

# **SANDIA REPORT**

SAND2010-6458

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September 2010

## **Multivariate Analysis of Progressive Thermal Desorption Coupled Gas Chromatography-Mass Spectrometry**

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# Multivariate Analysis of Progressive Thermal Desorption Coupled Gas Chromatography-Mass Spectrometry

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## Abstract

Thermal decomposition of poly dimethyl siloxane compounds, Sylgard<sup>®</sup> 184 and 186, were examined using thermal desorption coupled gas chromatography-mass spectrometry (TD/GC-MS) and multivariate analysis. This work describes a method of producing multiway data using a stepped thermal desorption. The technique involves sequentially heating a sample of the material of interest with subsequent analysis in a commercial GC/MS system. The decomposition chromatograms were analyzed using multivariate analysis tools including principal component analysis (PCA), factor rotation employing the varimax criterion, and multivariate curve resolution. The results of the analysis show seven components related to offgassing of various fractions of siloxanes that vary as a function of temperature.

## **ACKNOWLEDGMENTS**

This work was funded by Sandia Laboratory Directed Research and Development Office. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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## NOMENCLATURE

ALS	alternating least squares
DOE	Department of Energy
GC-MS	gas chromatography-mass spectrometry
MCR	multivariate curve resolution
PCA	principal component analysis
PDMS	poly dimethyl siloxane
SNL	Sandia National Laboratories
TD	thermal desorption

# 1. INTRODUCTION

Thermal desorption coupled with gas chromatography-mass spectrometry (TD/GC-MS) is a powerful analytical technique for analyzing chemical mixtures. It has great potential in numerous analytical areas including materials analysis, sports medicine, in the detection of designer drugs; and biological research for metabolomics. Data analysis is complicated, far from automated and can result in high false positive or false negative rates. We have demonstrated a step-wise TD/GC-MS technique that removes more volatile compounds from a sample before extracting the less volatile compounds. This creates an additional dimension of separation before the GC column, while simultaneously generating three-way data.

Sandia's proven multivariate analysis methods, when applied to these data, have several advantages over current commercial options. It also has demonstrated potential for success in finding and enabling identification of trace compounds. Several challenges remain, however, including understanding the sources of noise in the data, outlier detection, improving the data pretreatment and analysis methods, developing a software tool for ease of use by the chemist, and demonstrating our belief that this multivariate analysis will enable superior differentiation capabilities. In addition, noise and system artifacts challenge the analysis of GC-MS data collected on lower cost equipment, ubiquitous in commercial laboratories.

This research has the potential to affect many areas of analytical chemistry including materials analysis, medical testing, and environmental surveillance. It could also provide a method to measure adsorption parameters for chemical interactions on various surfaces by measuring desorption as a function of temperature for mixtures.

## 1.1. Thermal Desorption Gas Chromatography-Mass Spectrometry

TD/GC-MS is a flexible experimental technique that permits the direct analysis of volatile organic species from liquid or solid substrates. TD/GC-MS also facilitates the indirect analysis of organic species when collected on a suitable adsorbent.

Thermal desorption is a sample preparation process that heats a sample to a specified temperature under an inert gas chromatography carrier gas. The volatile species desorbed from the sample substrate are collected and concentrated on an adsorbent-packed trap, which is typically held at a sub-ambient temperature during desorption from the original substrate. After desorption from the sample is complete, the trap is heated to volatilize the adsorbed species and introduce them to the gas chromatography-mass spectrometer for separation and identification. Thermal desorption permits the direct analysis of volatile species from samples with little sample preparation; since no extraction solvents are used, dilution, solubility issues, and loss of analytes that may be part of a solvent extraction method are avoided.

Typically, TD/GC-MS is performed using a single, predetermined sample desorption temperature. This allows the chemist to extract materials that may be of interest, while not damaging the collection medium or generating decomposition products. Another issue is to select a temperature that will not decompose the target analytes. A disadvantage to this technique is that all of the target materials are driven out of the sample in aggregate. An

alternative strategy, which depends on the variable volatility of different species, is to step the desorption temperature to generate a series of desorptions.

The technique of stepping through a series of temperatures works as follows: (1) Perform an initial desorption at a temperature slightly above ambient temperature that is easy to maintain by the temperature controller. (2) Concentrate these higher-volatility species in the trap and then introduce them into the GC-MS. (3) After collection of the full-mass spectrum-chromatogram, step the temperature up to the next desired level and return to step one. (4) Repeat until the maximum desired desorption temperature is achieved. This process allows one to progressively extract the sample, removing the target species from the matrix as a function of volatility and/or adsorption affinity.

The methods and instrumentation used in this study are widely available, unspecialized, and of a relative low cost. This is by design so that the methods developed can easily be replicated by the widest possible audience responsible for analysis or performing forensic investigations. As such, the GC-MS conditions are not optimized toward particular targets or species, but in fact are unrestricted in order to detect the widest possible range of marker compounds. For example, the scan range was set from 50 to 380 atomic mass units (amu) and scanned at each time increment. In the case of a forensic investigation targeted methods may be used to look in an optimized way for specific species, such as selected ion monitoring methods and smaller scan ranges or temperature ramps. For unknowns, critical information can be overlooked or not even detected.

## 1.2 Multivariate Data Analysis

### 1.2.1. Data Scaling

Prior to performing factor analysis, GC-MS data must be appropriately scaled so that it approximates the assumptions of the factor analysis technique. The factor analysis techniques used here are based on the method of least squares, which assumes that the errors are independent and identically distributed (*i.i.d.*) normal. Since these GC-MS data are collected as counts from a quadrupole mass spectrometer, the first principles assumption is that the data are actually Poisson distributed.<sup>1-3</sup> SNL has extensive experience with optimal scaling of multivariate Poisson-distributed data.<sup>4-6</sup> Briefly, the data can be scaled using the inverse of the square root of the mean mass spectrum.

Consider some GC-MS data in the  $m \times n$  matrix  $\mathbf{D}$  oriented as mass spectral domain by chromatographic domain with mean  $m/z$  spectrum  $\bar{\mathbf{d}}_m$  given by

$$\bar{\mathbf{d}}_m = \frac{1}{n} \mathbf{D} \mathbf{1}_n \quad (1)$$

where  $\mathbf{1}$  is an  $n$ -vector column of ones. Now, the data can be scaled in  $\mathbf{D}$  using the diagonal matrix  $\mathbf{H}$  whose diagonal elements are  $\bar{\mathbf{d}}_m^{-1/2}$  using

$$\tilde{\mathbf{D}} = \mathbf{H} \mathbf{D} \quad (2)$$

where  $\tilde{\mathbf{D}}$  is the data scaled for Poisson statistics. This scaling decreases the effect of large variations in the data due solely to noise in intense spectral regions. It is important for

subsequent factor analysis as it effectively down-weights the effect of variance due to noise in intense spectral features and concomitantly up-weights minor spectral features, which in the raw data are smaller in magnitude than noise elsewhere.

### 1.2.2. Principal component analysis (PCA)

PCA is a statistical method that decomposes a matrix into two sets of orthogonal of basis vectors, ordered by decreasing variance, that model the row and column spaces of the matrix.<sup>7-8</sup> It is often used as an initial data reduction method, whose subspace representation may be readily factor-analyzed by additional statistical treatments.<sup>4</sup> PCA can be represented in matrix form as

$$\tilde{\mathbf{D}} = \tilde{\mathbf{T}}\mathbf{P}^T + \tilde{\mathbf{E}} \quad (3)$$

where  $\tilde{\mathbf{T}}$  is an  $m \times p$  matrix which describes the row (or mass spectral) space of the scaled data in  $\tilde{\mathbf{D}}$ ,  $\mathbf{P}$  is an  $n \times p$  matrix describing the column (or chromatographic) space of  $\tilde{\mathbf{D}}$ ,  $\tilde{\mathbf{E}}$  is an  $m \times n$  matrix of scaled residuals or noise, and the superscript “T” indicates the transpose of the preceding matrix or vector. We use  $p$  to define the size, or pseudorank, of the subspace model that describes the chemically meaningful information contained in  $\tilde{\mathbf{D}}$ ; simply put, the number of distinguishable chemical species in  $\tilde{\mathbf{D}}$ .  $\tilde{\mathbf{T}}$  is orthogonal and  $\mathbf{P}$  is orthonormal having the properties:

$$\begin{aligned} \mathbf{\Lambda} &= \tilde{\mathbf{T}}^T \tilde{\mathbf{T}} \\ \mathbf{I} &= \mathbf{P}^T \mathbf{P} \end{aligned} \quad (4)$$

where  $\mathbf{I}$  is a  $p \times p$  identity matrix and  $\mathbf{\Lambda}$  is a  $p \times p$  diagonal matrix of eigenvalues ordered from largest to smallest. One can also compute a “full set” of eigenvalues of length  $\min(m, n)$  for fairly low computational cost. These eigenvalues can be used to estimate the pseudorank,  $p$ , in numerous ways.<sup>7</sup> Commonly, a semi-logarithmic plot of eigenvalue versus factor number is produced and the number of factors selected where a “knee” occurs in the plot.<sup>9</sup>

