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Thermal degradation of New and Aged Urethane Foam and Epon 826 Epoxy

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Thermal degradation of New and Aged Urethane Foam and Epon 826 Epoxy

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Abstract

Thermal desorption spectroscopy was used to monitor the decomposition as a function of temperature for the foam and epoxy as a function of temperature in the range of 60°C to 170°C. Samples were studied with one day holds at each of the studied temperatures. Both new (FoamN and EpoxyN) and aged (FoamP and EpoxyP) samples were studied. During these ~10 day experiments, the foam samples lost 11 to 13% of their weight and the EpoxyN lost 10% of its weight. The amount of weight lost was difficult to quantify for EpoxyP because of its inert filler. The onset of the appearance of organic degradation products from FoamP began at 110°C. Similar products did not appear until 120°C for FoamN, suggesting some effect of the previous decades of storage for FoamP.

In the case of the epoxies, the corresponding temperatures were 120°C for EpoxyP and 110°C for EpoxyN. Suggestions for why the aged epoxy seems more stable than newer sample include the possibility of incomplete curing or differences in composition.

Recommendation to limit use temperature to 90-100°C for both epoxy and foam.

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NOMENCLATURE

| | |
|------|--|
| AMU | Atomic Mass Unit |
| BAG | Bayard-Alpert ionization gauge, a vacuum gauge |
| MS | Mass Spectroscopy |
| m/z | mass over charge ratio |
| P | pressure |
| RGA | residual gas analyzer, in this case a quadrupole mass spectrometer |
| SNL | Sandia National Laboratories |
| SPME | Solid Phase Micro Extraction |
| T | temperature |
| TC | thermocouple |
| TDS | Thermal Desorption Spectroscopy |
| TGA | Thermal Gravimetric Analysis |
| TMP | turbomolecular (vacuum) pump |
| UHV | Ultra-High Vacuum |
| V | volume |

1. INTRODUCTION

Operational lifetimes and typical limits of operation are of concern in most engineering applications for materials, especially for commonly used foams and epoxies. Determining strict limits of operation for these materials is critical to prevent any degradation that may limit their lifetimes. In addition to typical ambient oxidation, hydrolysis, or other related age degradation mechanisms must be considered[1].

The purpose of this study is to twofold. First, use highly sensitive mass spectroscopy to determine acceptable thermal limitations for specific materials. Limits here will dictate upper temperature exposure for handling. Second, a comparison between newly prepared samples and materials that have been in storage for decades will be made. Relative differences in mass spectra vs. temperature may provide information regarding long-term thermal stability.

2. EXPERIMENTAL PROCEDURES

Thermal Desorption Spectroscopy is performed with a Sandia made TDS in 916. This TDS uses a Quad Elliptical Heating Chamber Model E4 (5528-02) powered by a Research Inc. single phase, phase angle controlled 240VAC 25A power controller. The temperature ramps and holds are generated using an Omega CN3000 controller and the internal thermocouple. For the experiments in this program, a ramp rate of 2K/min is used. The entire vacuum system is pumped by a Pfeiffer TMU 071 YP high compression ratio, 60 l/s (nominal) turbomolecular pump backed by a rotary vane pump and has a base pressure of $\sim 2 \times 10^{-9}$ Torr. The total pressure in the system is measured by a Granville-Phillips Series 370 STABIL-ION® gauge, a highly stable Bayard-Alpert ionization gauge with a NIST-traceable, nitrogen calibration. Also on the system is a Stanford Research System (SRS) 300 quadrupole residual gas analyzer, used to detect the different gas species desorbed.

Samples were placed at the mid-point of the furnace, in an alumina crucible, sealed within the quartz tube and pumped down for approximately 30 hours prior to the start of the thermal desorption. At this point the pressure is dropping very slowly as the sample continues slowly to degas dissolved water and air. The pressure is typically more than an order of magnitude lower than the pressure after the first temperature ramp to 60 °C.

The heating portion of the experiments lasted for ten days with 24 hour dwell times at each temperature (see Figure 2). This choice provided enough data to discern differences between off gassing due to adsorption, diffusion through material to the free surface, and decomposition of materials. Photographs taken before and after tests, recorded mass changes, mass spectroscopy, and pressure profiles were all recorded.

It is believed that the samples in the presence of a vacuum do not change degradation pathways, but rather cause volatilization of degradation products [2], however this study can neither confirm or deny such results. In light of this assumption the use of the TDS system was employed for several reasons. First, ultra-high vacuum (UHV) increases the sensitivity of measurement, by allowing low amounts of volatiles evolved to be detected. Second, UHV will also facilitate volatilization of degradation products, which might otherwise remain dissolved in the organic matrix. Since experiments only last approximately 10 days high sensitivity is necessary to resolve the low temperature limit of reactivity.

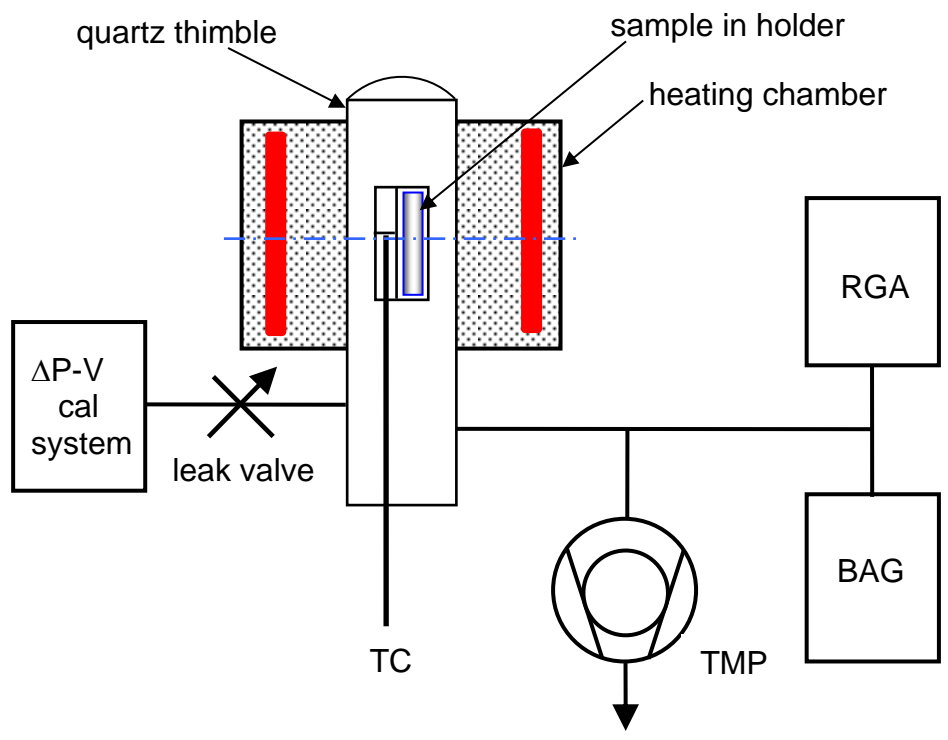


Figure 1: Schematic of TDS system

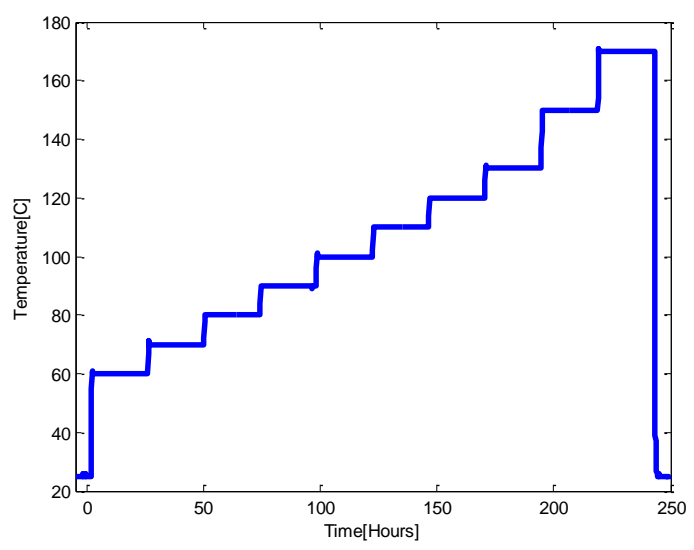


Figure 2: Temperature profile during TDS tests

3. FOAM RESULTS

The foam used in this study consists of two part rigid polyurethane foam, with the nominal density of 10 lb m/ft³. The blowing agent for the foam is water, which may contribute to observed water content. The glass transition temperature for foams occurred over the range from 110-140°C depending on age of the foam.

Two foams were compared with each sample extracted from locations of uniform density (i.e. away from regions of skin effects). Foam was prepared in the laboratory, which is called FoamN (foam new) and foam that was created in the past and has been in storage, called FoamP (foam past). Clearly there are some visual differences between new and old foams (Figure 3 and 4 as received). Despite some initial differences, foams lost similar mass over the course of the test (Table 1) with discoloration evident after heating to 170°C (see Figure 3 and 4).

Water released from the bulk was the dominant product detected during pump down, which was at room temperature. After increasing the temperature to 60°C, both foams degassed air, which is thought to be within the foam porosity as well as dissolved in the bulk. Evidence that AMU 28 is nitrogen and not a hydrocarbon is the constant ratio of masses 28 and 14. This fact, coupled with the relative absence of masses 13 and 15, which would represent the CH and CH₃ ions, provide further proof of nitrogen. At low temperatures, Figure 5, mass 28 is also associated with the presence of oxygen (O₂), although the oxygen level in FoamP is noticeably lower than it is in FoamN, which may indicate the presence of air off-gassing from the foam. A relative decrease in AMU 32 (likely O₂) with temperature (temperatures 24 hours different) is shown in Figure 5.

Table 2 provides the most intense peaks observed at each temperature. There was little difference between FoamN and FoamP at low temperatures (60-90°C). Within this temperature range, all detected species had a characteristic asymptotic decrease in intensity after each temperature step, typically attributed to the off-gassing of absorbed species by diffusion. Figure 6 and 7 have the time varying response for several masses: 18, 28, 44, 45, and 59 AMU. Masses 45 and 59 are representative of organic degradation products, while other detected products are commonly found in the atmosphere (i.e. water-18, nitrogen-28, and carbon dioxide-44). It is difficult to discern at elevated temperatures how much signal can be attributed to typical atmospheric products vs. organic components associated with decomposition (i.e. 28 can be CO or N₂). Clearly any products being detected only at higher temperatures are a result of decomposition, but it is unclear when the transition from desorption to decomposition product takes place for the more common masses or species.

At temperatures below 110°C the spectra of 45 and 59 is at the noise level. Evidence for these masses as decomposition products first becomes clear at 110°C. At temperatures of 150 and 170°C non-atmospheric products, specifically masses 45 and 59, become prominent. It is unclear what degradation pathways are occurring at high temperatures. Preliminary SPME mass spectroscopy experiments have detected small amount of propylene glycol, which has a primary peak at m/z of 45. It is still unclear at this time what molecule(s) are responsible for the presence of m/z 59.

The kinetics of reactions tends to increase in an Arrhenius fashion, making it difficult to identify an exact temperature threshold where thermal energy sufficiently overcomes kinetic barriers that facilitate reactions. Significant rate increase is observed from 100 to 110°C represented by relative concentration of masses 45 and 59 present. Visual inspection of Figures 6, 7, and 8 indicate FoamP begins degrading at 100°C, while FoamN only begins degrading at 110°C. Material aging in the form of a very slow deterioration may have occurred during FoamP's long storage at room temperature and only becomes detectable when the temperature is raised. Stated differently, it is possible that a high vapor pressure product has built up over time that can be volatilized only at 100 °C and above. In contrast to FoamP, FoamN has mainly new reaction product being generated. This suggestion may account for the difference in the shape of the mass 45 traces at elevated temperature for FoamN and FoamP as shown in Figure 8.

Results suggest that the thermal limit is around 100°C. When comparing this result to similar polyurethane foams in literature, temperature limits were typically identified to be higher, with degradation occurring around 240-260°C [2-4]. However, results from this work indicate that degradation temperatures tended to appear lower when under a vacuum, which is consistent with expectations from literature, as volatiles more readily off-gas [2]. Degradation temperatures determined under vacuum are a better representation of the appropriate operating range.

