

# Off-Gassing and Particle Release by Heated Polymeric Materials

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## ABSTRACT

Polymers are one of the major constituents in electrical components. A study investigating pre-combustion off-gassing and particle release by polymeric materials over a range of temperatures can provide an understanding of thermal degradation prior to failure which may result in a fire hazard. In this work, we report simultaneous measurements of pre-combustion vapor and particle release by heated polymeric materials. The polymer materials considered for the current study are silicone and Kapton. The polymer samples were heated over the range 20 to 400°C. Response to vapor releases were recorded using the JPL Electronic Nose (ENose) and Industrial Scientific's ITX gas monitor configured to detect hydrogen chloride (HCl), carbon monoxide (CO) and hydrogen cyanide (HCN). Particle release was monitored using a TSI P-TRAK particle counter.

## INTRODUCTION

Polymer materials are widely used in industry for electrical and thermal insulation applications. On prolonged use under high load conditions such as high voltage or temperature, these materials are known to fail and may be a fire hazard. The sequence and identity of events that occur prior to combustion is not well understood. Vapors are released while materials heat; there is a pyrolysis stage of thermal decomposition of materials where chemical vapors and particles are released; finally, combustion may occur. These thermal decomposition failures could occur during operation at diminished or elevated pressure as well as under atmospheric conditions.

Urban *et al.* [1,2] have studied the characteristics of particle release under low-gravity conditions by heating a set of polymer materials to simulate prefire overheat events. In these studies, it was found that the particle size distribution for smoke from low gravity fires is larger than in normal gravity.

There have been studies that have focused on the off-gassing from polymers during thermal decomposition [3-5]. Gases such as HCl, CO and HCN are some of polymer pyrolysis products, and can be used as pre-combustion event markers in addition to particle releases. It was observed that the degradation of polymer materials in vacuum occurs at a lower temperature as compared to their thermal degradation under ambient conditions [4]. In the case of Teflon pyrolysis and combustion processes [5], a qualitative shift to lower temperatures is observed for the decomposition process when an oxidative atmosphere is used in the combustion process. Understanding of pre-combustion event markers, such as off-gassing and particle release leading up to combustion, is important for crew safety on space vehicles.

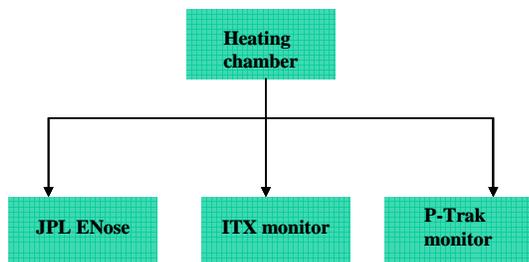
In the study discussed here, simultaneous measurements of vapor release and particle release have been made while heating polymeric materials. Materials investigated include silicone rubber and Kapton samples. These samples are heated in a chamber and responses to vapor releases are recorded by the JPL Electronic Nose (ENose) [6-15] and an Industrial Scientific ITX gas-monitor. Particles released are monitored by a TSI P-TRAK particle counter.

The JPL Electronic Nose (ENose) is an instrument designed to fill the gap between an alarm, such as a smoke alarm, and an analytical instrument such as a Gas Chromatograph – Mass Spectrometer (GC-MS). It identifies and quantifies vapors of chemical species to which it has been trained. In operation, a baseline of clean air is established, and deviations from that baseline are recorded as changes in resistance of the sensors.

This investigation is aimed at determining whether the JPL ENose can be used effectively as a monitor to detect pre-combustion events well before combustion and whether it could be used to develop necessary information to detect pre-fire events. Polymer heating experiments described here have provided us with information on the nature of events (vapor and particle release), sequence of events and conditions, such as temperature, under which these events have occurred.

## EXPERIMENTAL

The experimental setup is shown in the block diagram in Figure 1. This consists of a heating chamber connected to the JPL ENose, ITX gas monitor and the P-TRAK particle monitor.



**Figure 1:** Block diagram of experimental setup for polymer sample heating to monitor off-gassing and particle release

The heating chamber consists of an alumina tube wrapped with heating coils and covered with insulation. An inner quartz tube that accommodates the polymer samples is in contact with the alumina tube. The heater is connected to a power supply. A microprocessor temperature controller takes temperature input from the chamber and regulates the power to the heating elements based on the desired temperature set point and ramp rates. The heater was calibrated to provide determined temperatures within the quartz tube by setting a corresponding temperature on the controller.