There is a variety of methods to compute the PCA, among these are nonlinear iterative partial least square (NIPALS),<sup>10</sup> eigenanalysis,<sup>11-12</sup> and singular value decomposition (SVD).<sup>12-13</sup> SVD is very convenient since it decomposes the matrix  $\tilde{\mathbf{D}}$  as

$$\tilde{\mathbf{D}} = \tilde{\mathbf{U}}\mathbf{S}\mathbf{V}^T + \tilde{\mathbf{E}} \quad (5)$$

where  $\mathbf{U}$  and  $\mathbf{V}$  are, respectively, the  $m \times p$  and  $n \times p$  matrices of orthogonal left and right singular vectors and  $\mathbf{S}$  is the diagonal matrix of singular values. The singular values are the square roots of the eigenvalues, *viz.*

$$\mathbf{\Lambda} = \mathbf{S}^2 \quad (6)$$

We can combine equations (3) and (5) to show that

$$\begin{aligned} \tilde{\mathbf{T}} &= \tilde{\mathbf{U}}\mathbf{S} \\ \mathbf{P} &= \mathbf{V} \end{aligned} \quad (7)$$

We have been careful in this section to utilize notation that indicates which data domain bears the scaling, in this case the mass-spectral domain. This is important since after factor analysis we will want to return those factors to their native scale, specifically

$$\mathbf{T} = \mathbf{H}^{-1}\tilde{\mathbf{T}} \quad (8)$$

### 1.2.3. Orthogonal Factor Rotation

After performing PCA, one will have an orthogonal, rank- $p$  representation of the data that will probably not resemble any meaningful information to the chromatographer. Consequently, additional factor analysis is required to transform the PCA factors into interpretable factors. A reasonable approach to transforming the factors is to use a factor rotation method.

Factor rotation methods seek to maximize (or minimize) some criterion that is consistent with the nature of the data. In the case of GC-MS data, the varimax rotation<sup>14-16</sup> is an appropriate criterion for the chromatographic domain. The varimax criterion seeks an orthogonal rotation matrix,  $\mathbf{R}$ , which maximizes the row (or time) variance of the orthonormal matrix  $\mathbf{P}$ , thereby maximizing the "simplicity" of the rotated elution-time or chromatographic factors. In matrix form we have

$$\tilde{\mathbf{D}} = \tilde{\mathbf{T}}\mathbf{P}^T = \tilde{\mathbf{T}}\mathbf{R}\mathbf{R}^T\mathbf{P}^T = \tilde{\mathbf{T}}\underline{\mathbf{P}}^T \quad (9)$$

Generally, the factors of chromatographic domain are simple or sparse. For example, when a species elutes it produces a peak in the chromatogram, generating a chromatographic factor with a single peak, and zeros or noise at all other times. Unless another species co-elutes, all other factors will be zero-valued (or baseline-noisy) at the elution times encompassing that species peak. So, the chromatographic domain is, generally, sparse. Overlapping due to co-elution or the presence of a large background is a violation of this premise. By contrast, there is no reason to expect that the mass-spectral domain is sparse since many different compounds generate the same mass fragments, although not in the same *pattern*; so this violates the simplicity assumption.

### 1.2.4. Multivariate Curve Resolution (MCR)

If all species were to elute at different times such that none were overlapped, and no background arose from column packing loss and discharge, then PCA and varimax rotation would be sufficient to produce interpretable results. Unfortunately, one often has to deal with these and other problems, and so needs to find a method applicable to these issues. MCR, also called linear unmixing,<sup>16</sup> is a factor analysis method that utilizes an alternating least squares strategy while employing constraints;<sup>17-19</sup> the most common constraint used being nonnegativity.<sup>20-21</sup> MCR seeks to solve

$$\tilde{\mathbf{D}} = \tilde{\mathbf{M}}\mathbf{C}^T + \tilde{\mathbf{E}} \quad (10)$$

where  $\tilde{\mathbf{M}}$  is the nonnegative  $m \times p$  matrix modeling the row (or mass spectral) space of the scaled data in  $\tilde{\mathbf{D}}$ ,  $\mathbf{C}$  is the nonnegative  $n \times p$  matrix modeling the column (or chromatographic) space of  $\tilde{\mathbf{D}}$ . Combining equations (10) and (9), we can form the relationship

$$\tilde{\mathbf{T}}\underline{\mathbf{P}}^T = \tilde{\mathbf{M}}\mathbf{C}^T \quad (11)$$

which represents the dimension reduction of  $\tilde{\mathbf{D}}$  as well as the imposition of nonnegativity constraints on the rotated PCA factors. Finally, following MCR, we would rescale the factors in  $\tilde{\mathbf{M}}$  using the appropriate substitution into Eq. (8).



## 2. METHODS AND EXPERIMENTAL

### 2.1. Sample Preparation

Sylgard<sup>®</sup> 184 and 186 Silicone Elastomer (Dow Corning, Midland MI, USA) are poly-dimethyl siloxane (PDMS) polymers. They are two component silicone having low and high viscosities, respectively.<sup>22</sup> The principal monomeric species of the oligomer are dimethyl siloxane with methylhydrogen siloxane as a crosslinking agent.<sup>23</sup> They are both terminated with dimethylvinyl, dimethyl siloxane, and have differences in proportions of the major components and in some of the minor components. They are used in general electronics potting applications, such as transformers, resistors, and controls.<sup>24</sup>

### 2.2. TD/GC-MS

#### 2.2.1. Thermal desorption methods and instrumentation

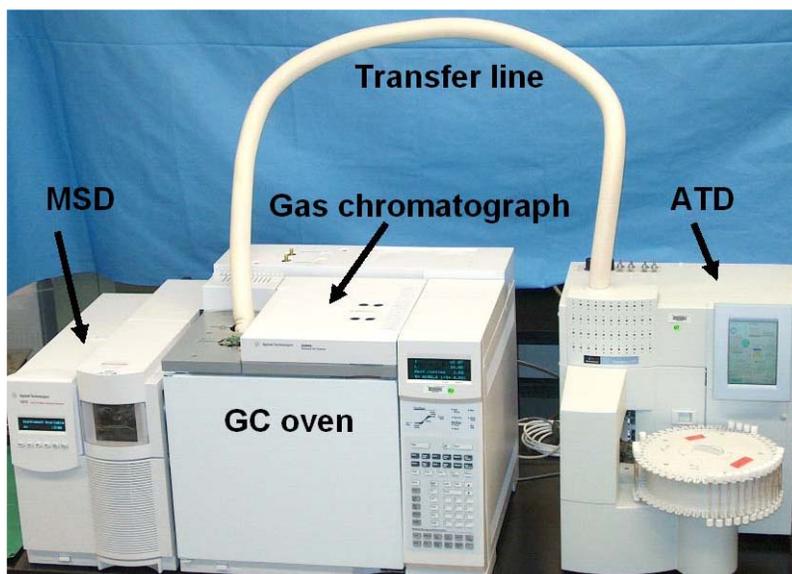
A 6.3 mg sample of Sylgard<sup>®</sup> 184 (27.4 mgs of Sylgard<sup>®</sup> 186) was placed into a desorption tube and inserted into a Perkin Elmer model TurboMatrix ATD thermal desorption unit. The sample was heated consecutively in the ATD at temperatures of 50°C, 65°C, 80°C, 105°C, 120°C, 135°C, and 150°C and chromatograms were acquired. The automated thermal desorption (ATD) was operated with an inlet valve temperature of 240°C, while maintaining the transfer line at 240°C. The sample trap low temperature was set at -30°C in order to collect the sample, and then ramped to 300°C at a heating rate 40°C/min to revolatilize the sample. The system used a purge time of one minute, a desorb time one minute, and a trap hold time of 5.0 min. A cycle time 60 min was chosen for these experiments, for compatibility with the expected elution times. The inlet split was off and outlet split on, and two-stage desorb mode was employed. The column pressure was set at 14.5 psi, outlet split of 36.3 mL/min, with desorb flow 46 mL/min, and inlet split of 197 mL/min.