Table 1: Mass loss after 10 day experiment at 170°C showed similar loss between the newly created and past foam. Foams were nominally the same starting mass and shape.

| Foam ID (starting weight) | Mass loss [%] |
|---------------------------|---------------|
| FoamN (246.7 mg) | 12.8% |
| FoamP (256.0 mg) | 11.9% |

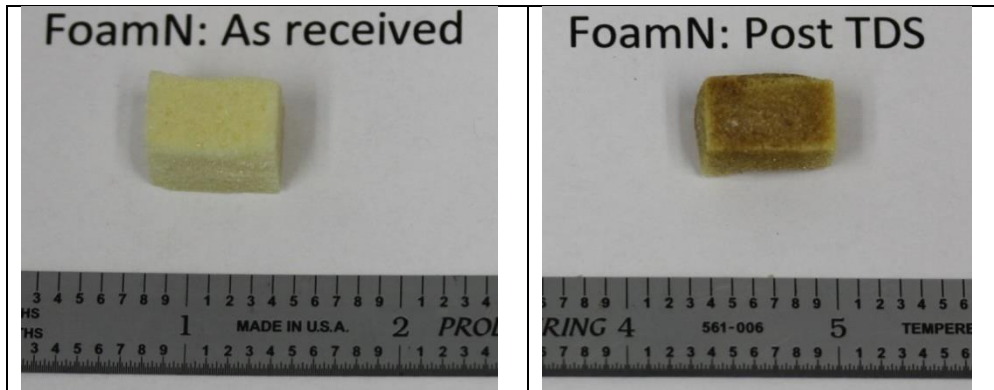


Figure 3: FoamN before and after TDS testing. Obvious discoloration and charring occurred after testing even under UHV. Puffing of sample may be related to production of internal degradation leading to a pressure differential at elevated temperatures.

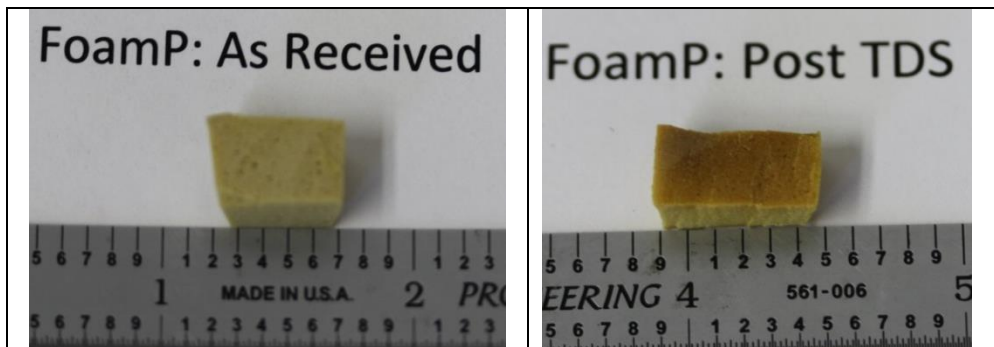


Figure 4: FormP before and after TDS testing. Qualitatively this foam was initially darker, likely due to sample age (created ~30 years ago) prior to TDS study.

Table 2: Four most intense masses averaged over 24 hours per temperature

| Most intense AMU detected (averaged over 24 hours) (Most Intense → Less intense) | | |
|---|----------------|----------------|
| Temperature | FoamN | FoamP |
| 60°C | 28, 32, 18, 44 | 28, 18, 2, 44 |
| 70°C | 28, 18, 44, 2 | 28, 18, 2, 44 |
| 80°C | 28, 18, 2, 44 | 28, 18, 2, 44 |
| 90°C | 28, 18, 2, 44 | 18, 28, 2, 44 |
| 100°C | 28, 2, 44, 18 | 18, 44, 2, 28 |
| 110°C | 44, 2, 18, 28 | 44, 2, 18, 28 |
| 120°C | 44, 18, 2, 28 | 44, 2, 28, 18 |
| 130°C | 44, 28, 18, 2 | 44, 28, 2, 45 |
| 150°C | 44, 28, 2, 45 | 44, 59, 28, 45 |
| 170°C | 44, 28, 59, 2 | 59, 44, 28, 31 |

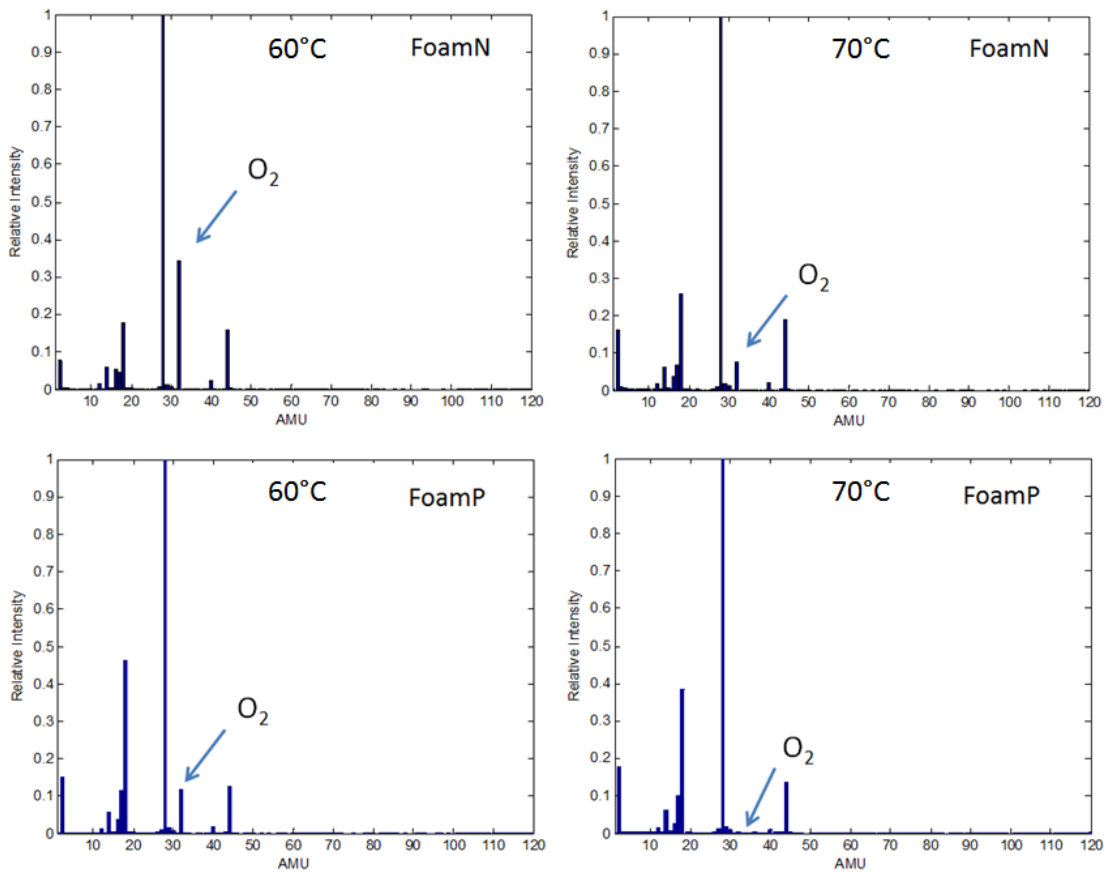


Figure 5: Oxygen is detected at low temperatures in both foams. The concentration detected, relative to m/z 28, suggests that products are likely the result of air within the samples (air was the storage atmosphere).

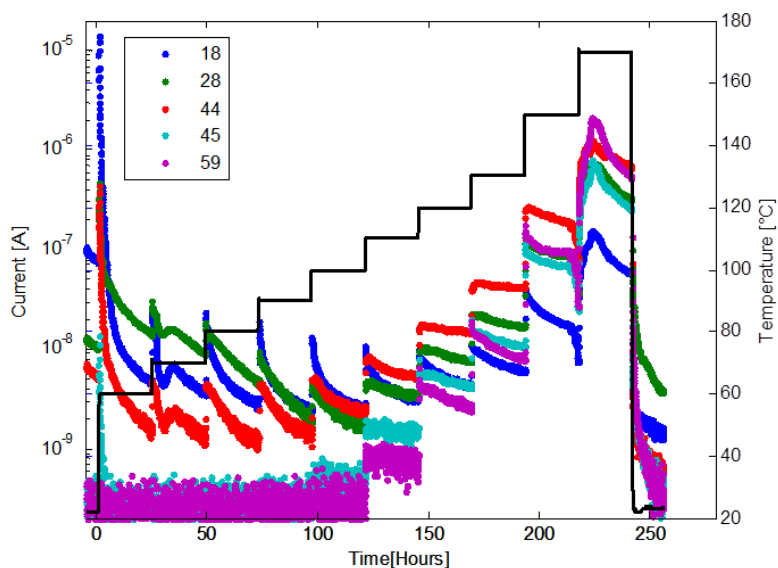


Figure 6: FoamP: Most prevalent masses detected. Change in curve shape at 170°C may indicate a change in reaction mechanism.

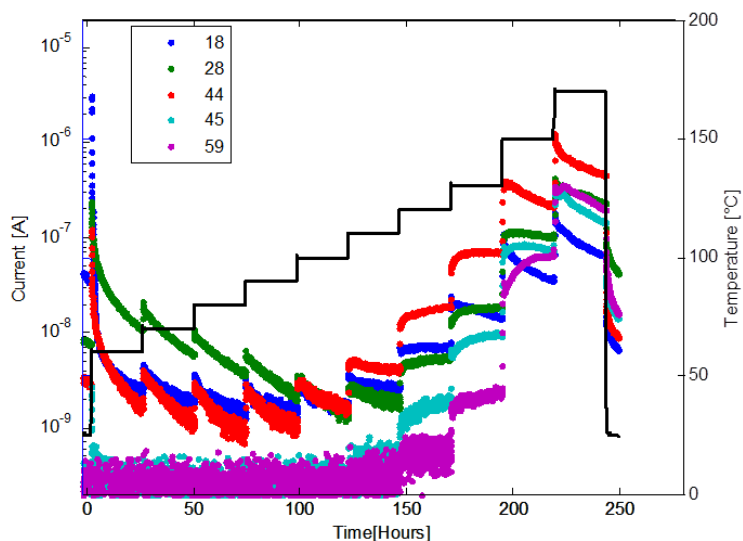


Figure 7: FoamN: Most prevalent masses detected. Transition from diffusion to degradation appears around 110°C as shown from changes in trace shape and appearance of m/z 45.

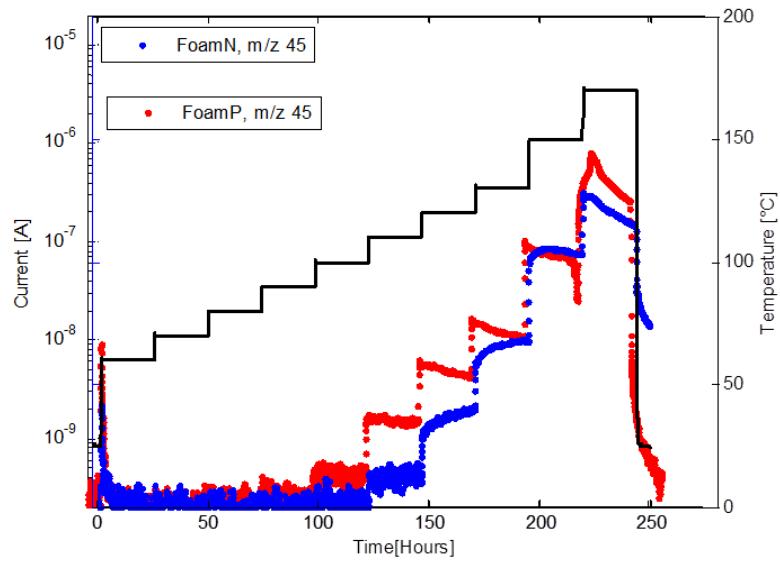


Figure 8: Smoothing function (moving average from MatLab©) applied to m/z 45 to show obvious off-gassing vs. temperature differences between FoamN and FoamP.

4. EPOXY RESULTS

Only one type of epoxy was investigated: an Epon 826 resin with a Z curing agent. As with the foams, EpoxyN and EpoxyP were tested and compared for relative differences. EpoxyN was created in the lab near the end of the year 2012 and tested several months later, while EpoxyP is a specimen that was made in the past. The onset of the glass transition temperature occurs around 130°C. None of the gases detected during this study arose from epoxy curing.

EpoxyP was a composite material, which is approximately 37% (by weight) Epon 826 (Z-cured) with the remaining 63% of the sample a glass filler material (determined from TGA conversion experiments). In this way the mass loss due exclusively to EpoxyP decomposition could be compared directly to mass loss determined from EpoxyN (Table 3).