The ITX gas monitor, manufactured by Industrial Scientific, has electrochemical sensors that are specific to CO, HCl, and HCN gases, and quantify at parts-per-million (ppm) concentration levels. The sensors have a resolution of about 1ppm and measure concentration in the range 0-30 ppm for HCl and HCN and 0-999 ppm for CO. The ITX was used in these experiments because it is the commercial version of the Compound Specific Analyzer-Combustion Products (CSA-CP) used by NASA in crew habitat to determine whether combustion products are present in breathing air.

The P-TRAK particle counter, manufactured by TSI, Inc., measures submicron to micron range particles (0.02-1 microns). This is a condensation particle counter (CPC). In this instrument, particles are drawn through the instrument by a pump and pass through a saturator tube where the particles mix with alcohol vapors. The mixture (alcohol /particles) is then drawn into a condenser tube, which cools the air/particle stream causing alcohol to condense on the particles and the particles grow into detectable droplets. The droplets then pass through a focused laser beam, producing flashes of scattered light. The scattered light flashes are sensed by photodetector and counted to determine particle number concentration (particles/cc). The maximum limit of detection by the P-TRAK is 500,000 particles/cc.

The experimental set up and protocols for experiments in this study were based on the microgravity combustion experiments which preceded the Smoke and Aerosol experiments (SAME) [1,2]. The SAME experiments were performed by resistively heating samples of silicone, Kapton, cellulose, and Teflon materials to produce smoke. The smoke was aged and then analyzed using industrial particle monitors (P-TRAK and DUSTTRAK) and a modified residential smoke detector to obtain the particle distribution characteristics.

In our experiments, prior to introducing the sample in the combustion chamber at room temperature, all instruments were baselined for 10 minutes. A polymer sample was introduced into the quartz tube of the heating chamber. The first measurement was made at room temperature with the polymer sample in the combustion chamber. Temperature scans were then performed on the polymer samples by ramping and soaking. Temperature ramps are performed from room temperature (21°C) to 50 °C and then 50°C to 400°C in increments of 50 °C. A ramp rate of 1.5-3.5 °C/min and soak time of 15-20 minutes was used. Vapors released during polymer heating were monitored by the JPL ENose and the ITX gas monitor, and particles released were monitored by the P-TRAK. During the temperature scan experiments, the instruments were operated at their normal pump capacities for sampling vapors and particles released from the combustion chamber.

## RESULTS AND DISCUSSION

### (i) *Silicone rubber heating*

To understand the kind of events and sequence of events as a function of time and temperature, the results for vapor and particle releases are analyzed by overlapping responses from the ENose and ITX gas monitor and P-TRAK. The results from heating silicone rubber are shown in Figure 2 (a)-(c).

In Figure 2(a), normalized P-TRAK particle counts are plotted vs. time with temperature soak periods shown as bars on the plot. The normalized particle count is defined as  $(N_p(t) - N_p(t=0)) / N_p(t=0)$ , where  $N_p(t=0)$  is the particle count at the start of the experiment ( $t=0$ ). The normalized particle count shows no significant change until the end of the 150°C cycle, following which there is a sharp rise in particle count. A normalized value of 80 corresponds to a particle count of about 500,000 particles/cc, which is the limit for the P-TRAK particle counter. For sample temperatures above 150°C to the soak at 200°C, the particle count remains high. At a sample temperature of 200°C; the P-TRAK was saturated. As a result, the P-TRAK had to be stopped and the condenser cartridge needed to be soaked in alcohol for reuse.

Figure 2(b) shows the results from the ITX gas monitor and the humidity sensor of the JPL ENose. In the temperature range 23 - 200°C, the ITX gas monitor did not detect any HCl/CO/HCN gases. In this same

temperature range (23 - 200°C), three significant humidity changes were detected by the JPL ENose. Note that the ITX monitor does not respond to these humidity events. For sample temperatures in the range 200-250°C, there is a sudden release of ~ 5ppm HCL accompanied by a humidity release. Following this first HCL release (after 200°C) the ITX response drifts, but recovers over time, when the sample temperature is about 250 °C. The drift could be due to the HCL sensors' cross sensitivity to other vapors released at the same time. In the temperature range above 250°C, the HCL concentration rose rapidly to about 15 ppm. At the same time, CO was detected, with concentrations increasing to about 5ppm after the 300°C soak.

Above 300°C, the experiment was stopped by discontinuing the heating; the rapid rise in HCL concentrations could damage the ITX sensors. Hence, the response of the ENose sensors to 5 ppm CO and HCL could not be recorded properly at temperature and times after the 300°C soak.