#### 2.2.2 GC methods and instrumentation

All separations were performed using an Agilent 6890N gas chromatograph with an Agilent model 5975 inert XL MSD mass spectrometer (Agilent Technologies, Santa Clara, CA). The instrument was equipped with a HP-1701 GC column, 60 m × 0.32 mm ID and 0.1 μm film thickness. Temperature profile parameters were 35°C, hold 2 min; ramp at 5°C/min to 150°C, hold for 2 min, then ramp at 8°C/min to 280°C and hold for 5 min, for a total time of 48.25 min. Mass spectrometer details were to scan 33 to 380 amu (4.27 scans/sec) with samples at 2, threshold equal to 150, and sampling rate 2<sup>2</sup>.

The photo in Figure 1 shows the instrumentation used in this work. The large tube above the instruments is the insulated capillary transfer line between the thermal desorption autosampler and the gas chromatograph's heating inlet. The glass sample tubes on the circular stage at right contain the glass wool on which the sample is deposited. The tubes are rotated into place and heated internally in the ATD unit and swept with helium to release chemical constituents. Within the ATD is a thermoelectrically cooled trap of small internal volume that cryogenically traps the constituents that are released. At a predetermined time, the trap is rapidly heated to release the constituents which travel through the transfer line into the gas chromatograph. Inside

the GC oven is a long capillary separation column that separates the constituents in time and introduces them into the mass spectrometer detector (MSD) for detection.



**Figure 1: Photo of TD/GC-MS instrumentation used in this work.** From left to right, mass spectrometer detector (MSD), gas chromatograph (GC), and automated thermal desorption (ATD).

### 2.3. Data Processing and Analysis

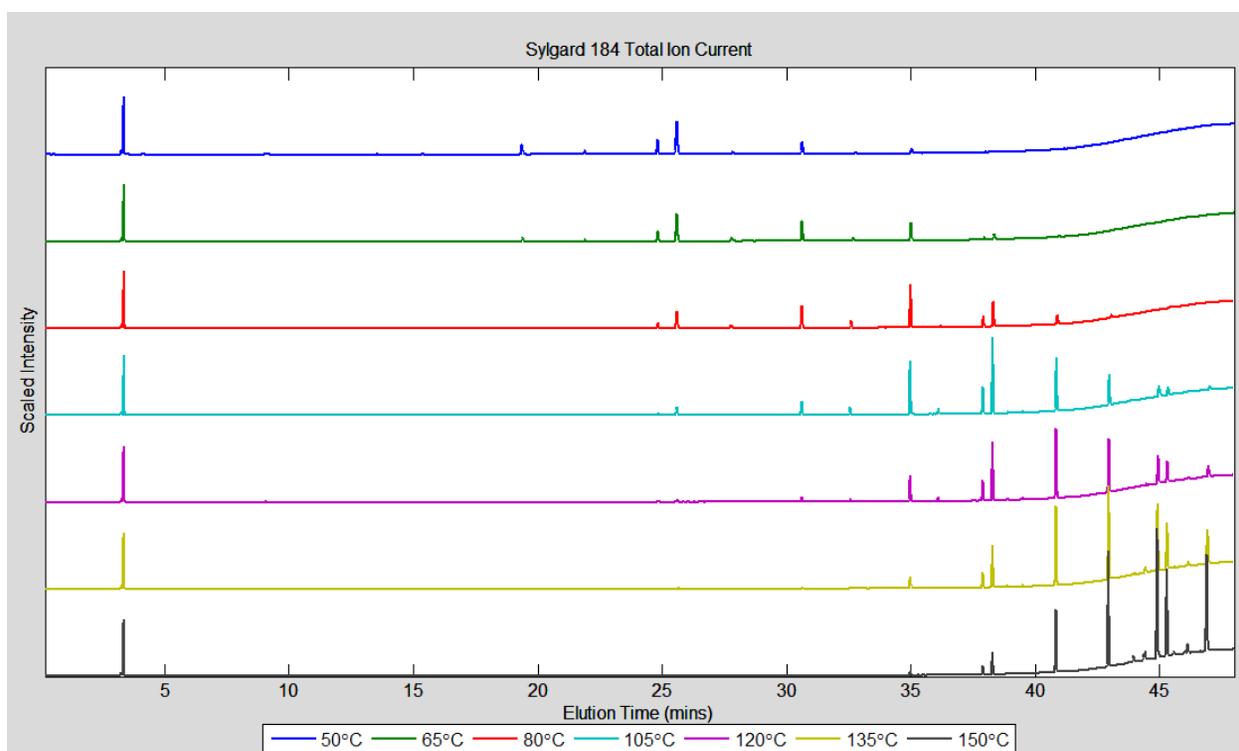
Agilent data were converted to MATLAB<sup>®</sup> file format using MassTransit software (Palisade Corp, Newfield, NY). All data processing and analysis were performed using SNL authored programs written in MATLAB<sup>®</sup> m-file language.<sup>25</sup> All computations were performed using Dell Precision 690 equipped with two, dual-core, 3.2 GHz Xeon processors and 4.0 Gbyte RAM; operating under Windows 7 Enterprise; and running MATLAB<sup>®</sup> version 7.10.0.499 (R2010a) and later. PCA was performed using a freely available SVD algorithm written in MATLAB<sup>®</sup> m-file format.<sup>26</sup> MCR was performed using code written in house employing fast combinatorial nonnegative least squares. The MCR algorithm utilized a PCA factored subspace rather than the full data set to improve performance and de-noise the data. MCR was initialized using the varimax rotated PCA components imposing simplicity in the elution time (chromatographic) domain.



