second segment that was fit, the adjustment removed the tail end of species 1 desorption from the data to be fit.

Table 2 contains the sequence of parameters as they appeared during the iteration. The ability of these parameters to reproduce the data is shown in figure 6. The error in the activation energy and initial mass terms is only a few percent, but the error in the deposition rate is as high as 11.5% for species 3. This may be due to compounding of errors during the subtraction of each species from the QTGA curve. Figure 7 clearly shows artifacts in the desorption rate after the subtraction process.

REFERENCES

1. Simpson, T. R., Hall, D. F., Ternet, G. K, "Extraction of Properties of Condensed Outgassed Species by Thermogravimetric Analysis," Proceedings of SPIE Vol 4774, 2002, pp. 151-159.

2. Bargeron C. B., Phillips, T. E., Benson, R. C., "Thermogravimetric Analysis of Selected Condensed Materials on a Quartz Crystal Microbalance," Proceedings of SPIE Vol 2261, 1994, pp. 188-199

TABLES

Table 1

Species	1	2	3
E/R	7000	7500	8000
M0	1200	800	600
phi	0.066667	0.044444	0.033333

Table 2

Guess 1	E/R	M0	Phi
M1	7143.71	1204.72	0.0000
M2	7514.05	901.66	0.0000
M3	8011.46	730.51	0.0000
Guess 2	E/R	M0	Phi
M1	7180.77	1261.15	0.0669
M2	7533.54	777.48	0.0501
M3	8024.52	531.02	0.0406
Guess 3	E/R	M0	Phi
M1	7148.71	1221.79	0.0701
M2	7530.03	784.45	0.0432
M3	8020.88	585.32	0.0295
Guess 4	E/R	M0	Phi
M1	7136.44	1231.29	0.0679
M2	7530.64	788.43	0.0436
M3	8021.86	570.53	0.0325

