

Final Report

In Situ Analysis of Organics with a Portable Mass
Spectrometer

Santosh Soparawalla
Final Report August 11th, 2011
Jet Propulsion Laboratory
Mentor: Luther Beegle
Signed _____

I. Introduction

The search for extra-terrestrial life starts at home. In order to find life on other planets, we start by examining life processes we understand on the earth. Though it may not be possible to see the life in the form of macroscopic organisms, telltale signs of life can exist in the form of small organic molecules such as peptides and amino acids. Our overall goal is to test a portable mass spectrometer (MS) system, the Mini 10.5, for astrobiological applications including in situ hydrocarbon analysis and sediments analysis using an additional automated sample processing system (ASPS).

The collaborative research focuses on two current projects in the field of astrobiology. Both projects are geared towards examining organics distributed in extreme environments. One portion of study attempts to qualitatively analyze the effect of volatile organic compounds (VOC) produced by diesel exhaust on lichens growing in the desert. This requires measurements to be taken by bringing the instrument to the Mojave Desert and monitoring atmospheric composition of VOCs in situ. The second project is to evaluate the miniature MS system as a detector for the ASPS extraction system. A major obstacle of any chemometric in situ analysis is the suppression of analyte signal by concomitant signal from the surrounding environment. The ASPS extraction device has been developed at JPL to extract amino acids from sediment samples and elute them in solution. The solution is eluted at a high pH and needs to be conditioned to a more neutral pH so that dissolved amino acids can be readily protonated and subsequently analyzed by electrospray MS.

II. Instrumentation Background

The fundamentals of MS center on measuring a particle mass to charge ratio and a typical MS system consists of an ionization method, a mass analysis, and signal detection. Our instrument is based on mass analysis through a planar version of the Paul trap mass analyzer. A rectilinear ion trap (RIT) is constructed of four planar electrodes that use RF to generate a quadrupolar electric field that traps and excites ionized molecules to a detector by function of mass. High vacuum conditions for trap operation limit the applicability of ion trap mass spectrometry to a laboratory setting. A field-portable RIT mass

spectrometer was developed by containing the analyzer and a detector in small stainless steel manifold of 470 cm³, a volume that can be kept at 10⁻⁵ torr using portable pumps. All components, including the electronics and vacuum systems are assembled into an aluminum case 32 cm in length, 22 cm in width and 19 cm in height. The total weight of the instrument is 22 pounds.

Analyzing trace organics from air samples is patently different than analyzing analytes in solution. To sample air borne analytes, a sorbent trap system (**Figure 1**) was fashioned to pre-concentrate air borne analytes and introduce them in smaller bolus samples. The system relies on cylindrical glass tubes (70 mm, *r* 3 mm) containing 10 mg of pre-packed sorbent material that can selectively bind chemicals in the air at ambient temperatures and release them into the instrument through direct outgassing via introduction into the low pressure regime of the ion trap manifold. To analyze the eluant output of the ASPS, we use an electrospray based method, nanospray, to create a spray plume of ions from a glass capillary with a 1-5 micron opening. A discontinuous atmospheric pressure inlet (DAPI) interface is used to take bolus ion samples at ambient pressure while the neutrals are pumped away before the trapped ions are mass analyzed.

All experiments were performed using a handheld Mini 10.5 mass spectrometer (rectilinear ion trap analyzer, dimensions $x_0 = 5.0$ mm, $y_0 = 4.0$ mm, axial length $z_0 = 43.2$ mm, operating RF ~ 1 MHz, resonant ejection at 350 kHz, excitation voltage ramped 0.01 V – 0.02 V). Electron impact ionization was used for VOC analysis. Electrons generated by thermionic emission from a rhenium filament (25 V bias, emission current ~ 20 μ A) are directed into the trap through a slit in the x-electrode and controlled by an external gate lens. Upon entering the trap, electrons take up additional kinetic energy from the RF field and ionize the neutral gaseous molecules. The resulting gas-phase ions are trapped and mass analyzed. Solution analysis was done by loading 10 μ L of solution into a glass nanospray emitter (tip size: 4 +/- 1 μ m) which is charged to 2-3 kV to induce an electrospray from the tip. The tip is positioned 1 cm from the DAPI inlet which is used to introduce ions from the ambient atmosphere into the vacuum of the RIT.