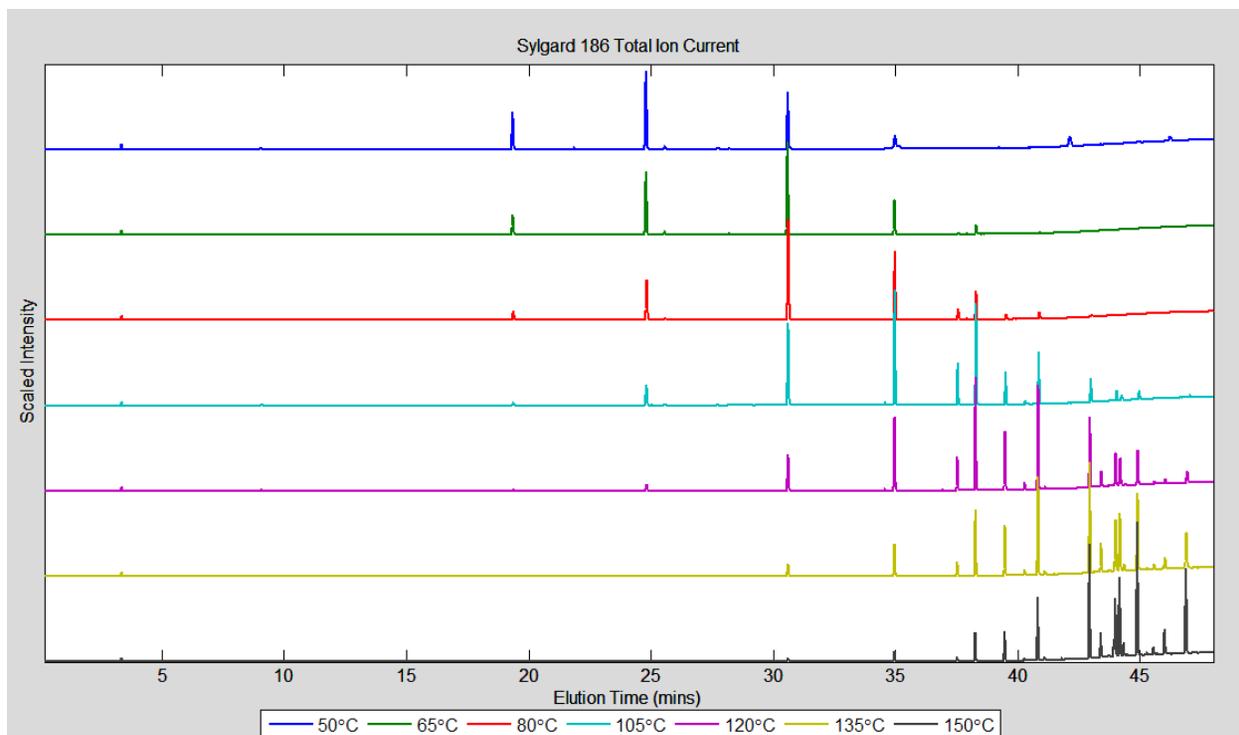
### 3. RESULTS

#### 3.1. TD/GC-MS Chemometric Analysis

Data were collected essentially as an array of mass counts and organized as mass spectral mode by chromatographic elution time by desorption temperature. Fractional mass channel data were summed into unit mass spectral elements. The total size of the Sylgard<sup>®</sup> 184 data array was 337 mass spectral elements (33-380 amu) by 3427 time elements (0-48 min, ~140 msec increments) by seven temperatures (50, 65, 80, 105, 120, 135 and 150°C). Figure 2 contains the plots of the total ion chromatograms (TICs) for the seven thermal desorption temperatures of Sylgard<sup>®</sup> 184. The Sylgard<sup>®</sup> 186 data array was 337 mass spectral elements (33-380 amu) by 12784 time elements (0-48 min, ~3.7 msec increments) measured at the same seven TD temperatures. Figure 3 contains the plots of the total ion chromatograms (TICs) for the seven thermal desorption temperatures of Sylgard<sup>®</sup> 186.



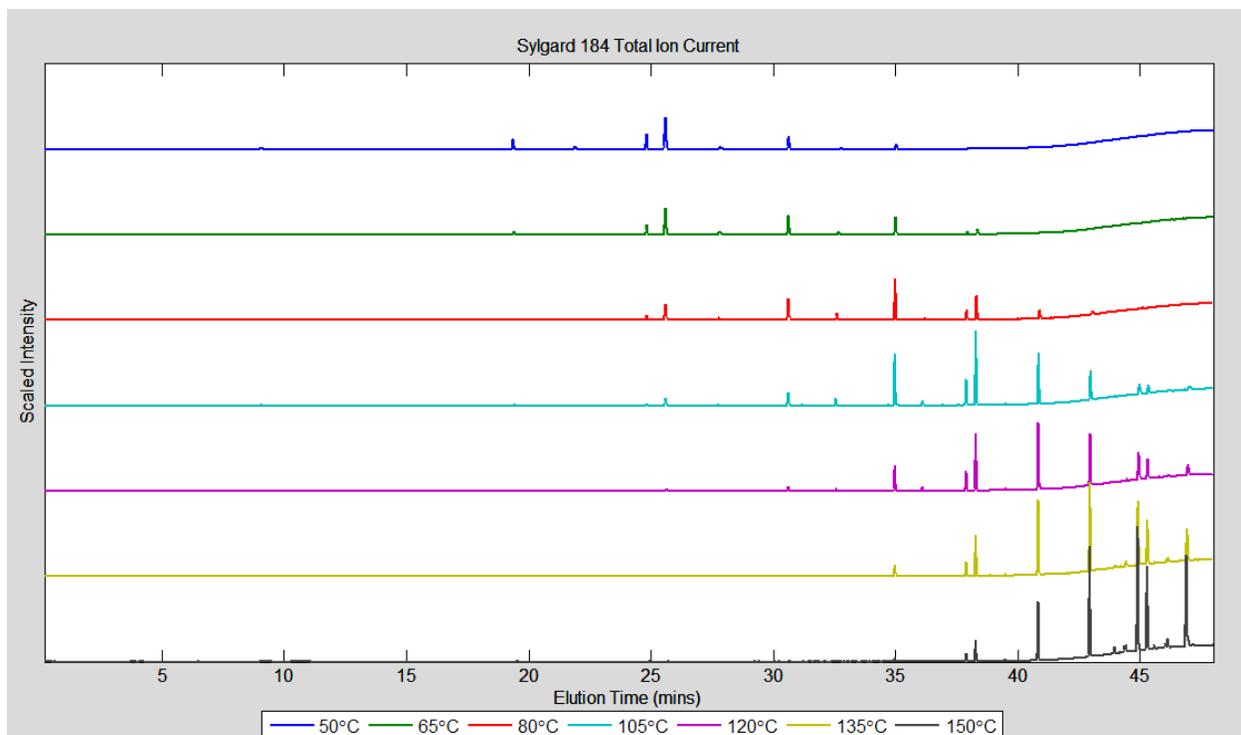
**Figure 2. Sylgard<sup>®</sup> 184 TICs for the seven TD temperature studies.**  
Intensities were scaled for convenience and ease of viewing.



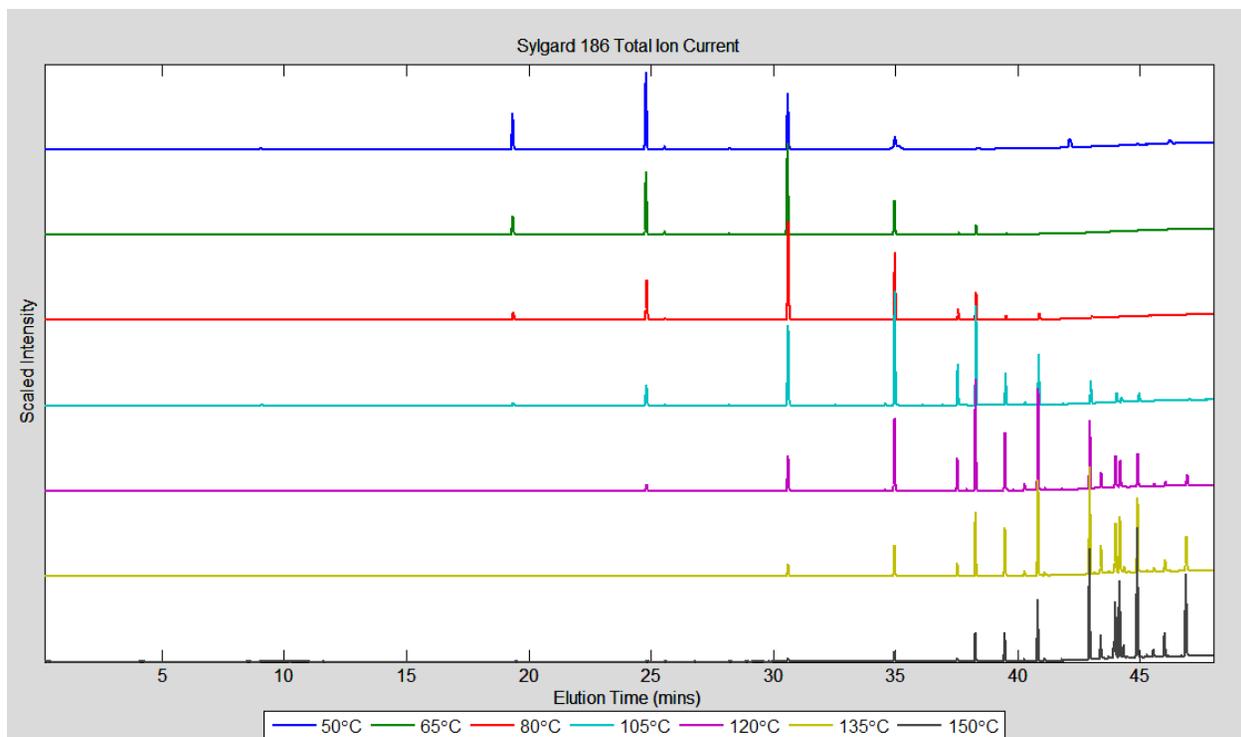
**Figure 3. Sylgard<sup>®</sup> 186 TICs for the seven TD temperature studies.**  
 Intensities were scaled for convenience and ease of viewing.