FIGURES

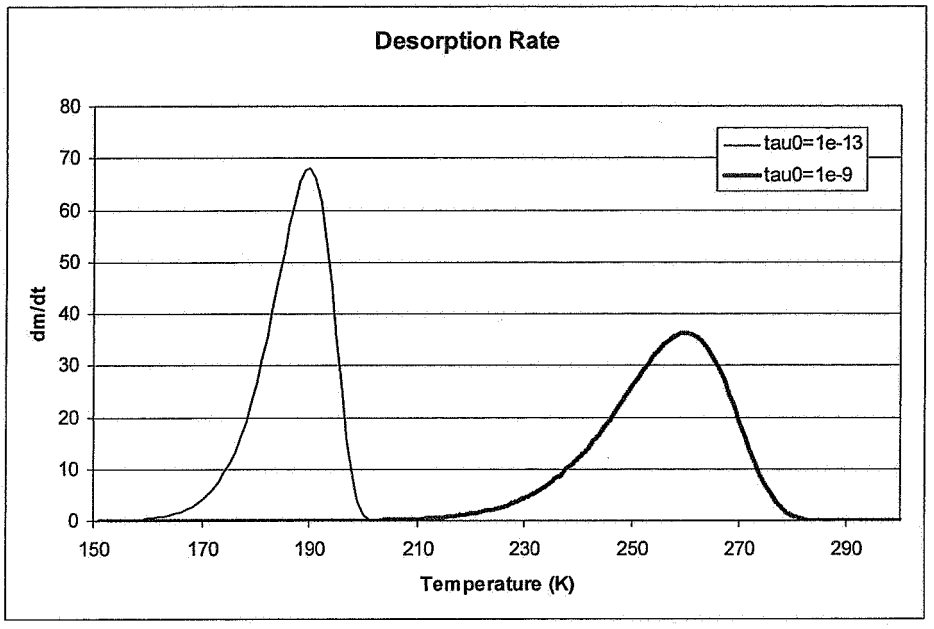


Figure 1

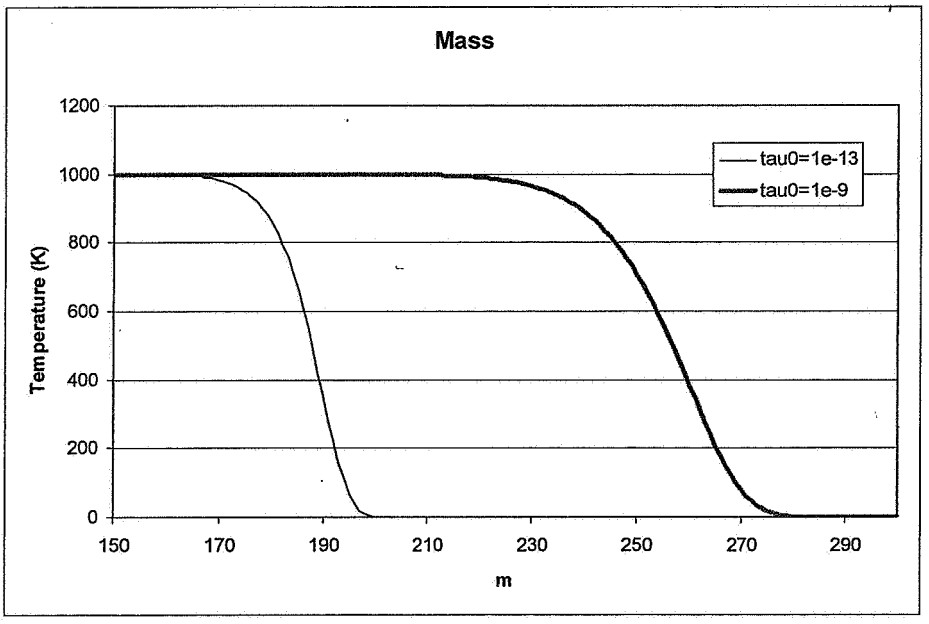


Figure 2

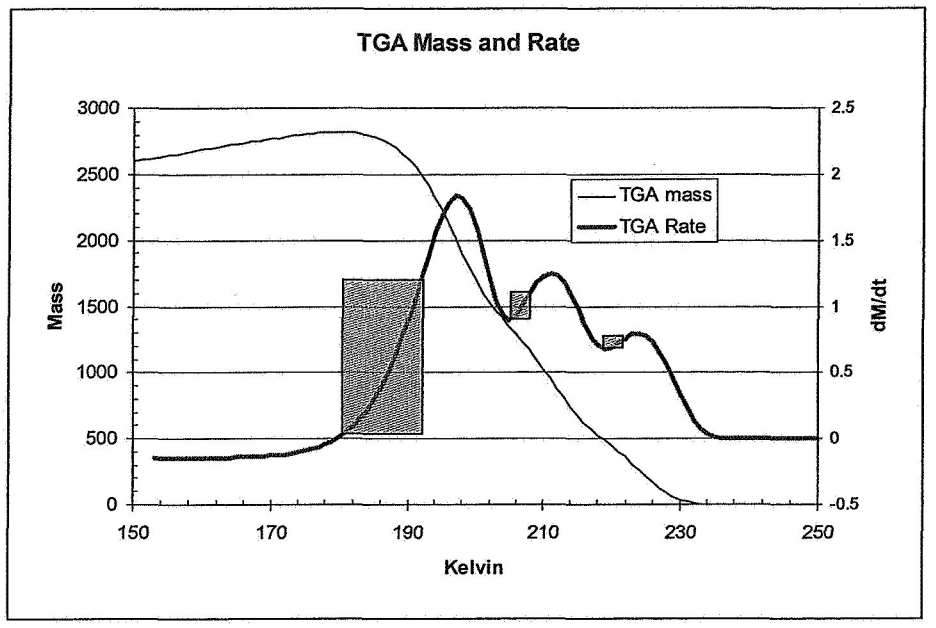


Figure 3

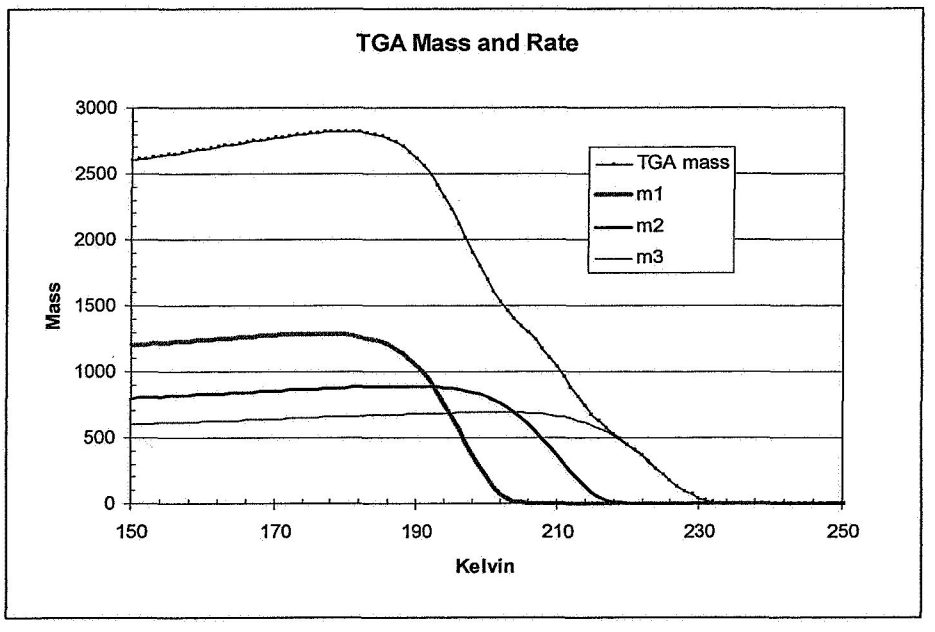


Figure 4

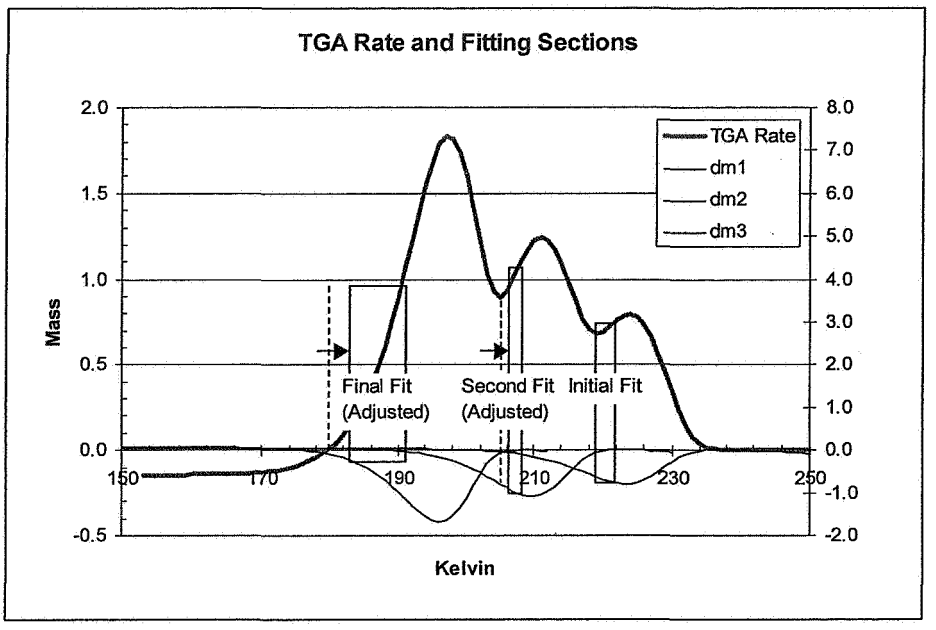


Figure 5

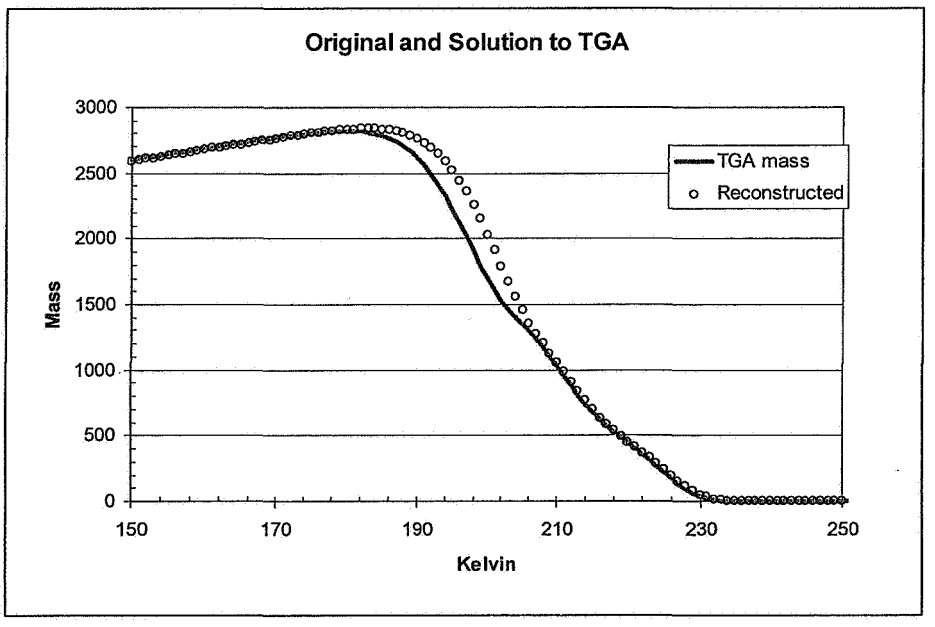
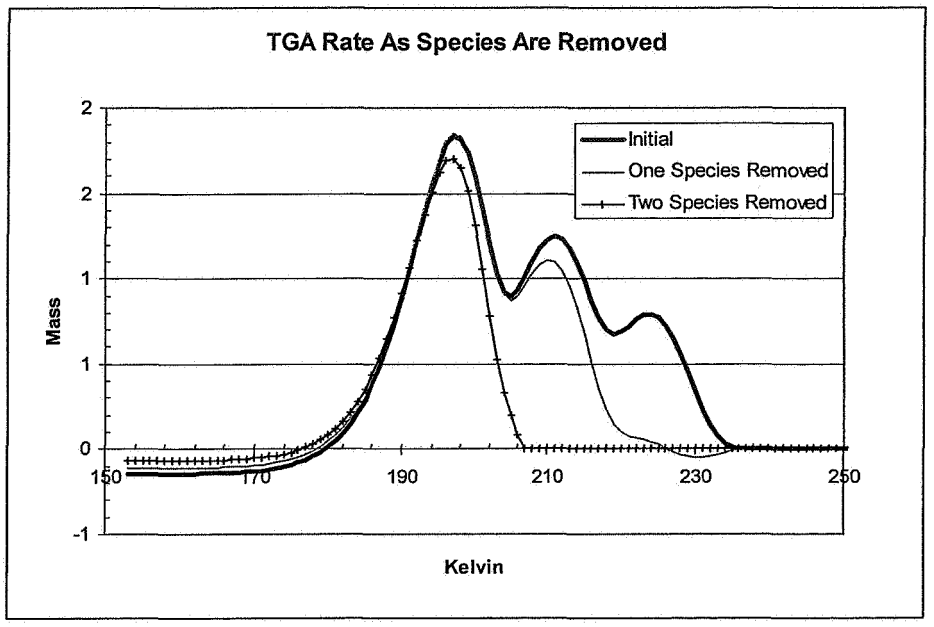


Figure 6

Figure 7


TGA Rate As Species Are Removed
Initial
One Species Removed
Two Species Removed
Mass
Kelvin
2
2
1
1
0
-1
150
170
190
210
230
250

24th Space Simulation Conference

David Hughes
HST Contamination Engineering Manager
NASA Goddard Space Flight Center
David.W.Hughes@NASA.gov

Paper Abstract:

QTGA Analysis With Concurrent Deposition

A method to analyze the species activation energies through QCM Thermo-gravimetric Analysis (QTGA) is presented. Through a simple iterative process, it is possible to determine the species parameters even with continuing deposition during the TGA.

Presentation Requirements:

PC with projector

Bio:

David Hughes is the Contamination Engineering Manager for the Hubble Space Telescope. He has 15 years of experience in aerospace contamination control and has been involved in each of the Hubble servicing missions. In addition to project support, his research interests include photopolymerization, improved contamination modeling techniques, and the design of slide rules. David has a Masters of Engineering Management from George Washington University and a Bachelors of Science from Carnegie Mellon University.