Mass loss observed was appreciably different between both epoxies. This result was unexpected in view of mass spectra and pressure data results. Figures 11 and 12 show that EpoxyN exhibits near constant off-gassing behavior starting at 110°C, while this behavior is not observed in EpoxyP until about 120°C. Despite this apparent difference the average masses detected at each temperature step (Table 4) were almost the same between the N and P series, which may indicate that reaction pathways may be the same for given temperatures, with slight differences in kinetics.

As an aside, the temperature spike in Figure 11 is real and thought to be caused by a temporary loss in flow of water used to cool the furnace. Flow loss occurred directly before the temperature transition from 110 to 120°C, which complicated the off-gassing spectra observed in EpoxyN. Regardless of this behavior, there is an indication that decomposition began at 110°C prior to this behavior as evidenced by the relative increase in mass 44 detected.

Similar to foams, the epoxy exhibited an increase in total ion current around 110-120°C, with increases present in typical atmospheric masses (i.e. water, nitrogen, etc.). As explained earlier it is difficult to assess how much of the signal is due to hydrocarbons vs. constituents such as water. Increase in total signal at higher temperatures is a direct result of decomposition processes.

Table 3: Mass loss after 10 day experiment at 170°C showed similar loss between the newly created and past epoxy.

| Epoxy ID (starting weight) | Mass loss [%] |
|---|---------------|
| EpoxyN (260 mg) | 10% |
| EpoxyP (138.4mg)* | 6%* |
| *Starting weight was 374mg initial and lost 7.9mg, Back calculated accounting for ceramic matrix. | |

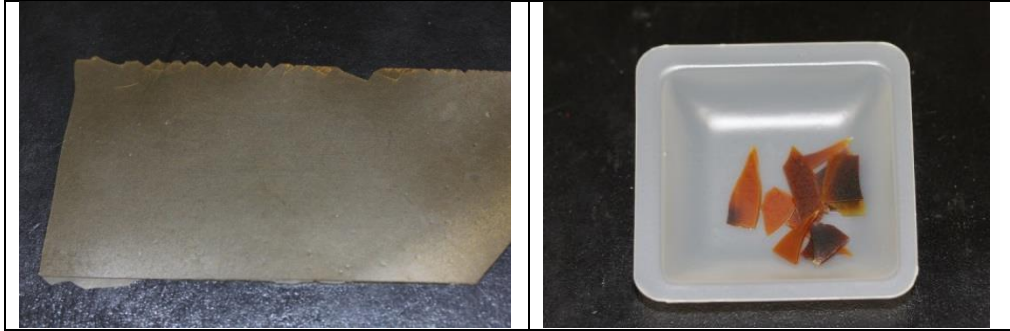


Figure 9: EpoxyN before and after TDS testing. Obvious discoloration and charring or pyrolysis occurred after testing even under UHV.

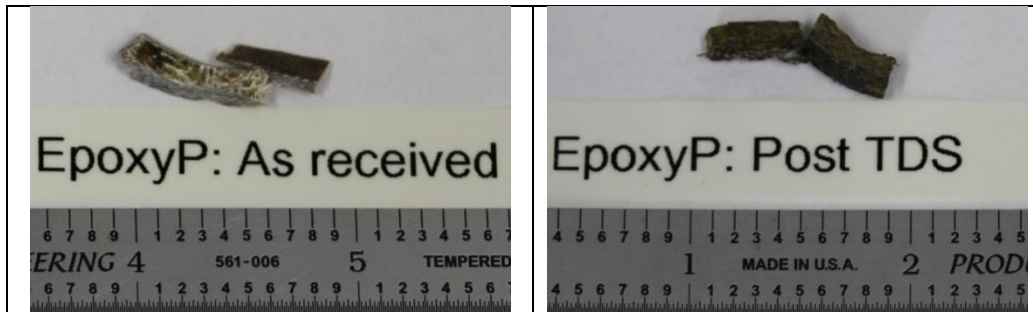


Figure 10: EpoxyP before and after TDS testing. Qualitatively this foam was initially darker, likely to from sample age (created decades ago) prior to TDS study

Table 4: Four most intense masses averaged over 24 hours per temperature on epoxy materials

| Most intense AMU detected (averaged over 24 hours) (Most Intense → Less intense) | | |
|---|----------------|----------------|
| Temperature | EpoxyN | EpoxyP |
| 60°C | 18, 30, 17, 44 | 18, 17, 2, 28 |
| 70°C | 18, 30, 17, 44 | 18, 28, 30, 17 |
| 80°C | 18, 30, 2, 44 | 18, 28, 30, 44 |
| 90°C | 18, 2, 30, 44 | 18, 28, 2, 44 |
| 100°C | 18, 2, 44, 28 | 18, 28, 2, 44 |
| 110°C | 18, 2, 44, 28 | 18, 28, 2, 44 |
| 120°C | 18, 2, 28, 17 | 18, 2, 28, 44 |
| 130°C | 18, 2, 28, 17 | 18, 2, 28, 17 |
| 150°C | 18, 2, 28, 17 | 18, 2, 17, 28 |
| 170°C | 18, 2, 28, 17 | 18, 2, 17, 28 |

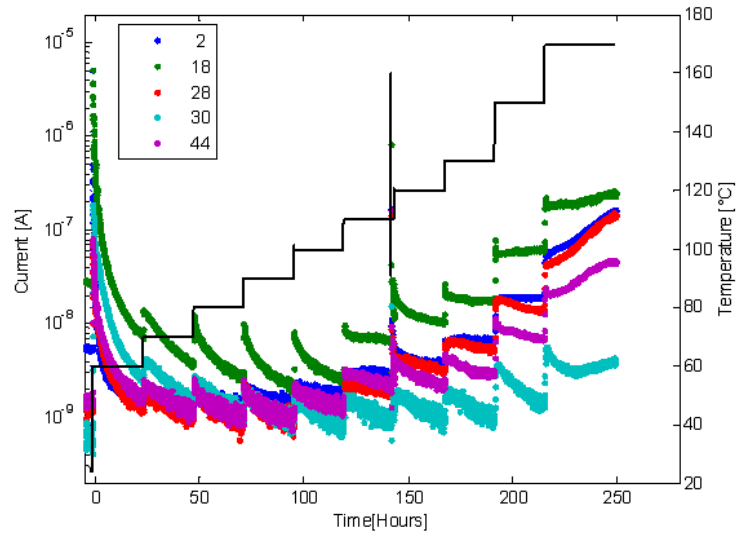


Figure 11: Five highest concentration masses detected in EpoxyN. Transition from diffusion to decomposition was detected at 110°C by change in spectra curves.

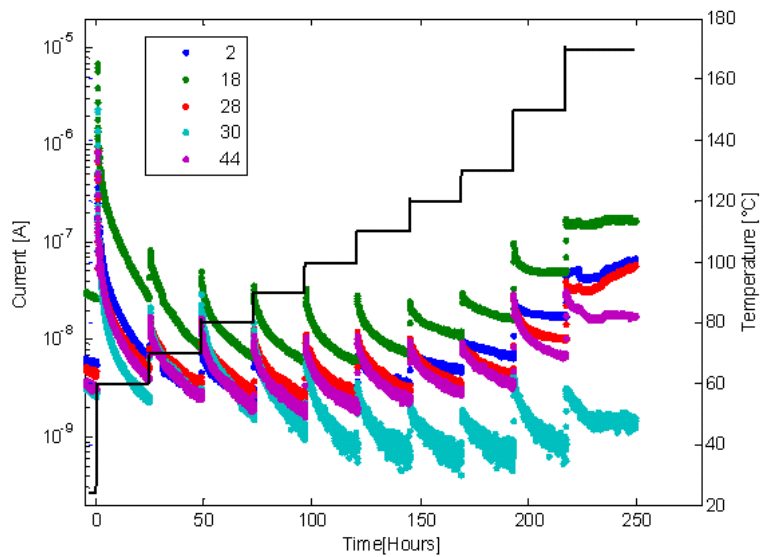


Figure 12: Five highest concentration masses detected in EpoxyP. Transition from diffusion controlled reactions to decomposition appeared to occur around 120°C

4. CONCLUSIONS

Two materials were tested experimentally using TDS, a urethane foam and Epon 826 epoxy. Both materials were tested from two vintages: newly made in the laboratory (FoamN or EpoxyN) or from stored reserves that were created in the past, decades ago (FoamP or EpoxyP). Samples were tested from 60-170°C, with dwell temperatures lasting one day per temperature step.

Both vintages of urethane foams lost 11-13% mass over the duration of experiments. Decomposition of both foams was indicated by the detection of m/z 45, thought to be propylene glycol, as determined from independent SPME analysis. Temperatures where this behavior occurred varied slightly: decomposition of FoamP at 110°C, with FoamN decomposition at 120°C. Decomposition in the way of m/z 59 (unidentified as of this time) became significant in the range of 130-150°C. Suggested upper temperature limit for the foams is 90-100°C based on these data.

Mass loss for vintages of Epon 826 was over the range of 6-10%. Glass-fill mixed with the EpoxyP made it difficult to quantify mass lost for the epoxy. Decomposition in epoxies was identified by change in the relative concentration of masses vs. time curves. EpoxyN exhibited degradation behavior at 110°C, while EpoxyP has degradation at 120°C. Suggested upper temperature limit of the epoxy, from these data, is 90-100°C.

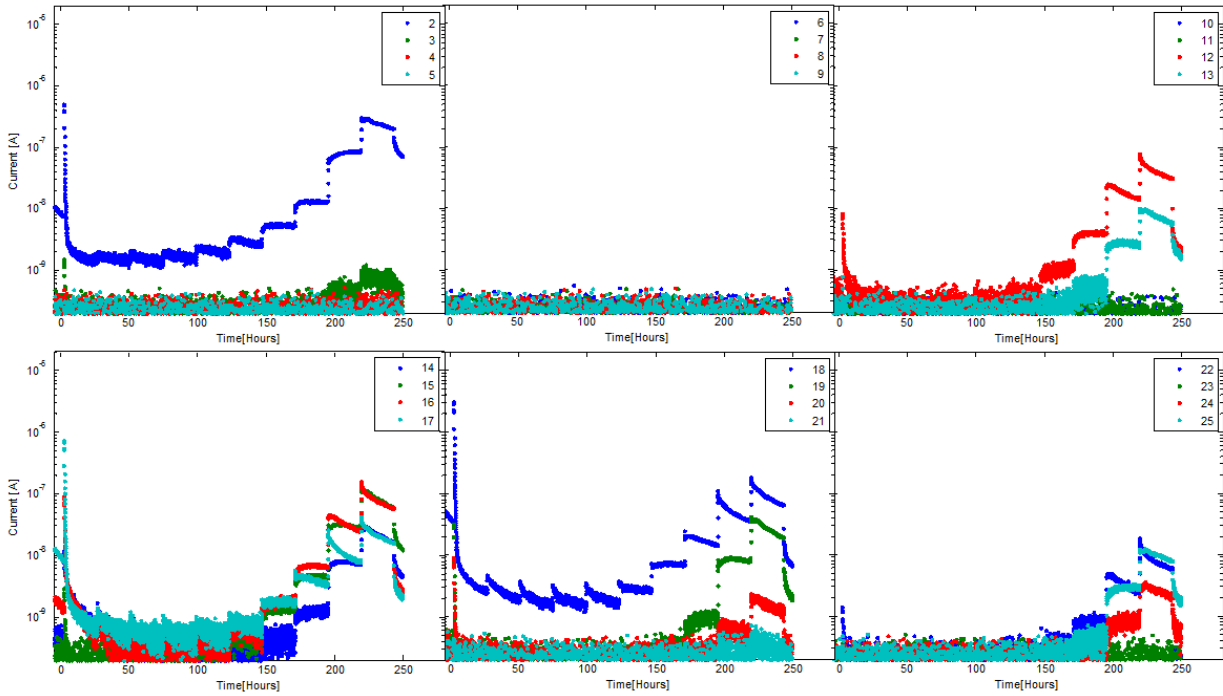
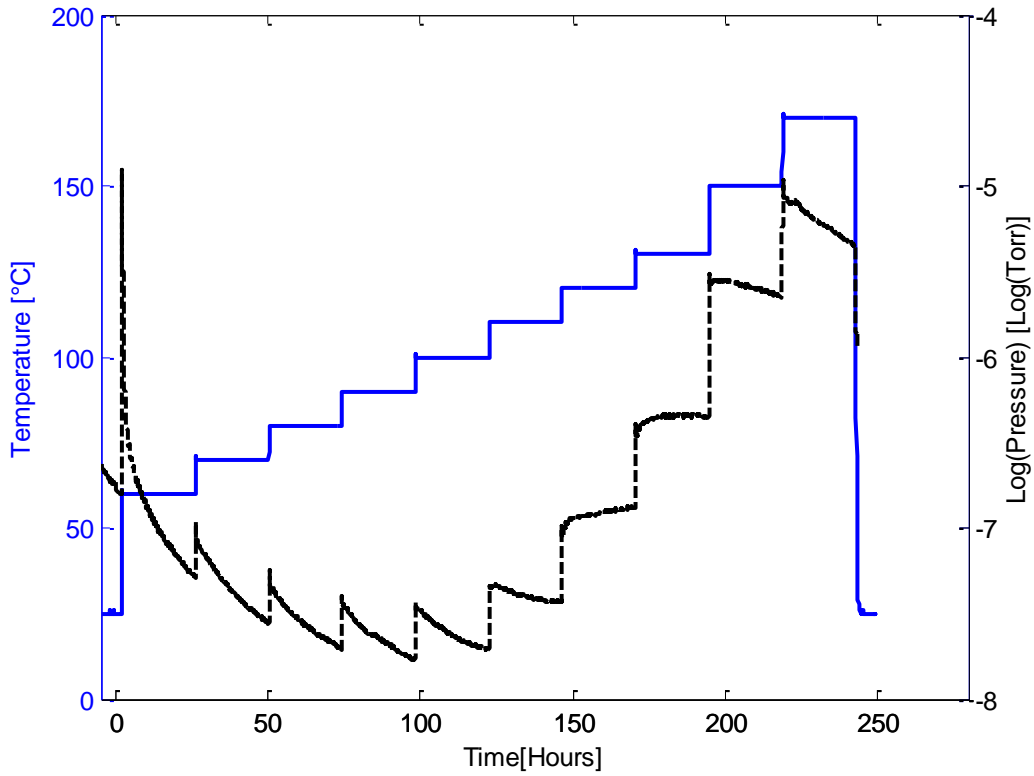
Future tests of interest are in no particular order:

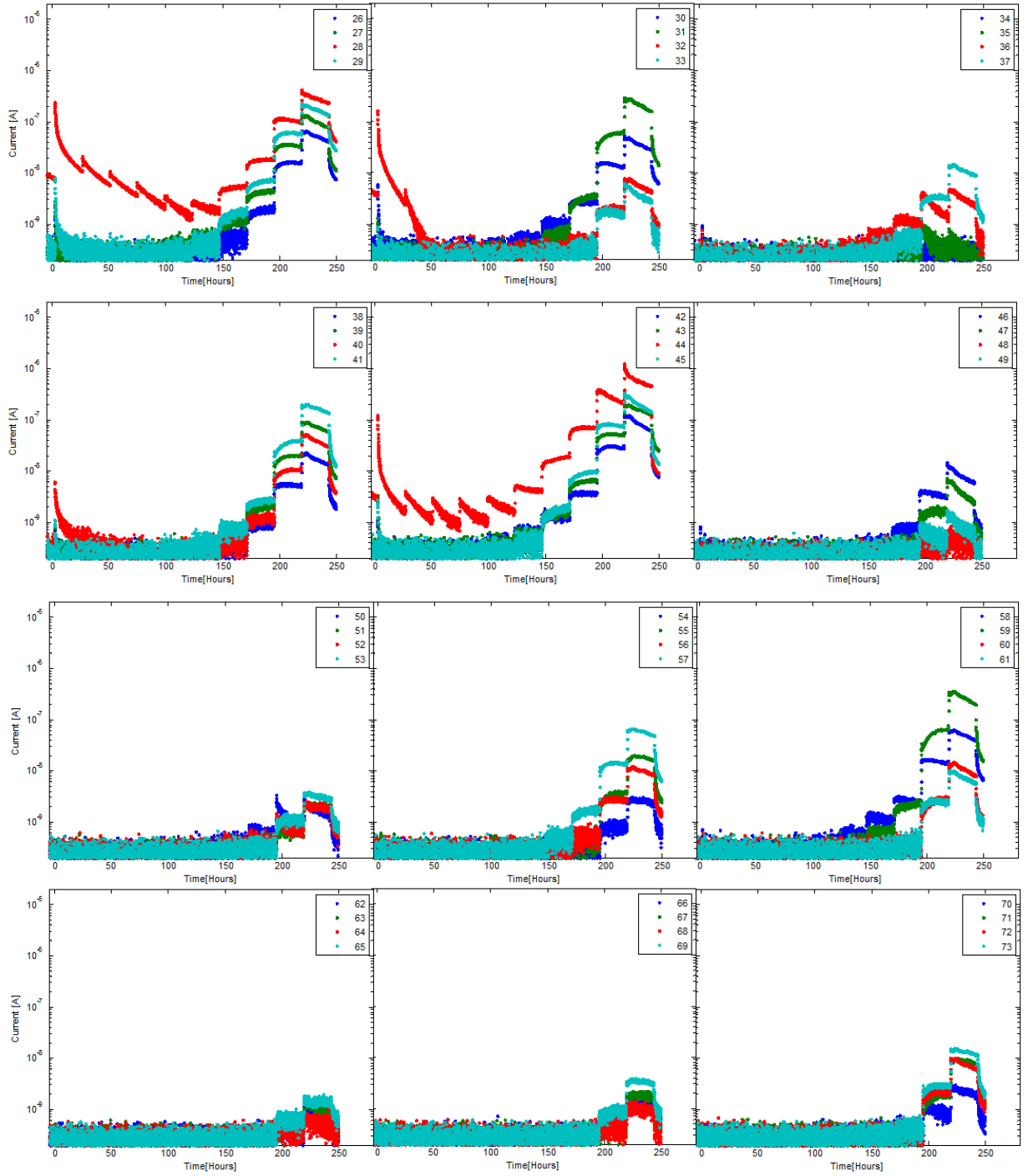
- Determine primary decomposition species, which would require higher temperature SPME; primarily of academic interest.
- Perform TDS to higher temperatures to understand if there is a change in dominant mechanisms; primarily of academic interest or for accidental situations (i.e. fires)
- Development of a principle component analysis method that would supplement TDS analysis. This would provide underlying patterns in data (i.e. help identify specific components of one molecule). The alternative to this method is purchasing a higher resolution mass spectrometer, which would be on the order of \$100k or more.

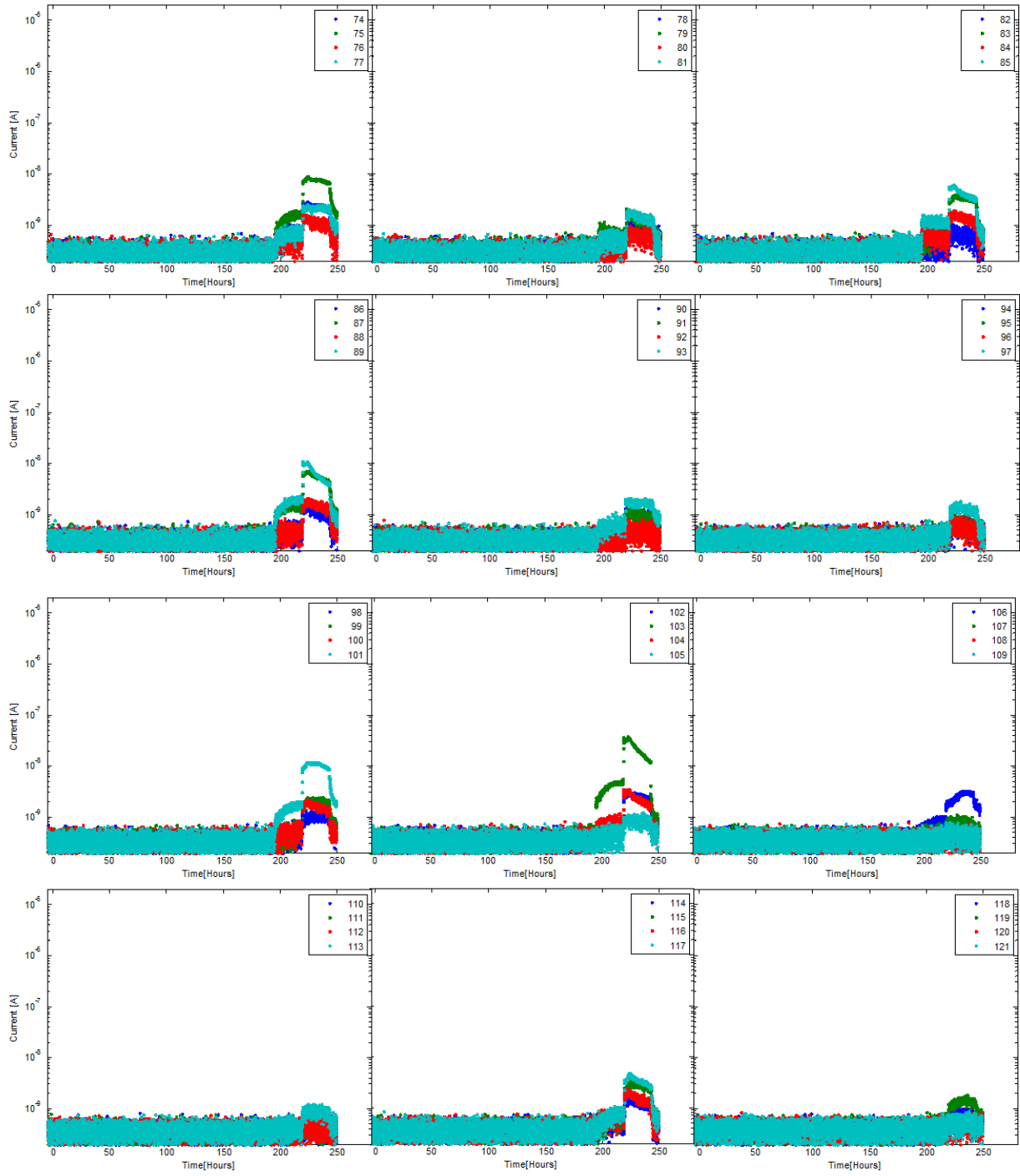
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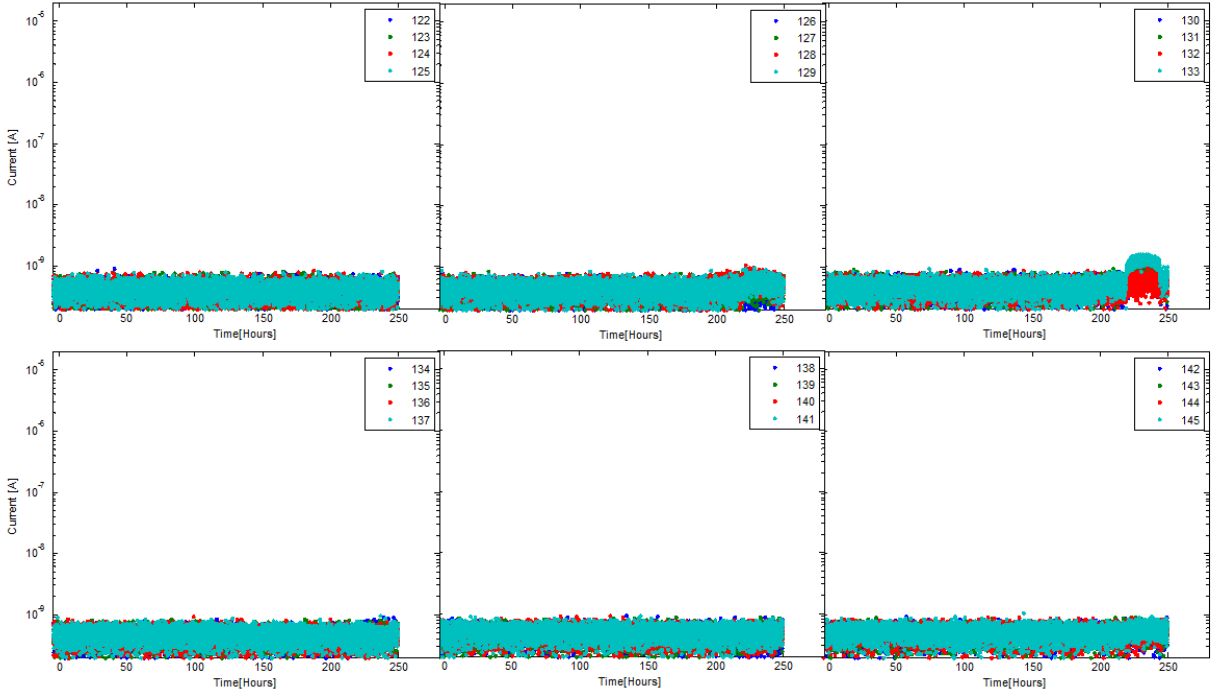
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2. Allan, D., J. Daly, and J.J. Liggat, *Thermal volatilisation analysis of TDI-based flexible polyurethane foam*. Polymer Degradation and Stability, 2013. **98**(2): p. 535-541.
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APPENDIX A: M/Z PROFILES FOR FOAM N (RAW DATA)