In Figure 2, and to a lesser extent in Figure 3, one can see a rather significant peak at ~3 minutes. This is actually two peaks whose largest mass peaks are 40 and 44 amu. Based upon their locations and mass spectra these peaks are CO<sub>2</sub> (at injection) and Ar (an air leak). In addition, a significant contribution of the background that crops up at around 30 minutes is column bleed from elevation of the column oven in the later stages of the elution, and has a very large mass peak at 207 amu. Given that we know these are essentially interferences in our analysis, we have eliminated masses 33-44 and 207 amu from these data. Removal of these mass channels reduce the mass spectrum dimension to 325 elements (mass channel 325 was already vacant). Figure 4 and Figure 5 contain the data in Figure 2 and Figure 3, respectively, after removing the offending masses. Note that the first peaks are gone, and close inspection reveals that the rising baseline is not as severe as before.

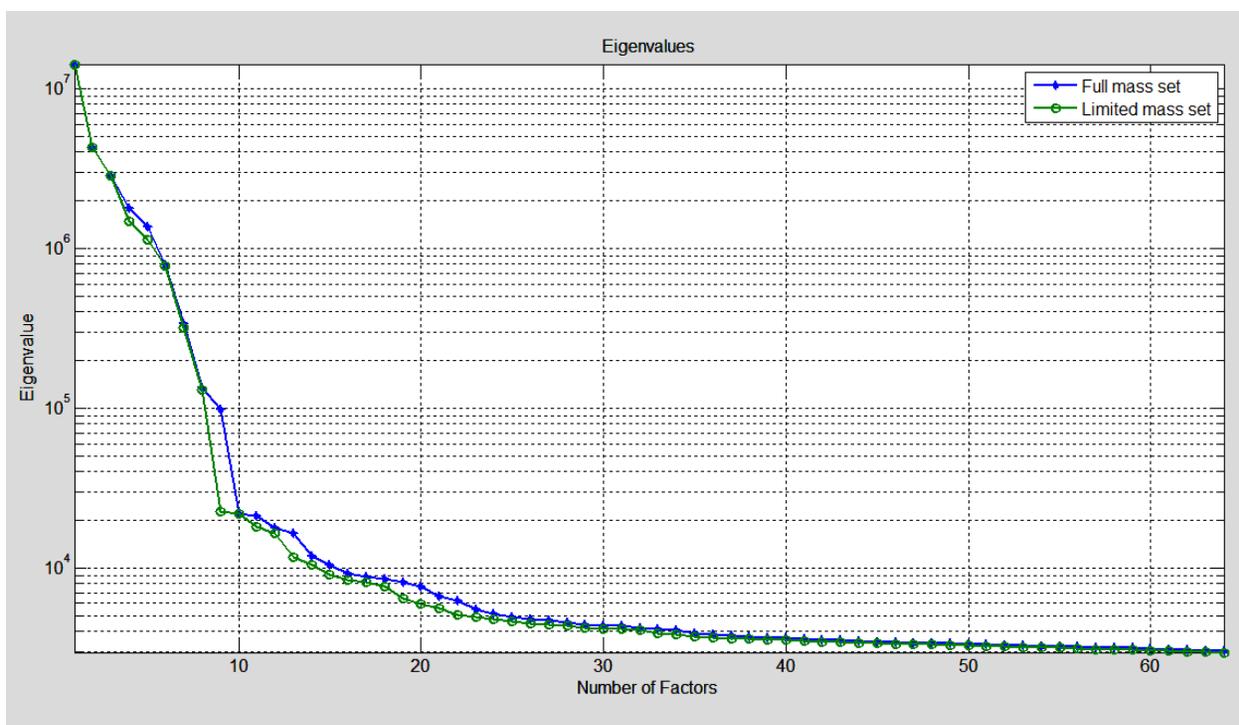
Analyses were performed on the two sets of data combined, *i.e.*, the data were organized as a large matrix whose dimensions were 325 mass channels by 113477 time-temperature-sample elements. Prior to multivariate analysis the data were Poisson-scaled using the mass spectral grand mean of the array as described in Eq. (2). Following scaling, the data were subjected to eigenanalysis to estimate the pseudorank. Figure 6 displays the results of eigenanalysis for data including all masses measured and excluding masses 33-44 and 207 amu. It appears that the rank for the full mass data is approximately nine, while the excluded mass data is approximately eight. One might suspect that the rank would drop by two when eliminating the CO<sub>2</sub> and Ar, but this is not the case because Ar is such a small contribution to the variance overall.



**Figure 4. Sylgard<sup>®</sup> 184 TICs for the seven TD temperature studies after removal of masses 33-44 and 207 amu.**  
 Intensities were scaled for convenience and ease of viewing.



**Figure 5. Sylgard<sup>®</sup> 186 TICs for the seven TD temperature studies after removal of masses 33-44 and 207 amu.**  
 Intensities were scaled for convenience and ease of viewing.

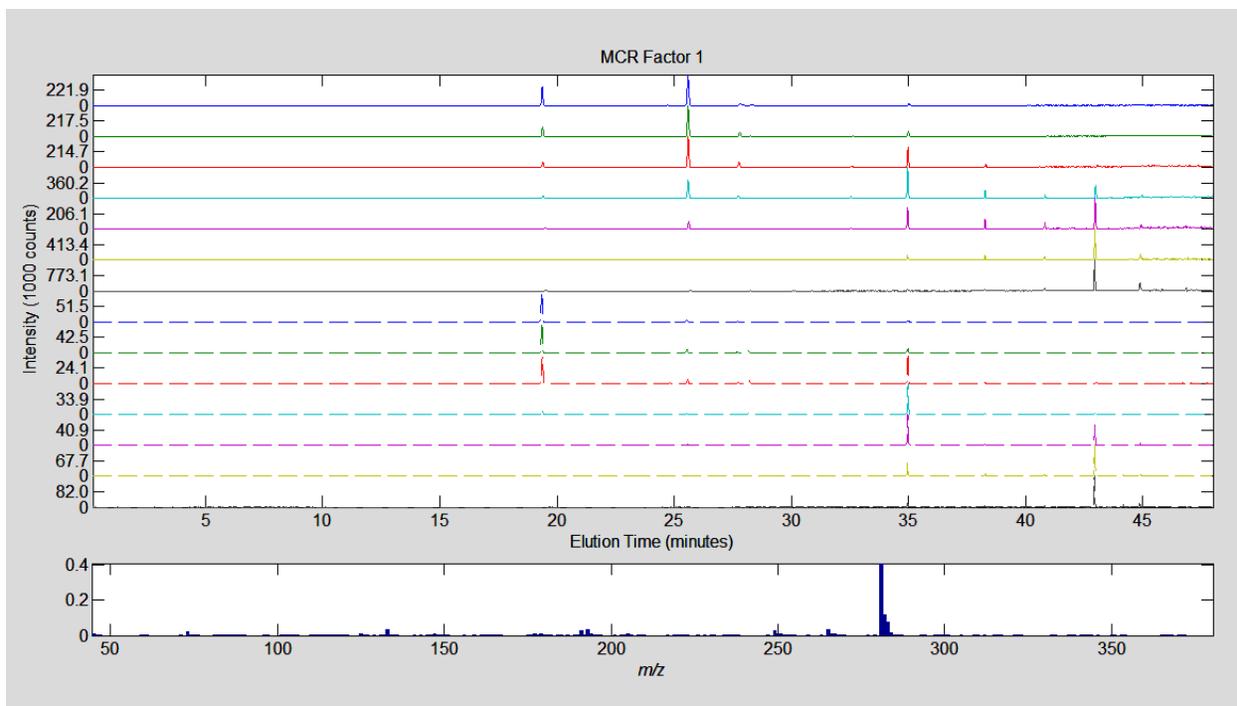


**Figure 6. Eigenvalues of combined Sylgard<sup>®</sup> 184 and 186 Poisson-scaled data.** Blue represents eigenvalues for combine data sets including all mass channels. Green omits mass channels 33-44 and 207 amu.