Comparing Figure 2(a) and Figure 2(b), we observe that the spike in particle release happens prior to the first HCL and CO events. The particle release events subsided, as indicated by the decrease in particle count when the HCL and CO events start.

Representative ENose sensor responses to vapors released from heated silicone rubber are shown in Figure 2(c). ENose sensors respond to all the humidity spikes prior to 200°C as well as to vapors released at the same time as HCL is detected by the ITX, after 200°C. During the 300°C soak, ENose sensors showed very weak or no response to low CO concentrations (~ 2-3 ppm).

It can be seen in Figure 2(c) that the magnitude of ENose sensor response to vapors released at a temperature just above 200°C is larger than sensor response to previous humidity releases of about the same concentration. Hence, we can say that the ENose sensor response at 200+ °C corresponds to vapors released at the same time as the sudden HCL release, and not only to the increase in humidity. The baseline drift of the ENose sensors during the temperature scans match the humidity trends recorded in the ENose sensing chamber (compare humidity trace in Figure 2b with sensor traces in Figure 2c).

Because the ENose is not yet trained to HCL, the sensor response pattern to HCL or HCL plus water is not known; it cannot be said unequivocally that the sensors are responding to HCL. It is possible that other vapors were released by the silicone rubber at the same time as HCL. Training the ENose to the HCL and the combination of gases released from silicone rubber at a temperature above 200 °C remains for future work, as does determining which gases are released at this temperature.

For silicone rubber, there is significant release of particles and water as the temperature rises to 200 °C, prior to release of HCL and CO vapors. The particle

count starts to subside when the HCL/CO gas events begin.

### (ii) **Kapton heating**

The results recorded by the three instruments after heating a sample of Kapton in the range 21–400 °C is shown in Figures 3(a)-(c)

The results from the P-TRAK for Kapton heating are shown in Figure 3(a). It can be seen that in the temperature range 21 - 350°C, there is no significant change in particle count. When the sample was held at 400°C there is a sudden increase in the particle count. The particle count reaches the maximum of 500,000 particles/cc during this time. Figure 3(b) shows the results from the ITX gas monitor and the humidity sensor of the JPL ENose. It can be seen that there is a humidity spike during the 100°C soak cycle. There is no HCL or CO detected over the entire range of temperature (21-400°C). If there are pre-combustion vapors released from Kapton, it will be necessary to do a temperature scan higher than 400°C.

Representative JPL ENose sensor responses to vapors released from Kapton heating are shown in Figure 3(c). It can be seen that the ENose sensors respond to the humidity spike seen during the 100°C soaking cycle. Like the silicone heating experiment we see a continuous decrease in chamber humidity, which correlates with the apparent drift of the baseline in ENose sensors.

## **CONCLUSIONS**

We have investigated the vapor and particle releases from silicone rubber and Kapton polymer samples over a temperature range of 23 to 350°C for silicone and 21 to 400°C for Kapton. The silicone sample released water at three temperatures, particles at temperatures below 200°C and HCL and possibly other vapors slightly above 200°C. The Kapton sample did not release vapors other than water; Kapton released particles only at 400°C. If Kapton's pre-combustion behavior is similar to that of silicone rubber, then the sample was not taken to a high enough temperature to develop pre-combustion vapor release.

The JPL ENose responds to all vapor releases recorded by other devices for the silicone rubber sample, and showed no additional responses to vapor releases. The ENose responded to the water release for the Kapton sample. While, at this point it cannot be said the ENose can be used to detect pre-combustion events caused by polymer heating, it show promise and the need for further testing. Further, more specific training of the ENose sensors is required to develop necessary information to detect pre-fire events.

In future work, the temperature range between 200 and 350°C will be further investigated in smaller temperature increments to understand the vapor and particle releases for the silicone polymer, and

temperatures above 400°C will be investigated for Kapton. In addition, vapor samples will be collected from both silicone and Kapton and analyzed using a standard chemical analytical technique such as mass spectroscopy to determine what vapors are released as the materials are heated. Further work will also include similar experiments on additional materials.

## ACKNOWLEDGMENTS

The research reported in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology under a contract with the National Aeronautics and Space Administration and supported by the Advanced Environmental Monitoring and Control Program, ESMD, NASA.. Thanks to Gary Ruff at Glenn Research Center for providing the initial polymer samples.