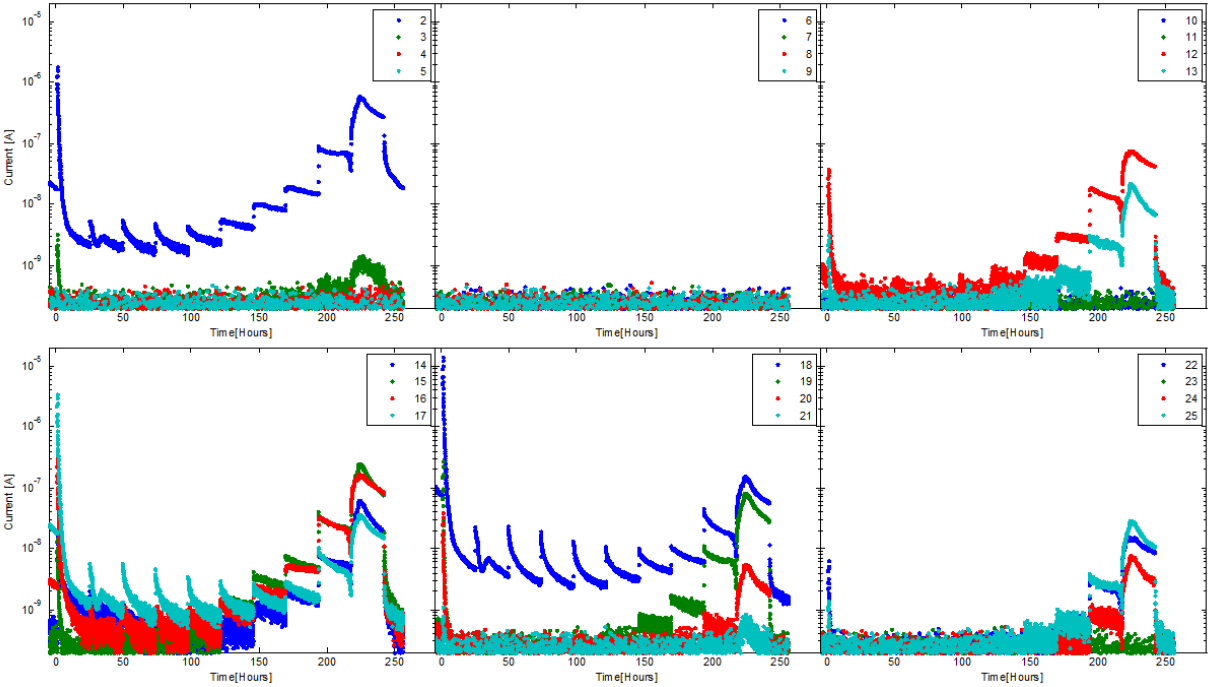
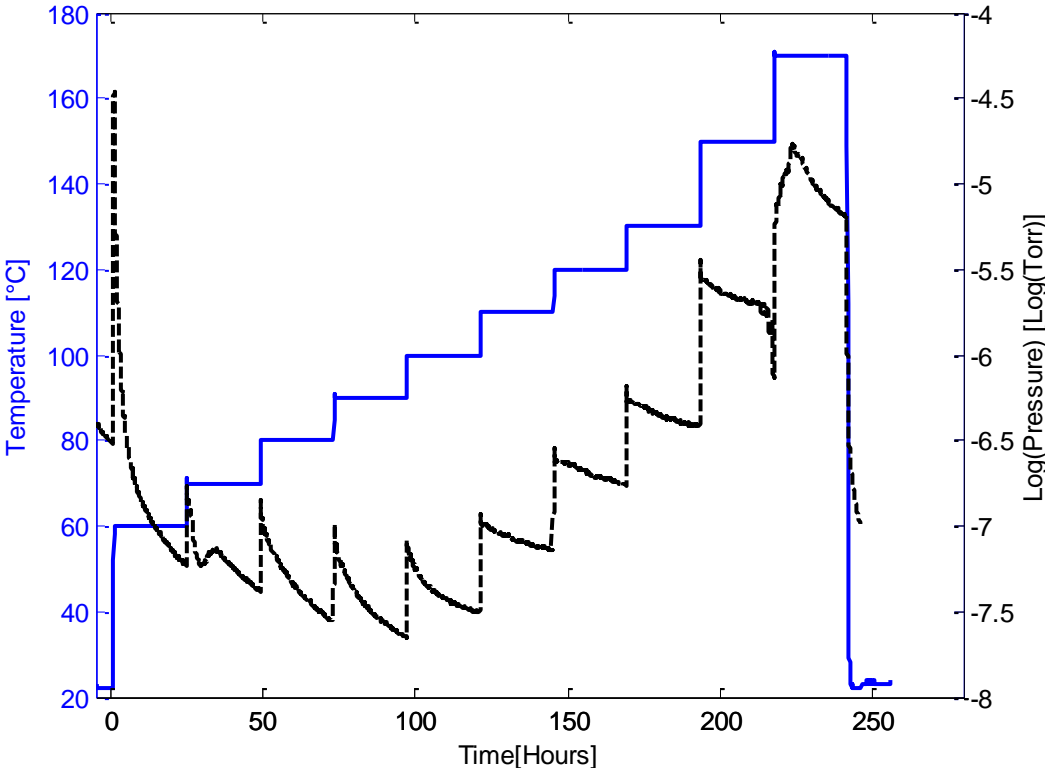