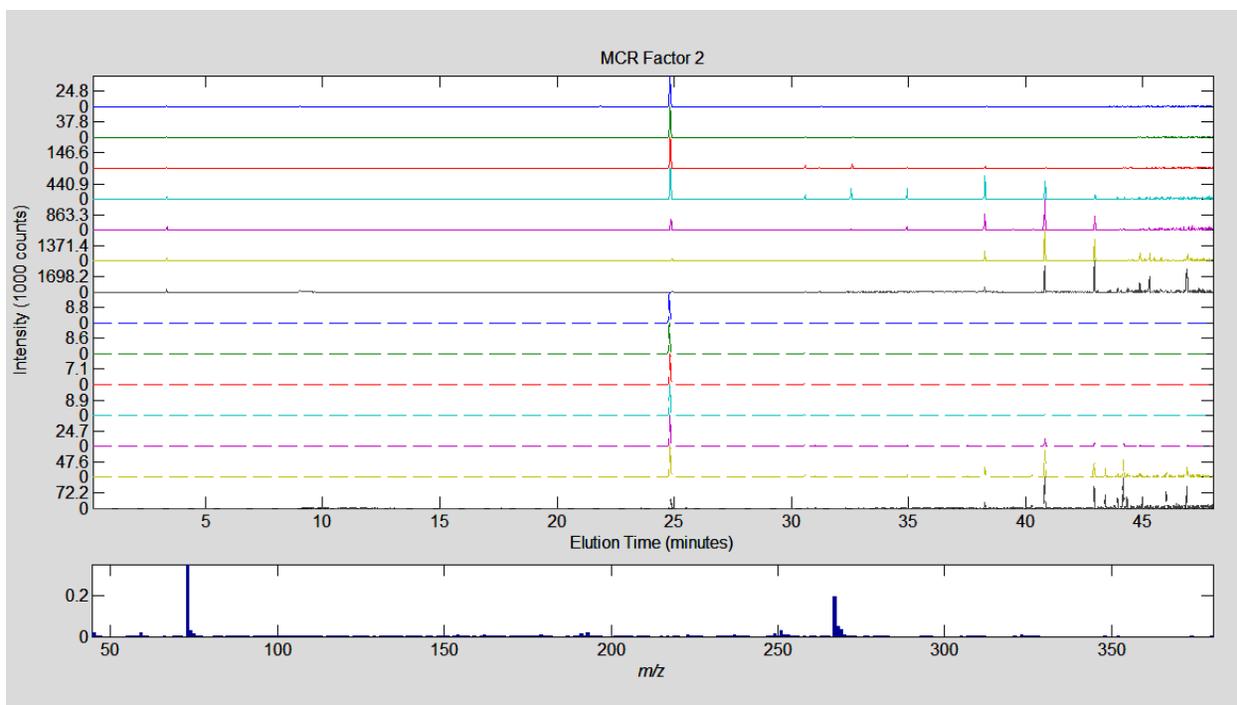
Figures 7 through 14 display the rank eight MCR model of the combined Sylgard<sup>®</sup> 184 and 186 TD/GC-MS data. In Figure 7, we find the first MCR factor has peaks at 19.3 and 25.6 minutes in the lower temperature events and at 35 and 43 minutes in the higher temperature events. The mass spectrum has one major group of peaks at 281-283 amu. It is possible that these peaks represent structural isomers of the major fragment for the species volatilized in the TD process. The second MCR factor, displayed in Figure 8, has major elution peaks at 24.8 minutes in the low and medium temperature events and 38.3, 40.8 and 42.9 minutes in the higher temperature events. The mass spectrum has major groups of peaks at 73-75 amu and 267-269 amu. Again, these are probably structural isomers of species volatilized at different temperatures.

Figure 9 models the background component, which is the siloxanes that emerge as a result of column bleed, which of course increased with the programmed oven temperature.

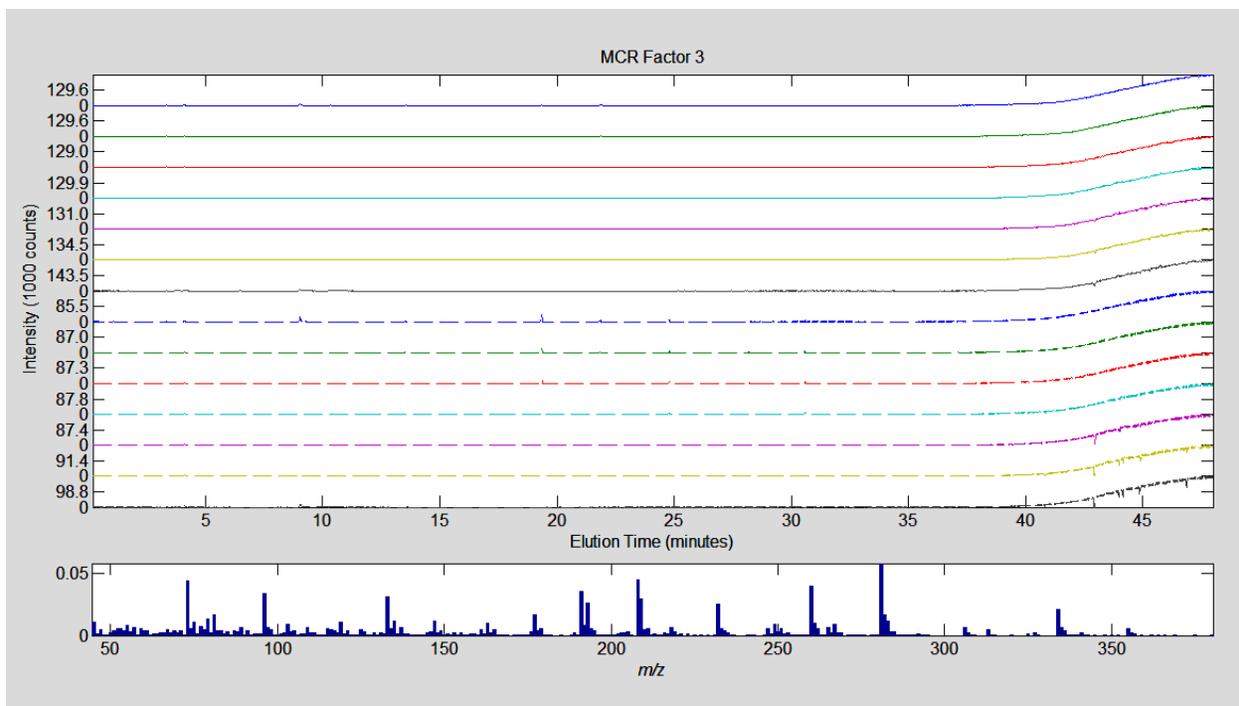
The remaining figures display factors four through eight, all of which have multiple elution peaks and multiple groups of mass peaks. They all seem to describe various fragments of siloxane molecules that are associated with decomposition of PDMS.