## REFERENCES

1. J. E. Brooker, D.L. Urban, G.A. Ruff, "ISS Destiny Laboratory Smoke Detection Model", 07ICES-113, *International Conference on Environmental Systems*, Chicago, (2007).
2. D.L. Urban, D. Griffin, G.A. Ruff, T. Cleary, J. Yang, G. Mulholland, Z.G. Yuan, "Detection of Smoke from Microgravity Fires", *International Conference on Environmental Systems*, Rome Italy, Paper # 2005-01-2930, SAE Transactions, pp 375-384 (2005).
3. V. Babrauskas, "Mechanisms and modes for ignition of low-voltage, PVC-insulated electrotechnical products", *Fire and Materials* 30,151-174 (2006).
4. D. L. Schweickart, "A Survey of Thermal Decomposition of Solid Insulations and its Relevance to Breakdown Mechanisms in Partial Vacuum", *Digest of Technical Papers Tenth IEEE International Pulsed Power Conference*, 2, 1482 - 1487 (1995).
5. J. A. Conesa and R. Font, "Polytetrafluoroethylene Decomposition in Air and Nitrogen", *Polymer Engineering and Science*, 41(12), 2137-2147 (2001).
6. M.A. Ryan, M.L. Homer, M.G. Buehler, K.S. Manatt, F. Zee, and J. Graf, "Monitoring the Air Quality in a Closed Chamber Using an Electronic Nose," *Proc. 27th Intl. Conf. on Environ. Systems*, SAE (1997).
7. M.A. Ryan, M.L. Homer, M.G. Buehler, K.S. Manatt, B. Lau, D. Karmon, and S. Jackson, "Monitoring Space Shuttle Air for Selected Contaminants Using an Electronic Nose," *Proc. 28th Intl. Conf. on Environ. Systems*, SAE (1998).
8. M.A. Ryan, M. L. Homer, H. Zhou, K. S. Manatt, V. S. Ryan, and S. Jackson, "Operation of an Electronic Nose Aboard the Space Shuttle and Directions for Research for a Second Generation

Device," *Proc. 30th Intl. Conf. on Environ. Systems*, SAE (2000).

9. M.A. Ryan, H. Zhou, M.G. Buehler, K.S. Manatt, V.S. Mowrey, S.P. Jackson, A.K. Kisor, A.V. Shevade, and M.L. Homer, "Monitoring Space Shuttle Air Quality Using the JPL Electronic Nose," *IEEE Sensors Journal*, 4, 337 (2004).
10. M.A. Ryan, A.V. Shevade, H. Zhou and M.L. Homer, "Polymer-Carbon-Composite Sensors for an Electronic Nose Air Quality Monitor," *MRS Bulletin*, 29, 714 (2004).
11. M.A. Ryan, M.L. Homer, H. Zhou, K. Manatt, A. Manfreda, A. Kisor, A. Shevade and S.P.S. Yen; "Expanding the Analyte Set of the JPL Electronic Nose to Include Inorganic Species;" *Journal of Aerospace, SAE Transactions*, 2005-01-2880 (2005).
12. M.A. Ryan, M.L. Homer, H. Zhou, K. Manatt, A. Manfreda, A. Kisor, A. Shevade and S.P.S. Yen; "Expanding the Capabilities of the JPL Electronic Nose for an International Space Station Technology Demonstration", *Proc. 36th Intl. Conf. on Environ. Systems*, SAE, 2179 (2006).
13. H. Zhou, M. L. Homer, A. V. Shevade and M. A. Ryan "Nonlinear Least-Squares Based Method for Identifying and Quantifying Single and Mixed Contaminants in Air with an Electronic Nose;" *Sensors*, 6, 1 (2006).
14. A.V. Shevade, M.A. Ryan, M.L. Homer, A.M. Manfreda, H. Zhou, K.S. Manatt, "Molecular Modeling of Polymer Composite-Analyte Interactions in Electronic Nose Sensors," *Sens. & Act. B*, 93, 84 (2003).
15. A.V. Shevade, M.A. Ryan, M.L. Homer, A.M. Manfreda, H. Zhou and K. Manatt, "Correlating Polymer-Carbon Composite Sensor Response with Molecular Descriptors," *J. Electrochem. Soc.*, 153, H209 (2006).