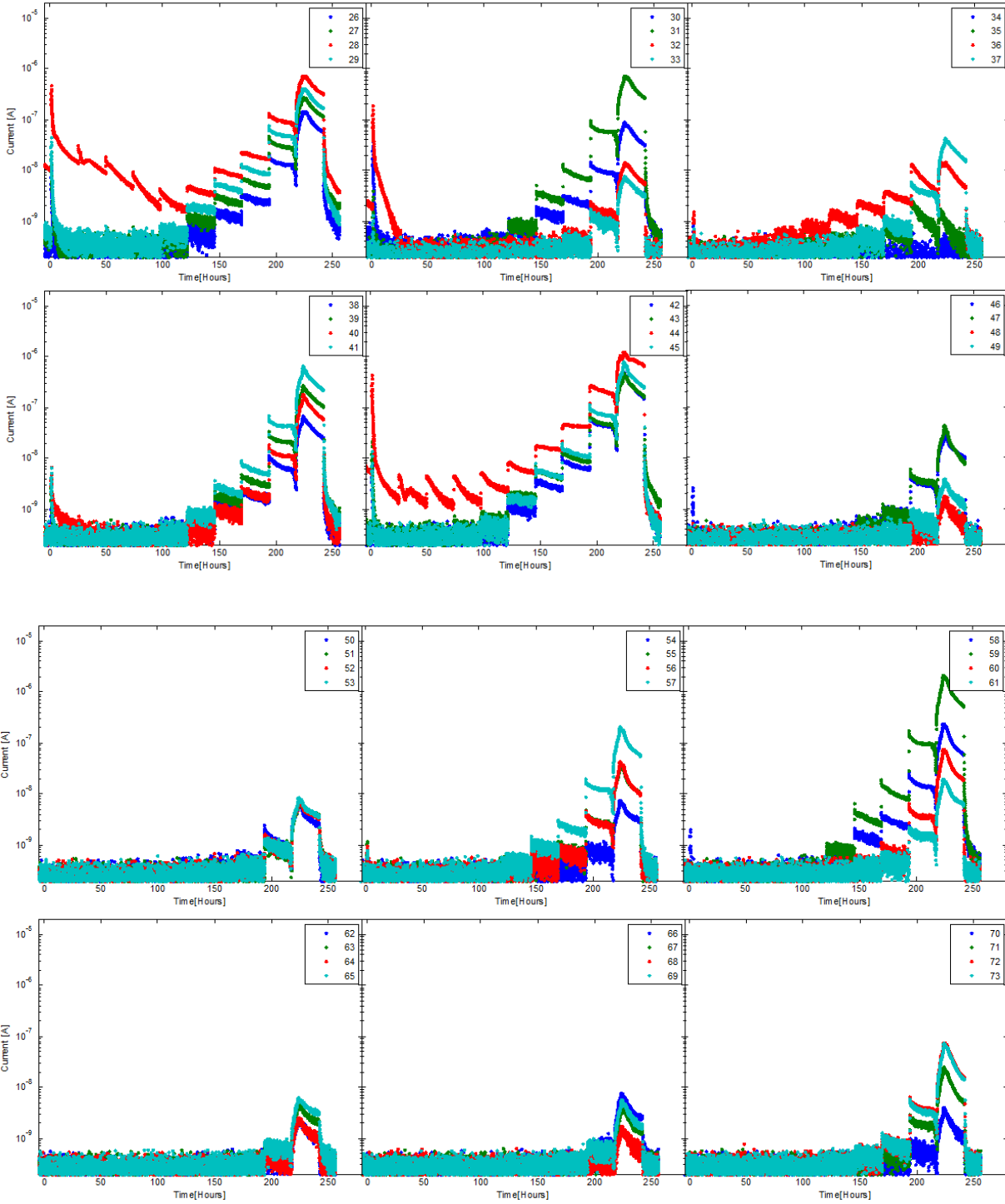


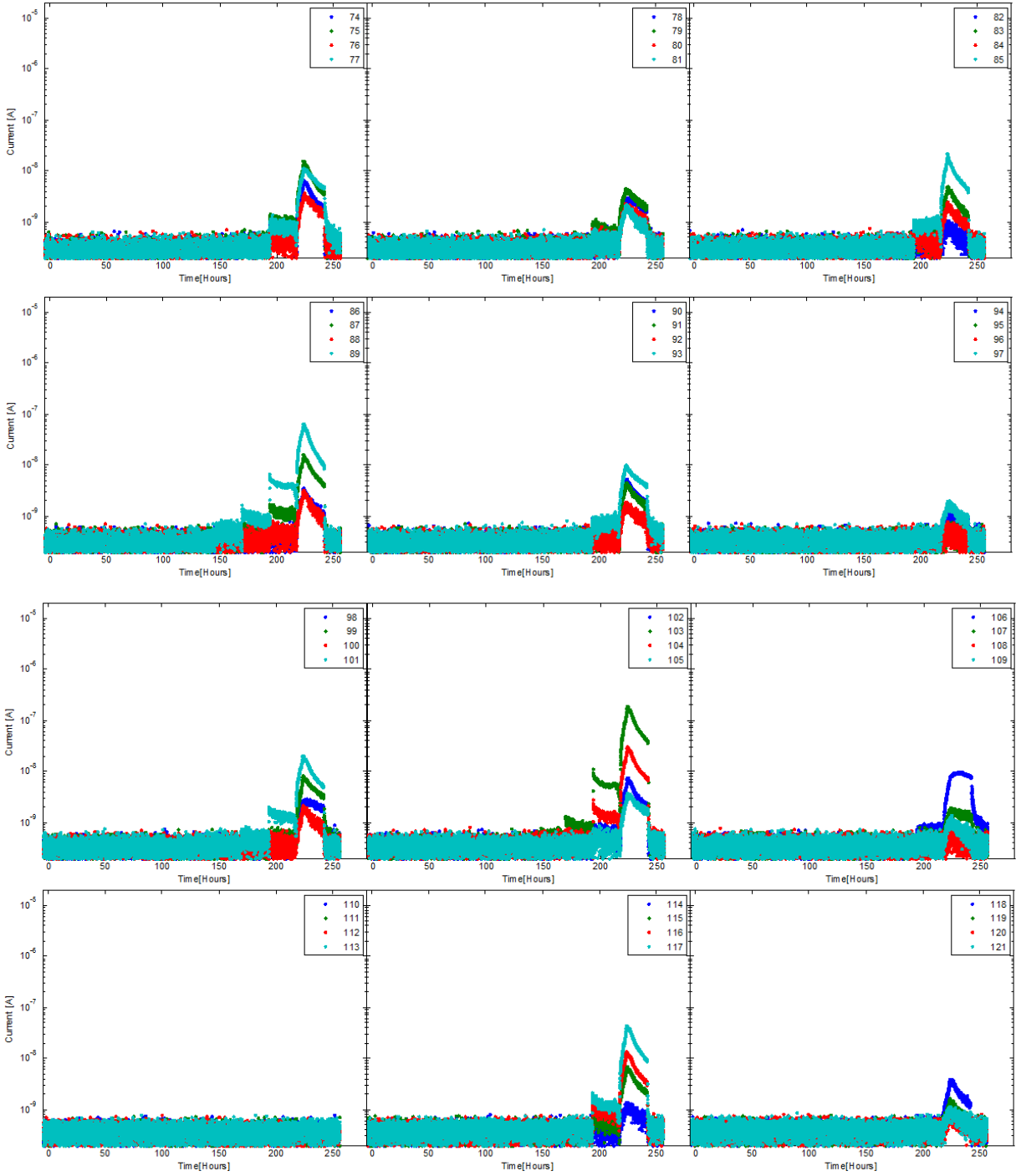


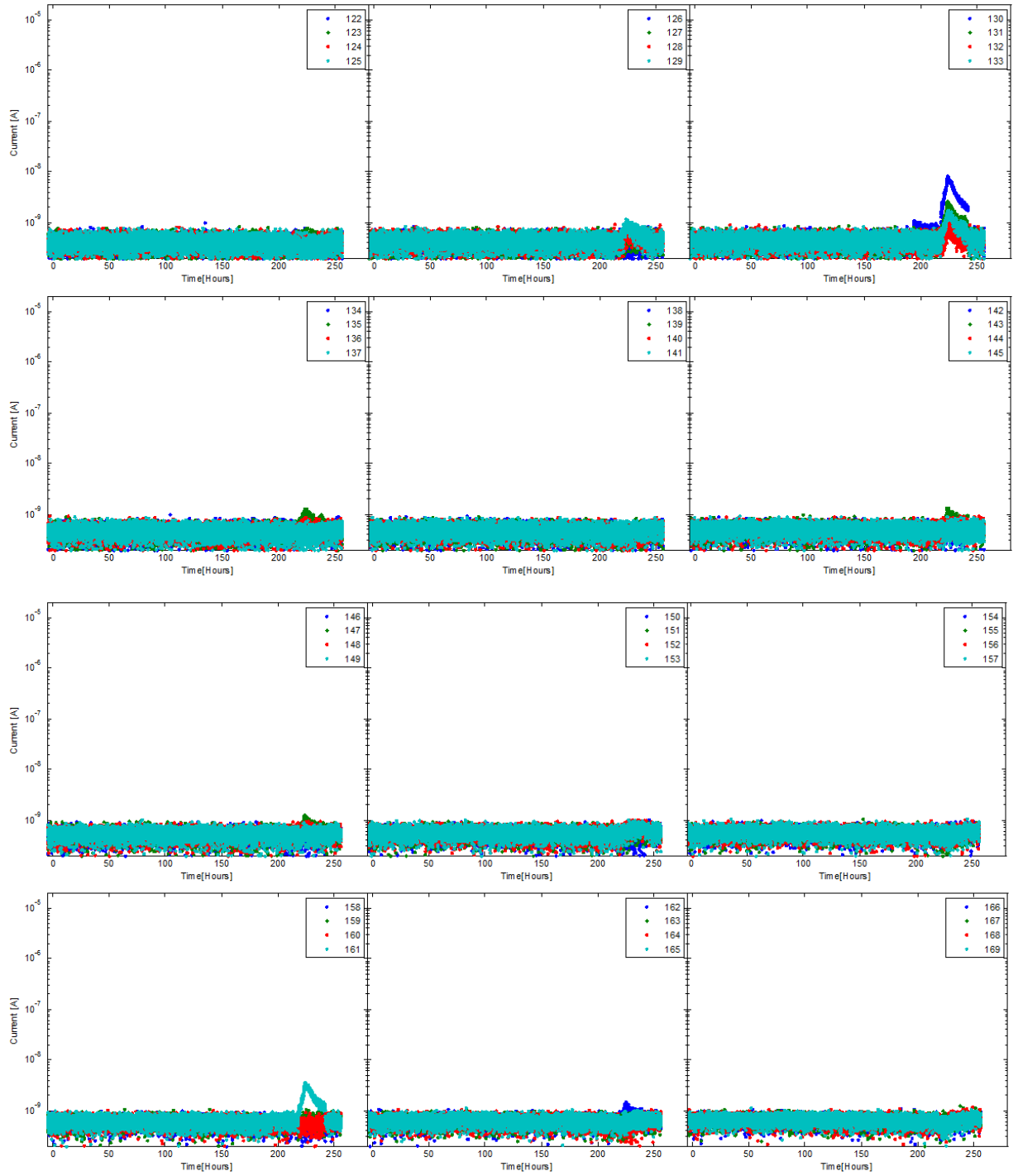


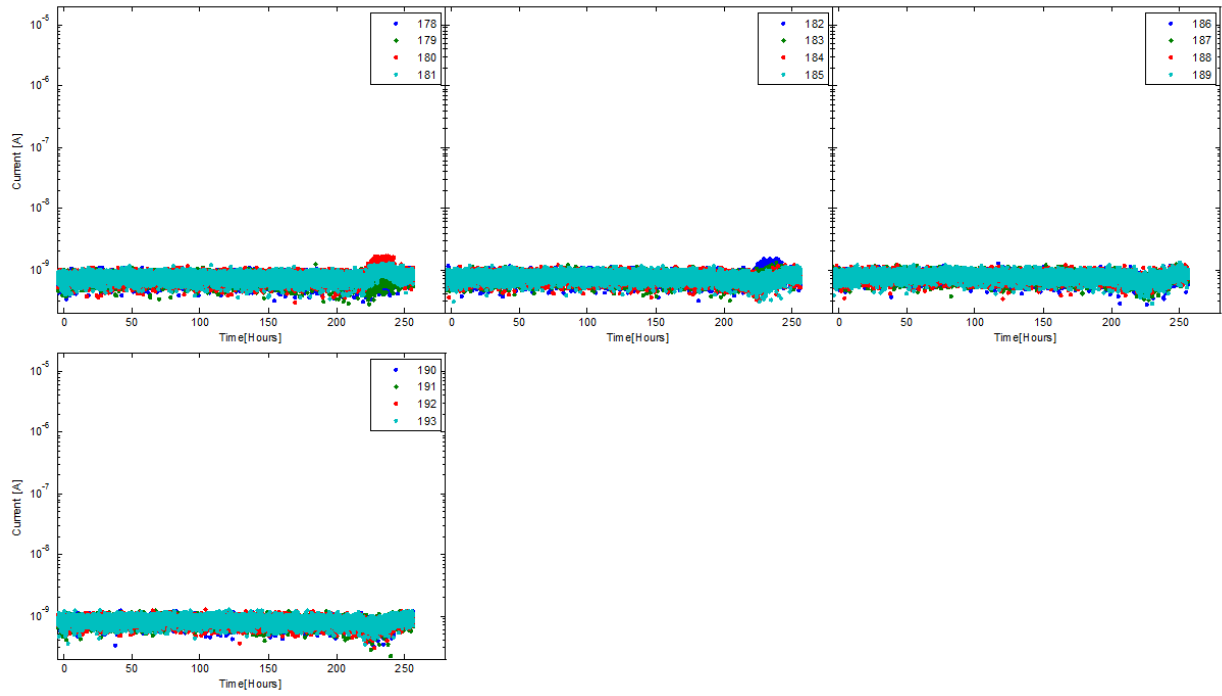
APPENDIX B: M/Z PROFILES FOR FOAMP (RAW DATA)



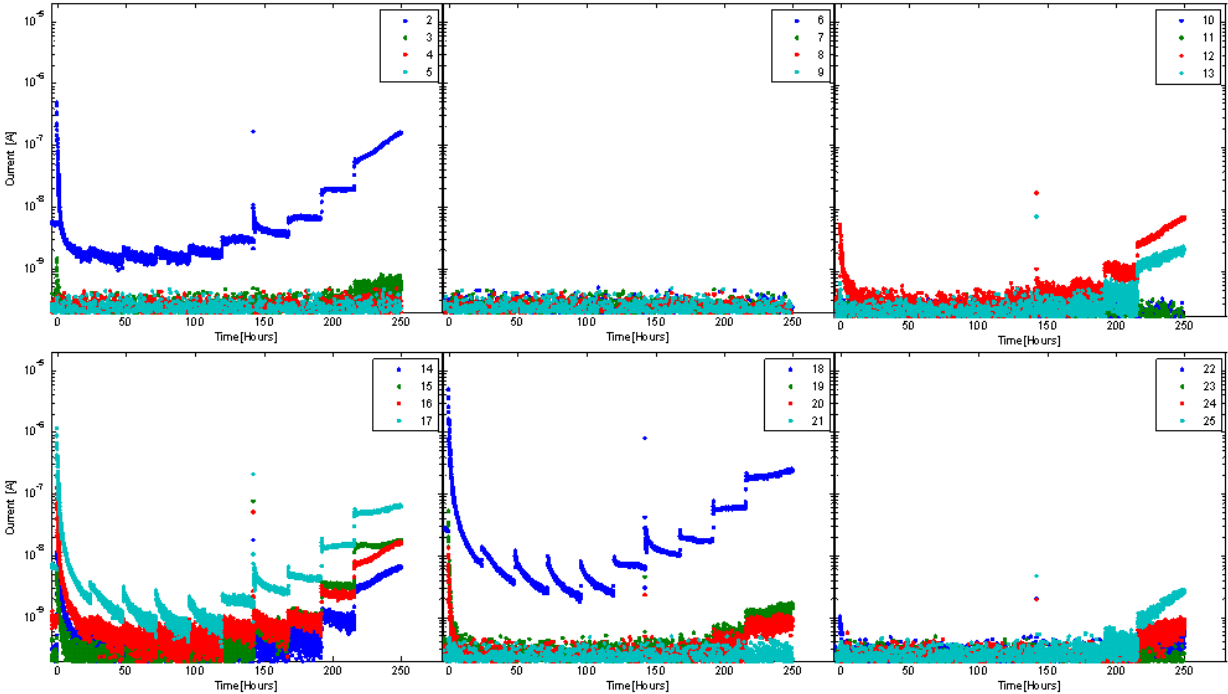
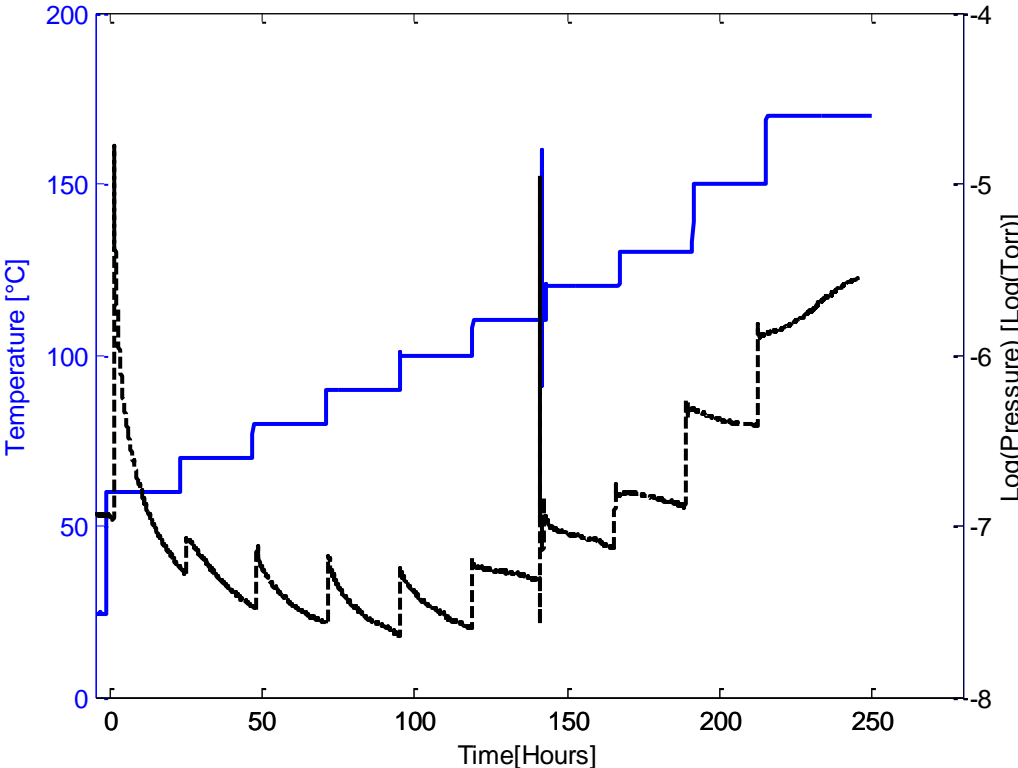