III. In Situ Analysis of Atmospheric Organics

Organisms living in extreme environments are good models for studying how life exists on other planets. This portion of our collaborative work examines the environment of lichens growing in the Mojave Desert. The lichen commonly referred to as the yellow acarospora (**Figure 2**) grows on basaltic rock surfaces in extreme heat and drought without any apparent source of organic nutrition. A possible source of organics for these species is from the byproducts of diesel combustion by vehicular traffic on nearby roads. Our goal is to characterize the carbon uptake of these organisms in situ using field portable analytical instrumentation, including a mass spectrometer (MS), to develop a methodology that can be applied to do automated analyses in a similar arid environment on Mars.

i. Scouting

Air samples were collected during a scouting trip geared toward finding lava rock with lichen growth. Air was sampled at sites with variable distance from automobile traffic. For air sampling in the desert the sorbent tubes were attached to a sample pump powered by rechargeable batteries. Air was drawn over these tubes at a rate of 2 liters/min for at least 15 minutes. Two different sorbents were used to sample at each site. A Hayesep D sorbent tube was used to check for non-polar midsize organics such as benzene. A PoraPak Q tube was used to check for similar compounds that were slightly more polar such as toluene and substituted organics.

During the first scouting trip, air sampling was done near Rainbow Basin near Barstow, CA, Salt Creek area of critical environmental concern (ACEC), CA, and Baker, CA (**Figure 3**). The Rainbow Basin site (N 35.104181, W -117.136688) is 12 miles away from the I-15 freeway and 10 miles away from any paved road. Salt Creek ACEC site (N 35.394088, W -116.127949) is 8 miles away from the I-15 freeway but adjacent to Hwy 127, a lightly traveled road. During the experiment only light vehicular traffic was seen with approximately 1 auto / 4 min. Baker, CA is a rest stop town on the I-15 freeway where the air sampling was done 100 yds from the freeway (N 35.265099, W -116.074768).

Air samples collected at Rainbow Basin showed the least overall signal intensity with both the Hayesep D and PoraPak Q resins. Three components were seen eluting from the Hayesep D and eight components from the PoraPak Q (**Figure 4**). The signal from m/z 72 and m/z 74 in the Hayesep D spectra can be sourced to C3-C4 substituted hydrocarbons. The Hayesep D and PoraPak Q spectra of the Salt Creek ACEC had the second highest signal response (maximum 800 counts). Five distinct components were seen in the PoraPak Q spectra and eight components from the Hayesep D spectra(**Figure 5**). Peaks seen in the higher mass ranges of m/z 108 – 130 likely originate from substituted aromatics. The strongest signal was seen from air sampling done near the I-15 freeway near Baker, CA. Signal was seen across the mass range m/z 60 – 120 with eight components from the Haysep D sampling and seven components from the Porapak Q. Both Haysep D and Porapak Q tubes gave a maximum signal response over 1400 counts (**Figure 6**). The trend in signal intensity across the different samples suggests that the amount of organic atmospheric components decrease with increasing distance from automobile thoroughfares. This experiment laid the groundwork for the in situ measurements.

ii. In Situ Analysis

The sorbent material adopted for the final field experiment was Carbopack C. Carbotrap C gives good recoveries for polyaromatic hydrocarbon (PAH) analytes from naphthalene to chrysene. This was chosen to complement data obtained from a UV laser spectrophotometer which targeted aromatic hydrocarbons. Air was sampled 10 feet from the freeway using a sample pump to draw the air over the sorbent tubes at a rate of 2 liters/min for 60 minutes. The miniature instrument was powered by a Duracell DPP-600HD Powerpack.