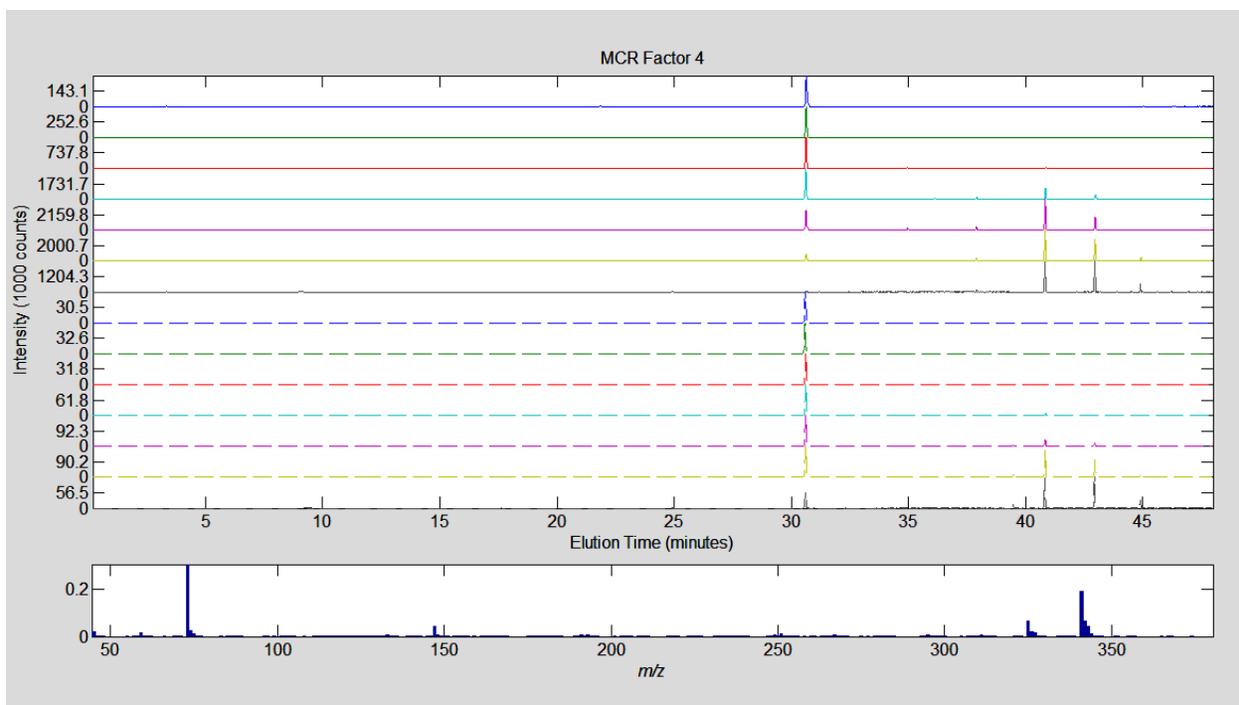
**Figure 7. MCR factor 1 of combined Sylgard<sup>®</sup> 184 and 186 Poisson-scaled data.** Top is the chromatographic mode for each of the 14 TD-sample trials; solid for Sylgard<sup>®</sup> 184 and dashed for 186. Bottom is the mass spectral mode. Data is Poisson-scaled and omits mass channels 33-44 and 207 amu.



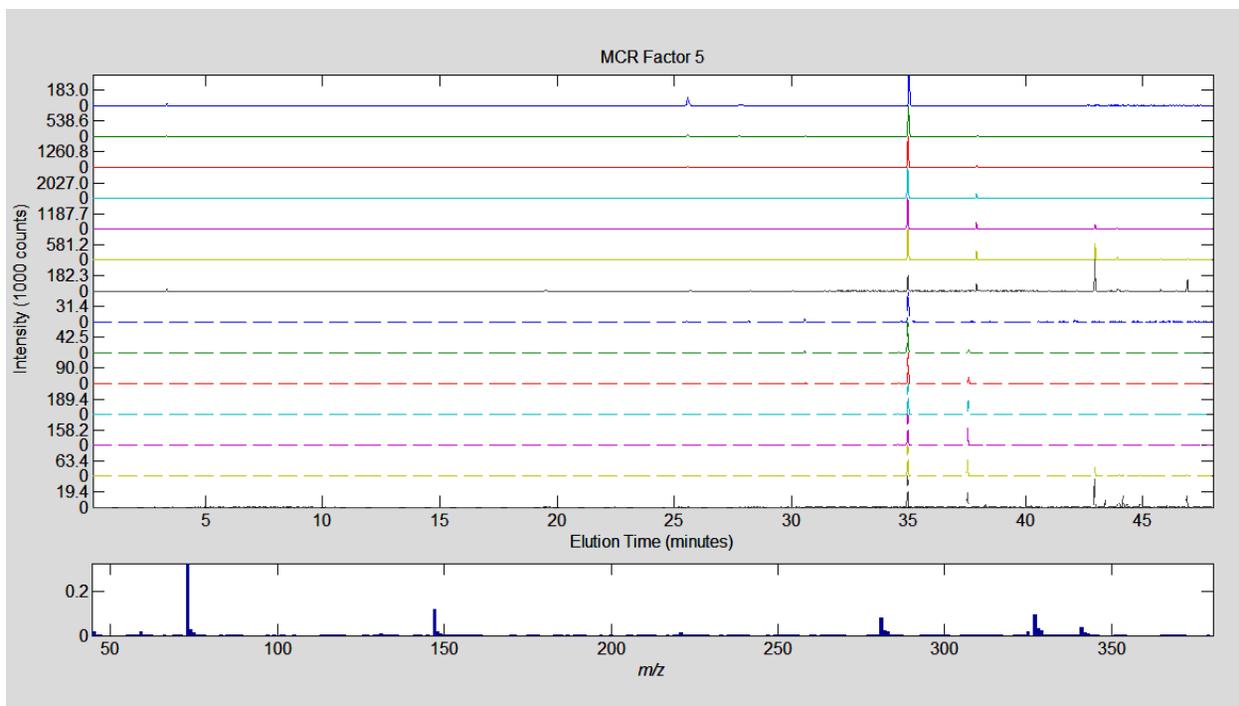
**Figure 8. MCR factor 2 of combined Sylgard<sup>®</sup> 184 and 186 Poisson-scaled data.** Top is the chromatographic mode for each of the 14 TD-sample trials; solid for Sylgard<sup>®</sup> 184 and dashed for 186. Bottom is the mass spectral mode. Data is Poisson-scaled and omits mass channels 33-44 and 207 amu.



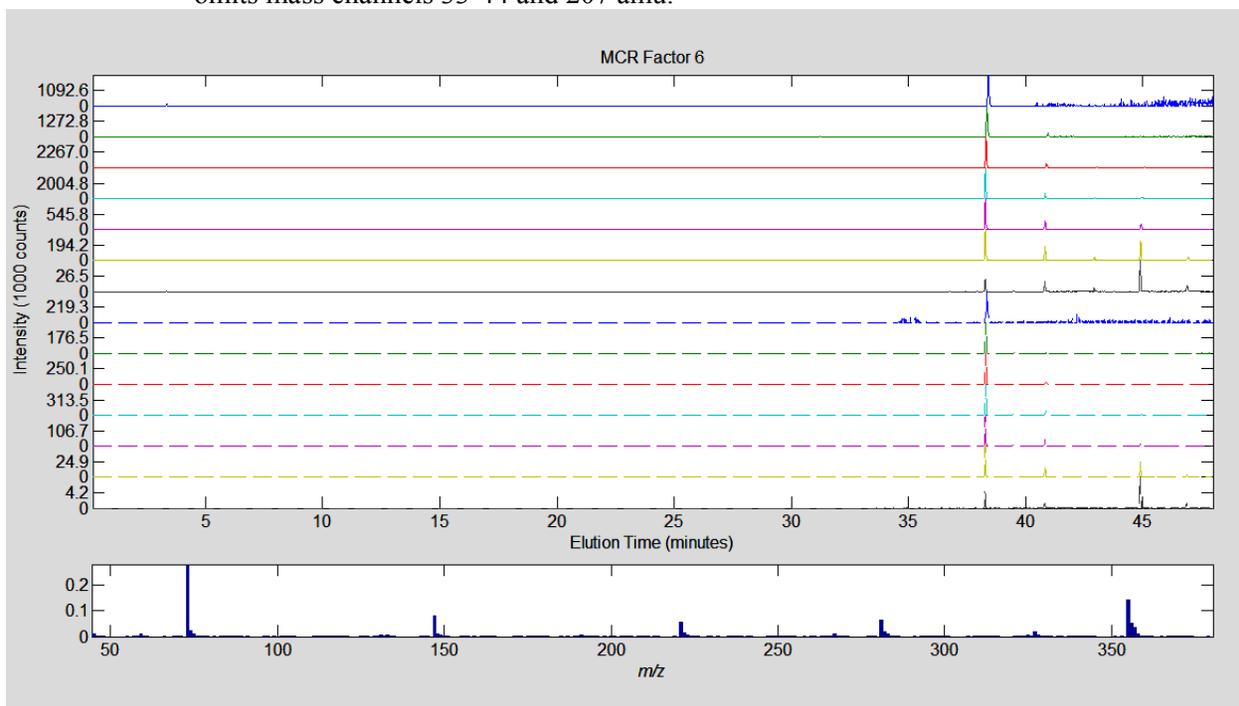
**Figure 9. MCR factor 3 of combined Sylgard® 184 and 186 Poisson-scaled data.** Top is the chromatographic mode for each of the 14 TD-sample trials; solid for Sylgard® 184 and dashed for 186. Bottom is the mass spectral mode. Data is Poisson-scaled and omits mass channels 33-44 and 207 amu.