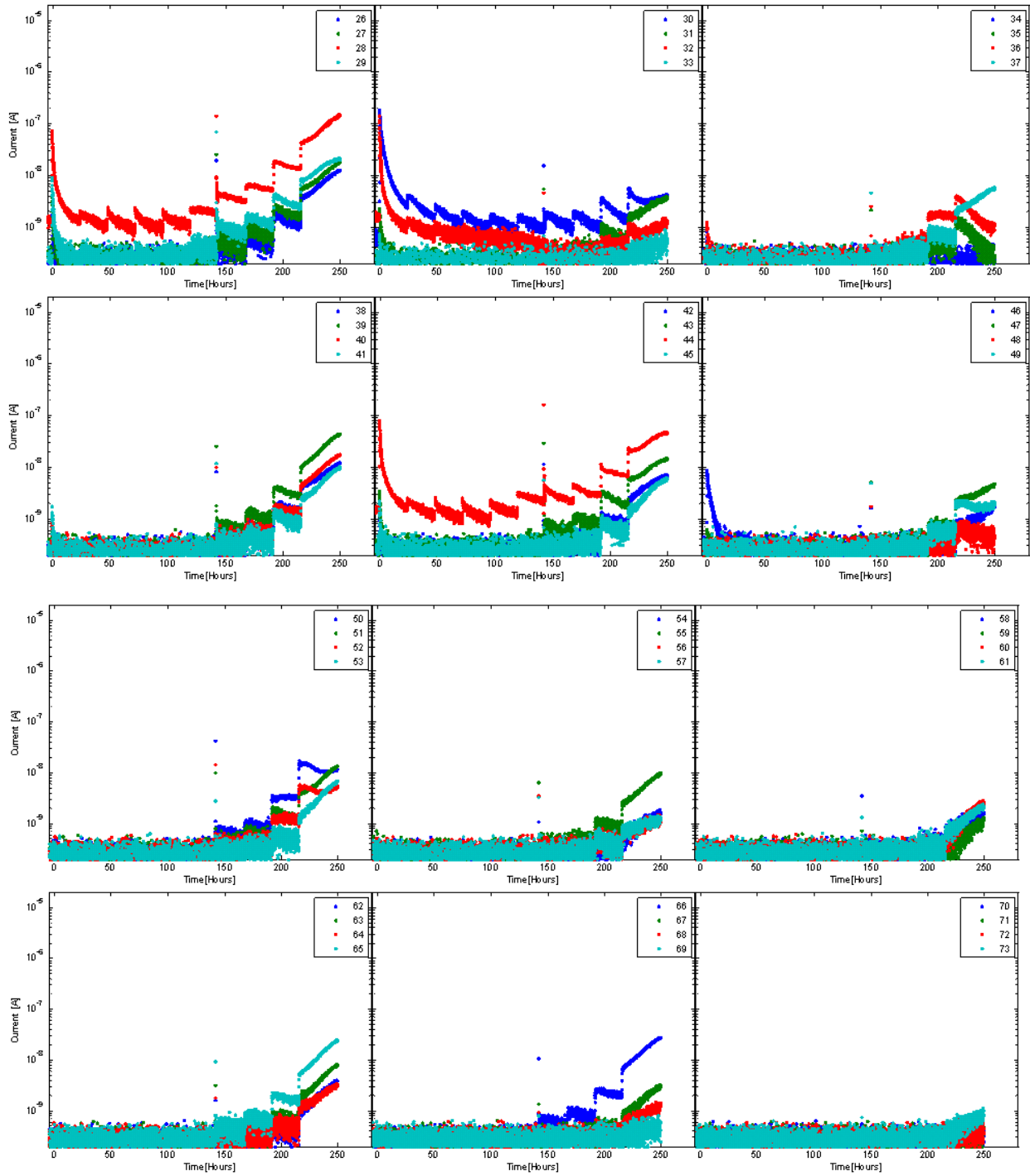


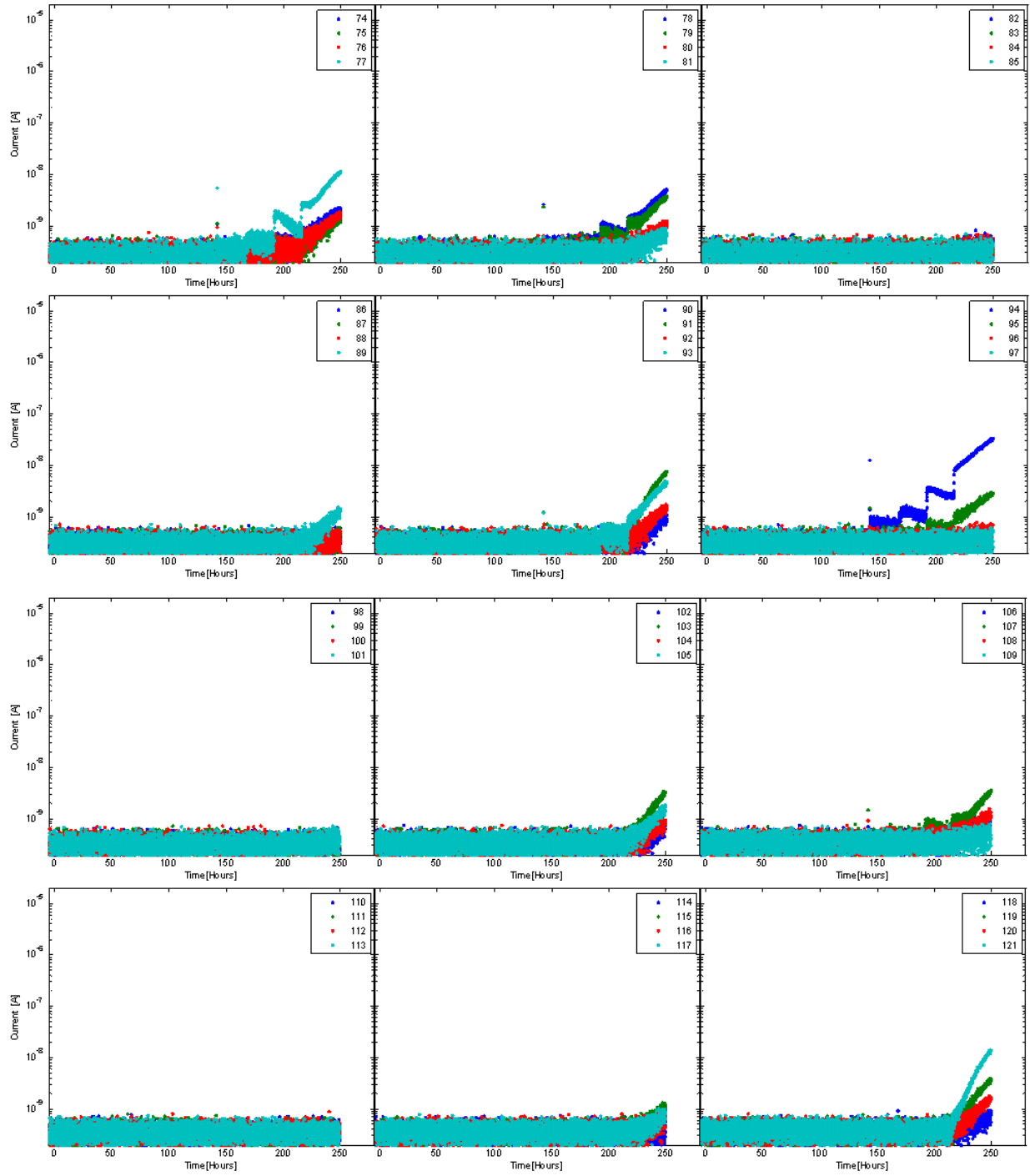


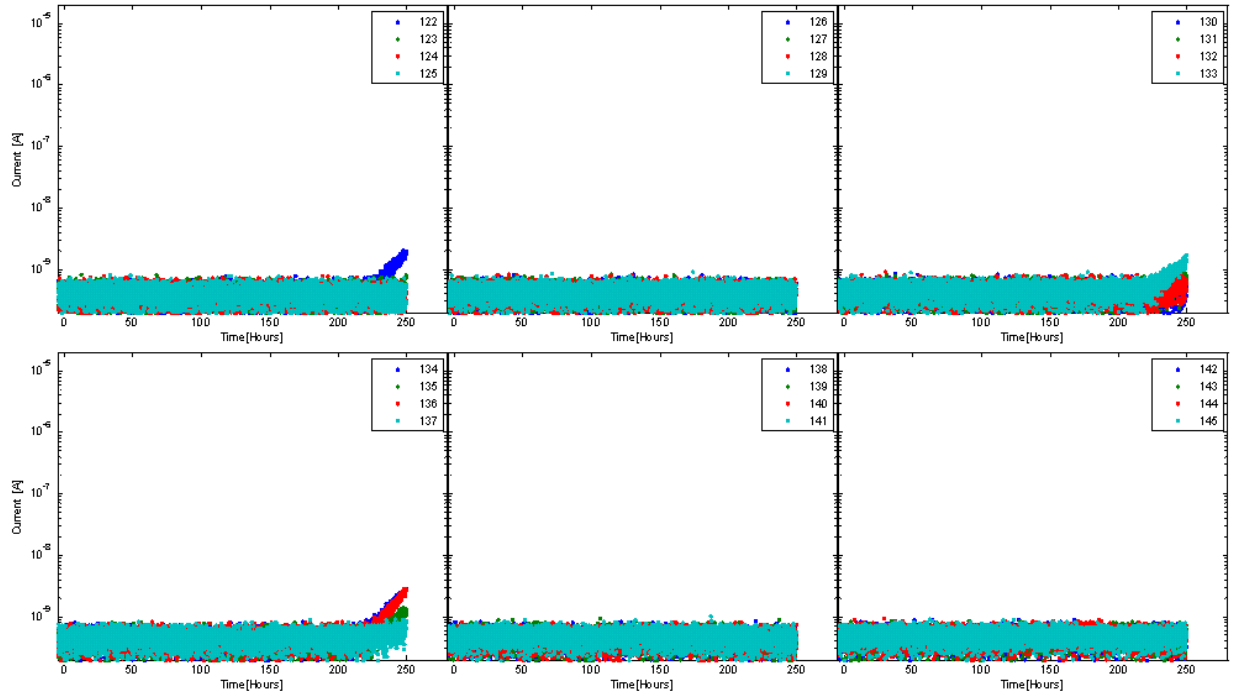


APPENDIX C: M/Z PROFILES FOR EPOXYN (RAW DATA)