## ABBREVIATIONS

ENose: Electronic Nose

ITX gas monitor: Industrial Scientific gas monitor

P-TRAK: TSI particle counter  
(measures particle count)

DUSTTRAK: TSI particle counter  
(measures particle concentration)

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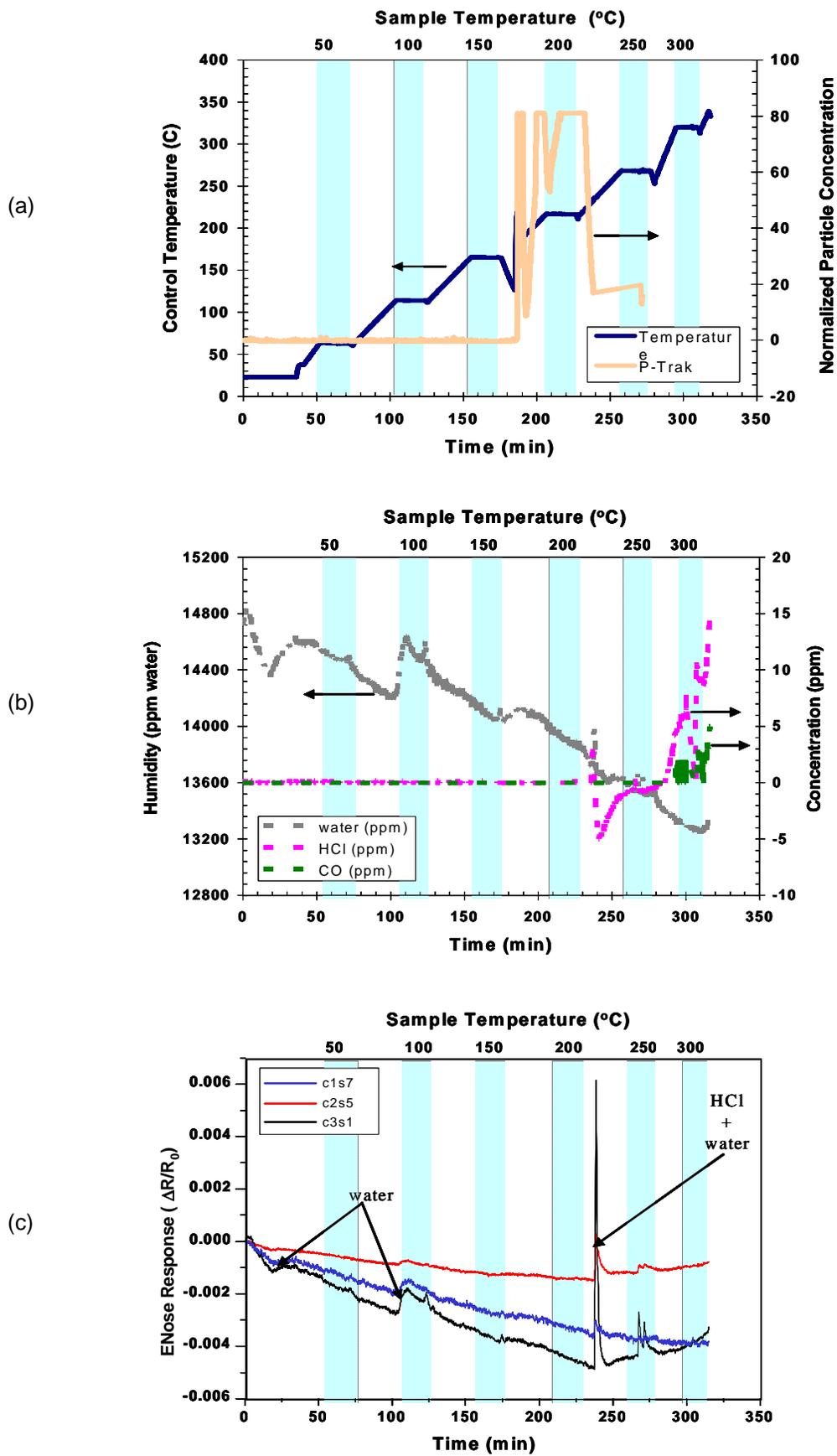


Figure 2: Silicone rubber heating results showing (a) temperature scans and P-TRAK particle count data (b) ITX gas monitor and ENose humidity data (c) ENose sensor data.