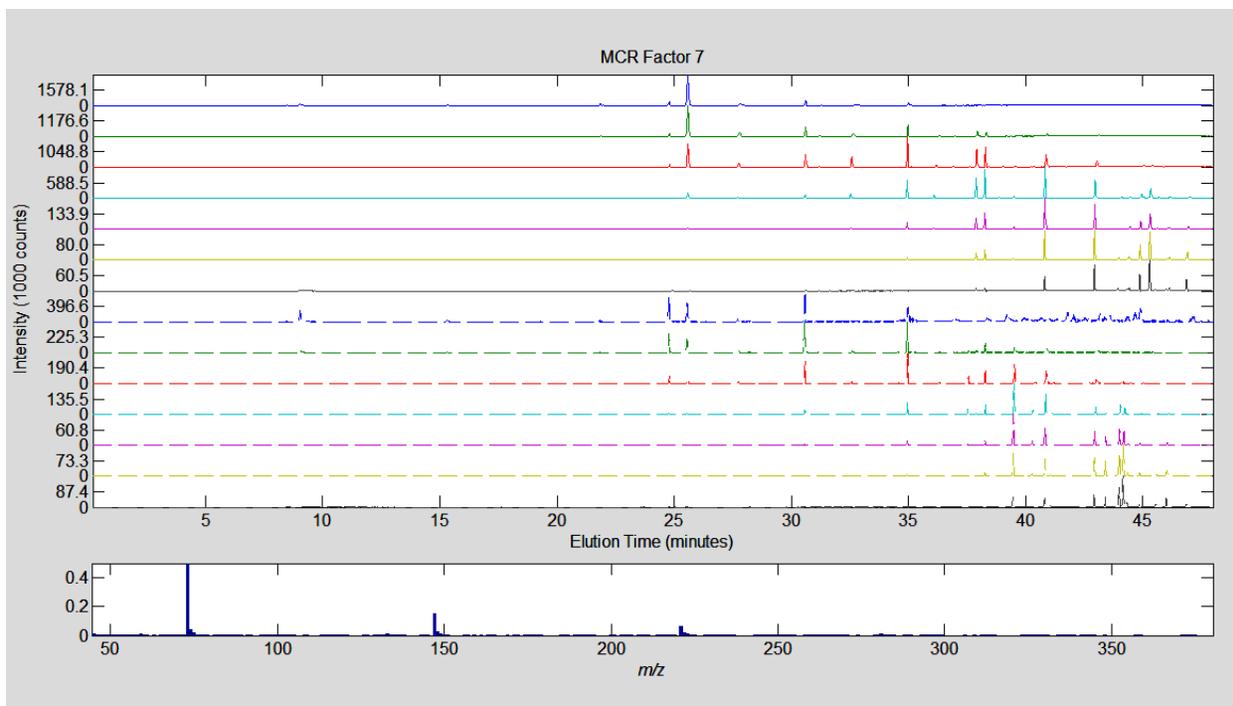
**Figure 10. MCR factor 4 of combined Sylgard® 184 and 186 Poisson-scaled data.** Top is the chromatographic mode for each of the 14 TD-sample trials; solid for Sylgard® 184 and dashed for 186. Bottom is the mass spectral mode. Data is Poisson-scaled and omits mass channels 33-44 and 207 amu.



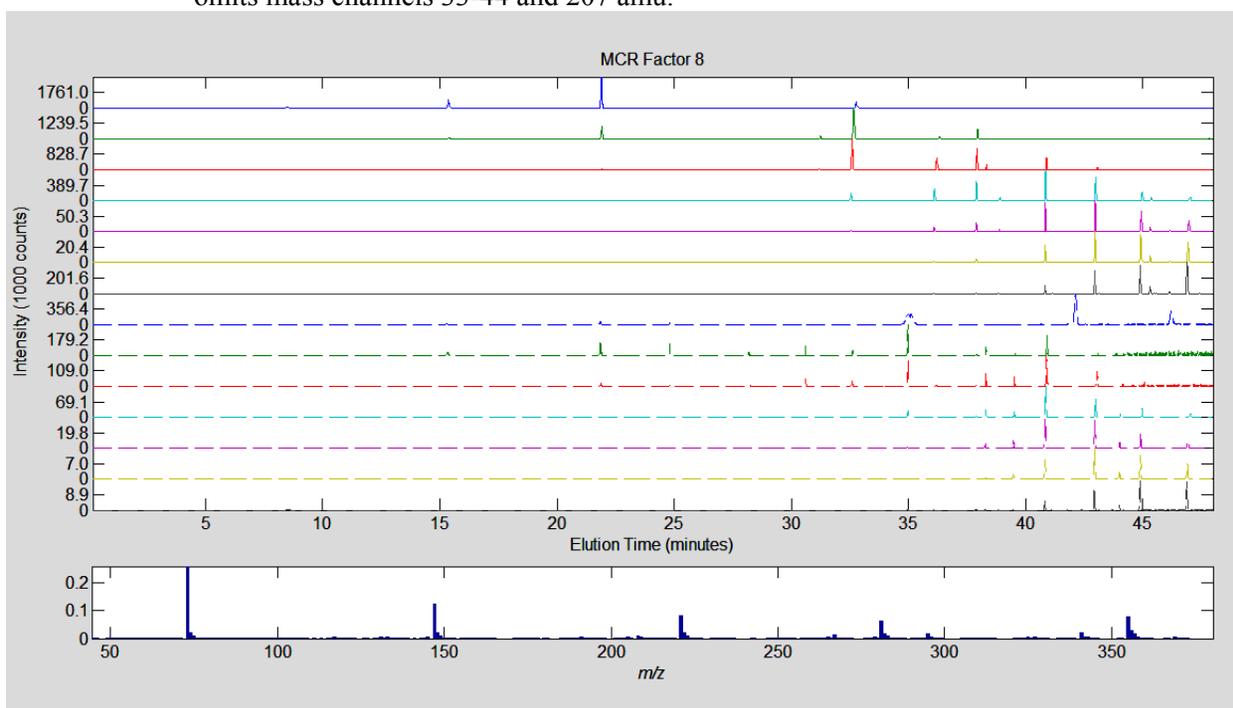
**Figure 11. MCR factor 5 of combined Sylgard® 184 and 186 Poisson-scaled data.** Top is the chromatographic mode for each of the 14 TD-sample trials; solid for Sylgard® 184 and dashed for 186. Bottom is the mass spectral mode. Data is Poisson-scaled and omits mass channels 33-44 and 207 amu.



**Figure 12. MCR factor 6 of combined Sylgard® 184 and 186 Poisson-scaled data.** Top is the chromatographic mode for each of the 14 TD-sample trials; solid for Sylgard® 184 and dashed for 186. Bottom is the mass spectral mode. Data is Poisson-scaled and omits mass channels 33-44 and 207 amu.



**Figure 13. MCR factor 7 of combined Sylgard<sup>®</sup> 184 and 186 Poisson-scaled data.** Top is the chromatographic mode for each of the 14 TD-sample trials; solid for Sylgard<sup>®</sup> 184 and dashed for 186. Bottom is the mass spectral mode. Data is Poisson-scaled and omits mass channels 33-44 and 207 amu.



**Figure 14. MCR factor 8 of combined Sylgard<sup>®</sup> 184 and 186 Poisson-scaled data.** Top is the chromatographic mode for each of the 14 TD-sample trials; solid for Sylgard<sup>®</sup> 184 and dashed for 186. Bottom is the mass spectral mode. Data is Poisson-scaled and omits mass channels 33-44 and 207 amu.



### **3. CONCLUSIONS**

We have presented results of a novel method for examining offgas products of a common PDMS material. Our method involves utilizing a stepped TD/GC-MS data acquisition scheme that may be almost totally automated, coupled with multivariate analysis schemes. This method of data generation and analysis can be applied to a number of materials aging and thermal degradation studies.



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