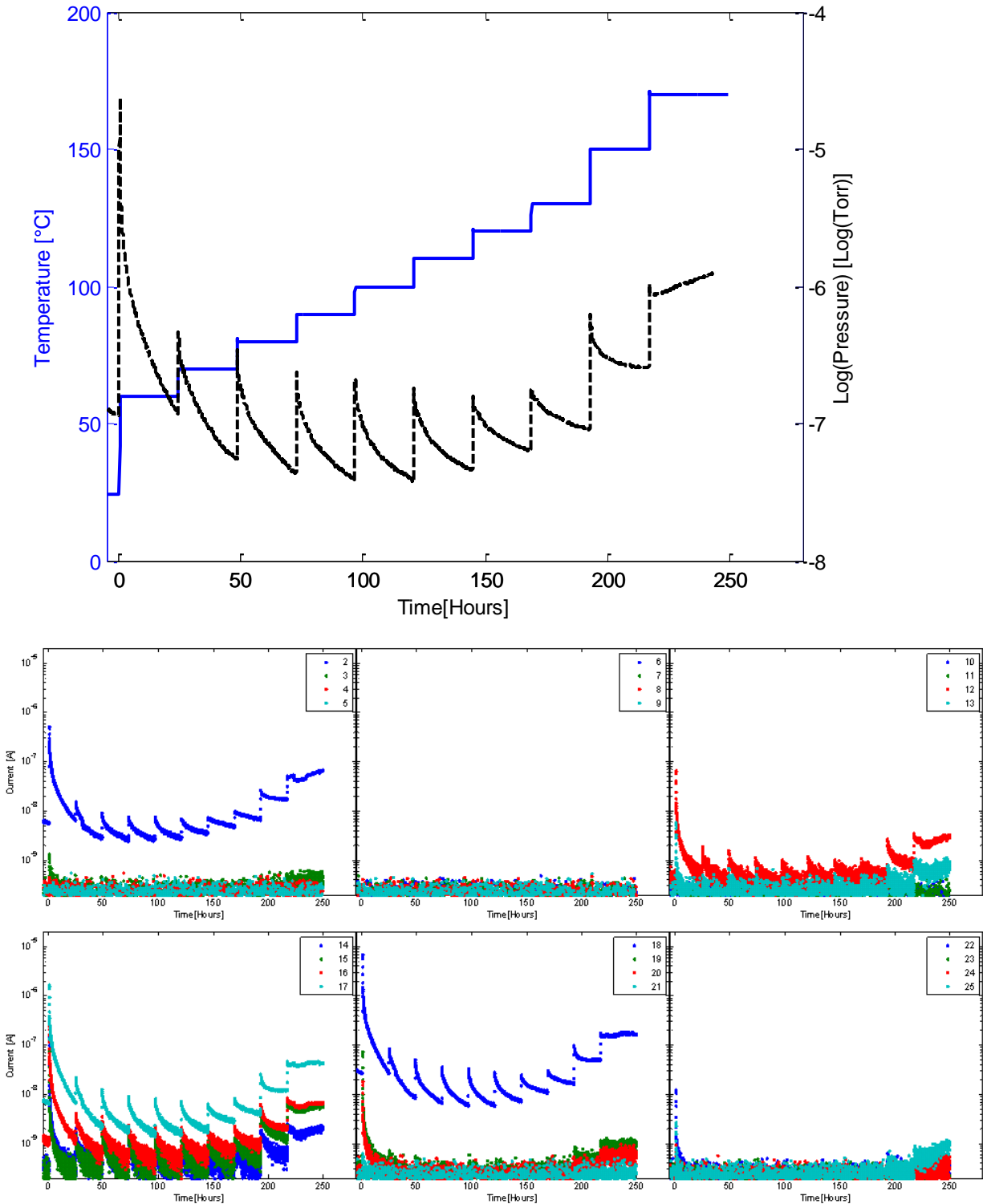


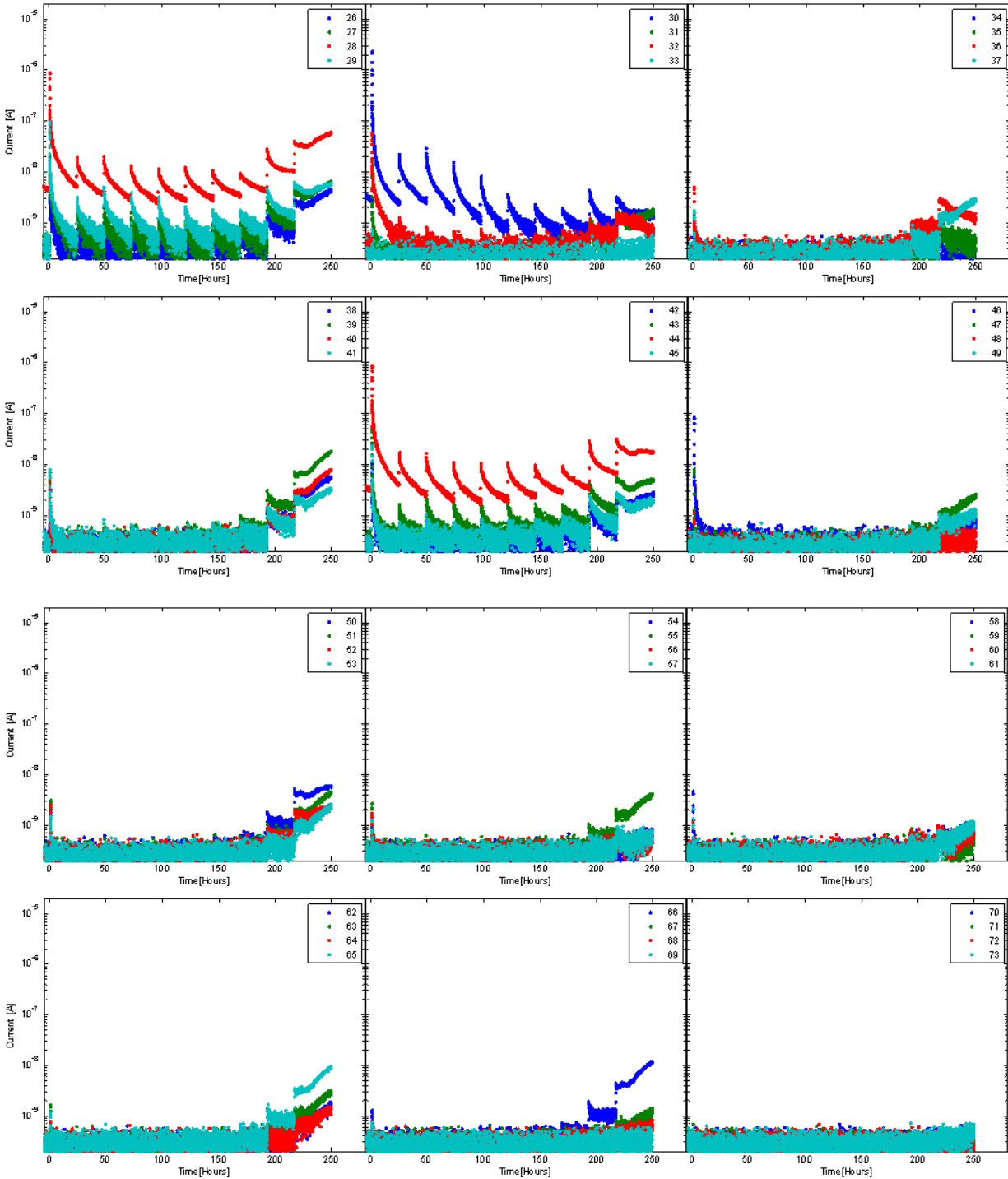


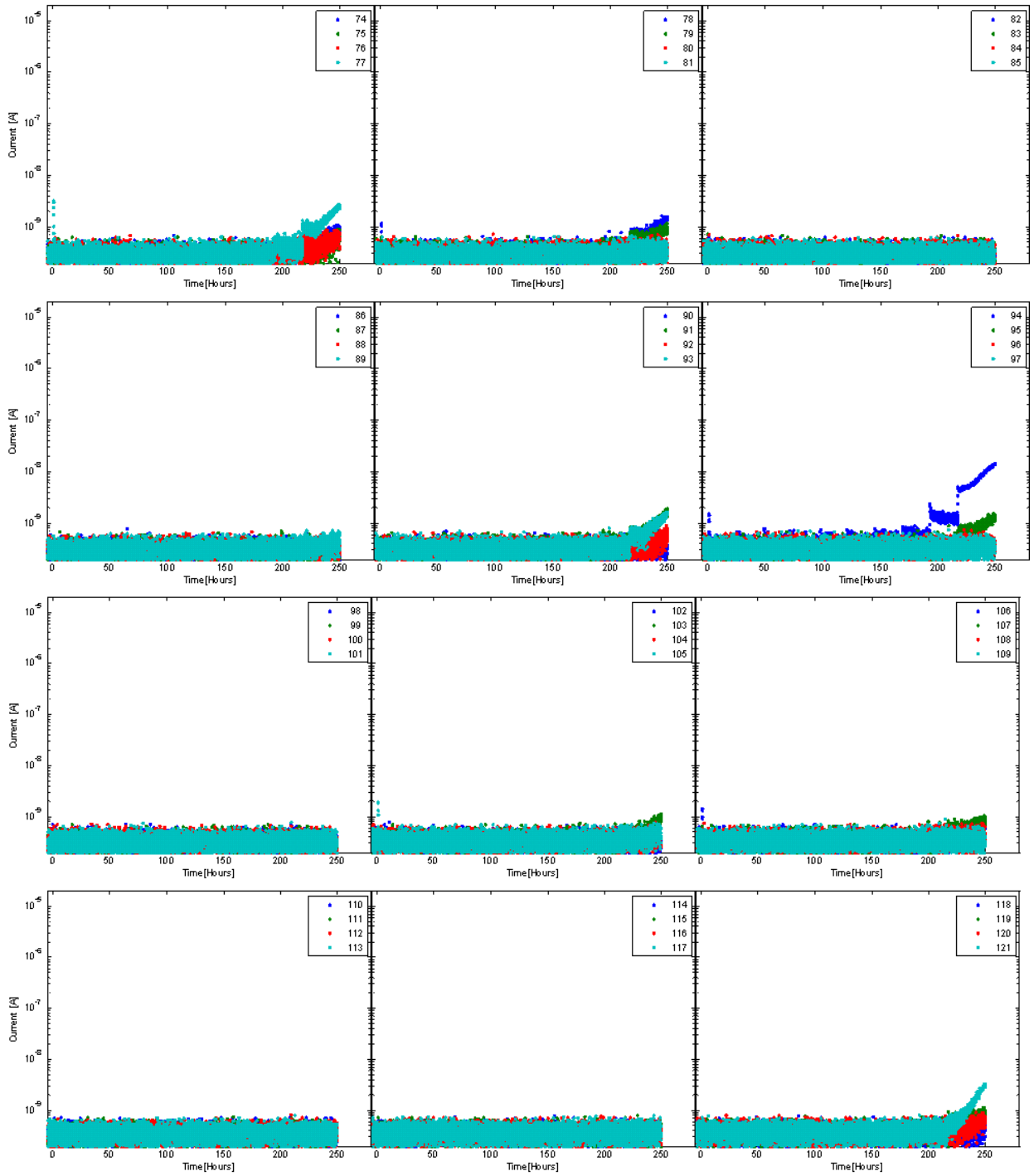


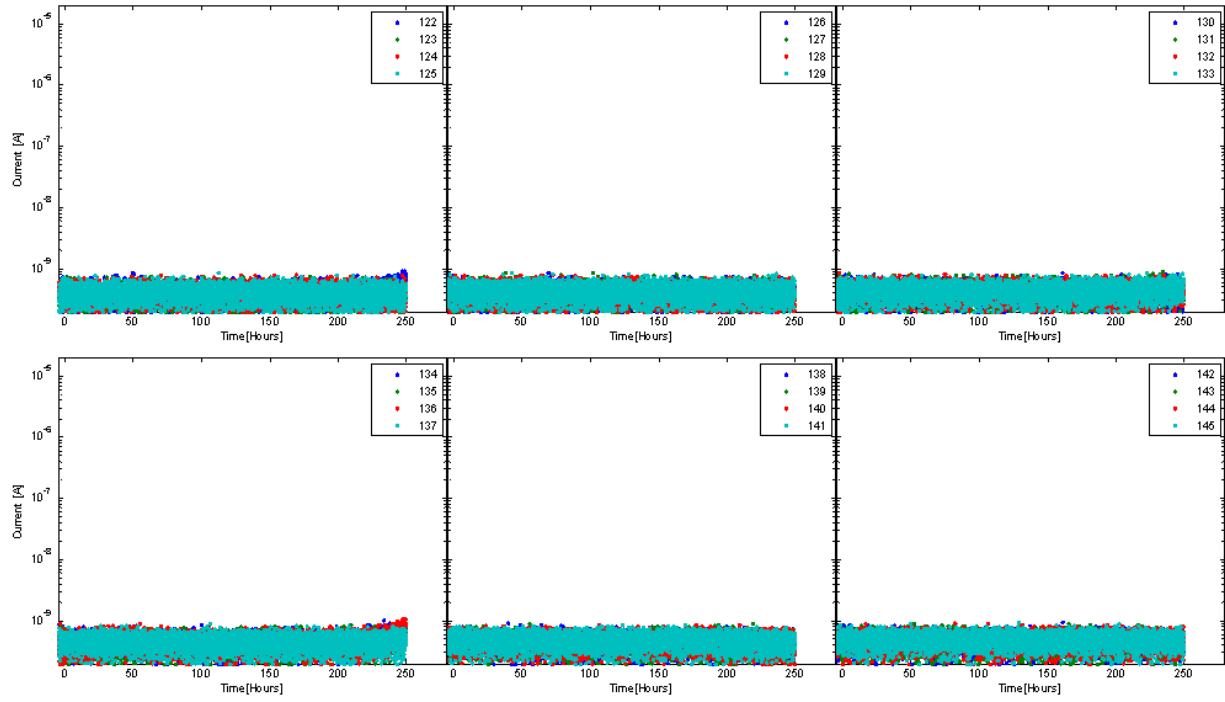


APPENDIX D: M/Z PROFILES FOR EPOXYP (RAW DATA)









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