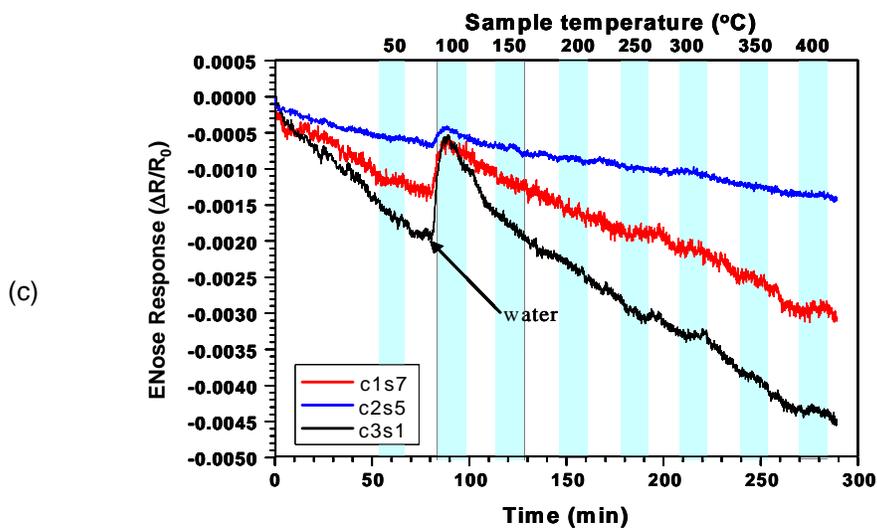
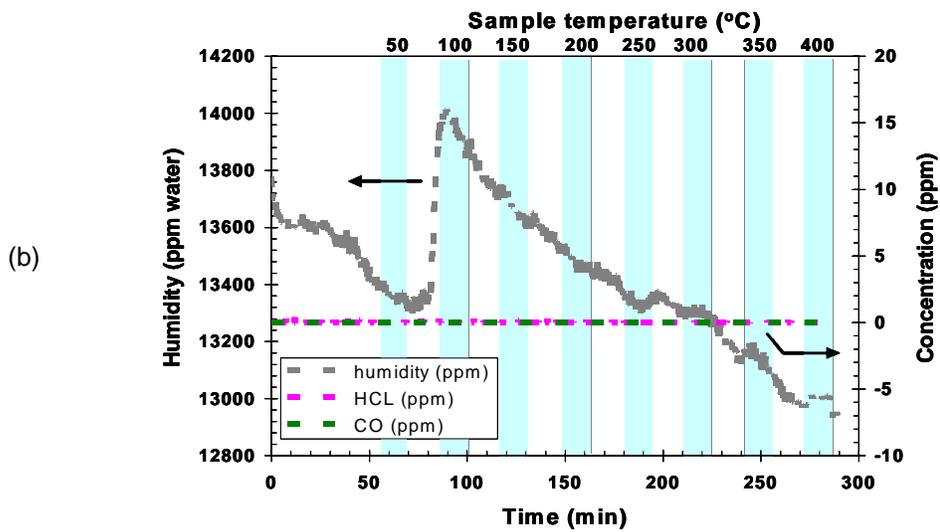
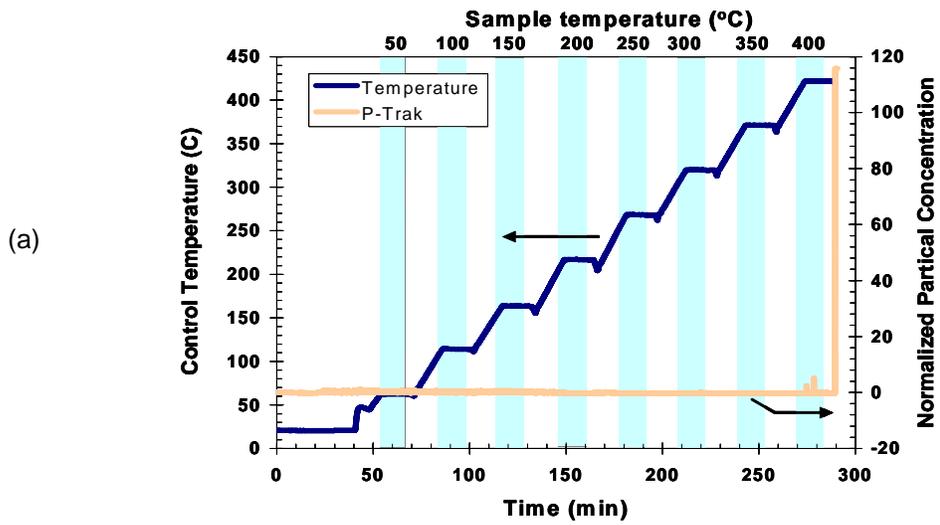


Figure 3: Kapton heating results showing (a) temperature scans and P-TRAK particle count data (b) ITX gas monitor and ENose humidity data (c) ENose sensor data.