The miniature MS system was able to detect the two most abundant components of diesel exhaust, naphthalene and acenaphthene. Background chemical noise was accounted for by taking the spectrum of a preconditioned blank Carbotrap C tube (**Figure 7**) before analyzing the sampled tube (**Figure 8**). Signal from larger species is also limited in part because thermal desorption was not used

during this experiment. The major aromatic components of the exhaust are toluene, phenylacetylene, styrene, indene, naphthalene, and acenaphthalene. The background subtracted spectra shows two clear peaks (**Figure 9**) at m/z 128 and m/z 154. The peak at m/z 128 corresponds to the radical cation of naphthalene and the peak at m/z 154 corresponds to acenaphthene. The small peak at m/z 104 is from radical cation of styrene.

IV. Analysis of ASPS Elution

Mass analysis requires the molecules being analyzed to be ions bearing a net positive or negative charge. One concern of using the automated sample processing system is the interference of high pH in subsequent MS analysis of the extracted, desalinated amino acids. After a cation exchange column of AG50W-X8 resin is prepped with 10mL 3.0 M HCl, a solution containing a mixture of salts and amino acids is introduced. Amino acids in solution bind to the resin in the column. The column is then desalted using oxalic acid to remove any excess Fe and Al. The amino acids are finally extracted from the resin using 2.5M NH₄OH. Therefore, the final solution of amino acids is at pH of 11.9. For MS analysis, any analyte species must bear a net charge. Since the miniature MS instrument is capable of positive mode detection, the easiest way to achieve this is through protonation. Unfortunately, at this pH, protonation of the amino acids via electrospray method is inhibited. One solution is to reduce the pH using acid.

Initial experiments examined using a strong acid HCl as a neutralizing agent prior to MS analysis. When neutralizing 2.5M NH₄OH with 6.0 M HCl a salty solution, 1.75 M NH₄Cl, was an inevitable outcome. No amino acid signatures were detected in the nanoESI-Mini MS spectra of the 1.75 M NH₄Cl. This is likely due to charge competition from the salts in the solution during electrospray. An alternative strategy was explored by reducing the pH by dilution of the NH₄OH. 1% acetic acid was also added to bring down the pH and facilitate protonation of the analytes. This results in a buffered solution of sodium acetate. Sodium acetate has been shown to be useful for buffer loading to counteract metal salt-induced signal suppression in electrospray ionization.

If we assume that only 2.5 ml of the 2.5 M NH_4OH is required to completely elute amino acids then a starting 10 ml of 100 μM AA sample solution can be eluted to a 4x higher concentration in the NH_4OH . In the simulated eluant, the 2.5 ml 400 μM AA in 2.5 M NH_4OH was diluted 2 fold and spiked with 1% Acetic Acid for a final solution of 200 μM amino acid in 1.25 M NH_4OH . In a hundred scan average, 4 of the 5 amino acids can be seen as molecular ions $[\text{THE}+\text{H}]^+$, $[\text{LYS}+\text{H}]^+$, $[\text{HIS}+\text{H}]^+$, $[\text{ARG}+\text{H}]^+$ (**Figure 11**). The $[\text{TYR}+\text{H}]^+$ signal was intermittent and seen frequently in individual scans (**Figure 12**).

V. Conclusion

The inclusion of a miniature MS on future interplanetary exploration missions could improve the chemical analysis of organic materials due to its sensitivity and specificity. These results underscore the utility and potentially broad applicability of handheld mass spectrometers for the detection and identification of gaseous and solid species in the field. The current study emphasizes that the pumping limitations of small mass spectrometers can be overcome with creative sample preparation techniques.

VI Acknowledgment

This research was carried out at the Jet Propulsion Laboratory, California Institute of Technology, and was sponsored by JPL Graduate Fellowship Program and the National Aeronautics and Space Administration.

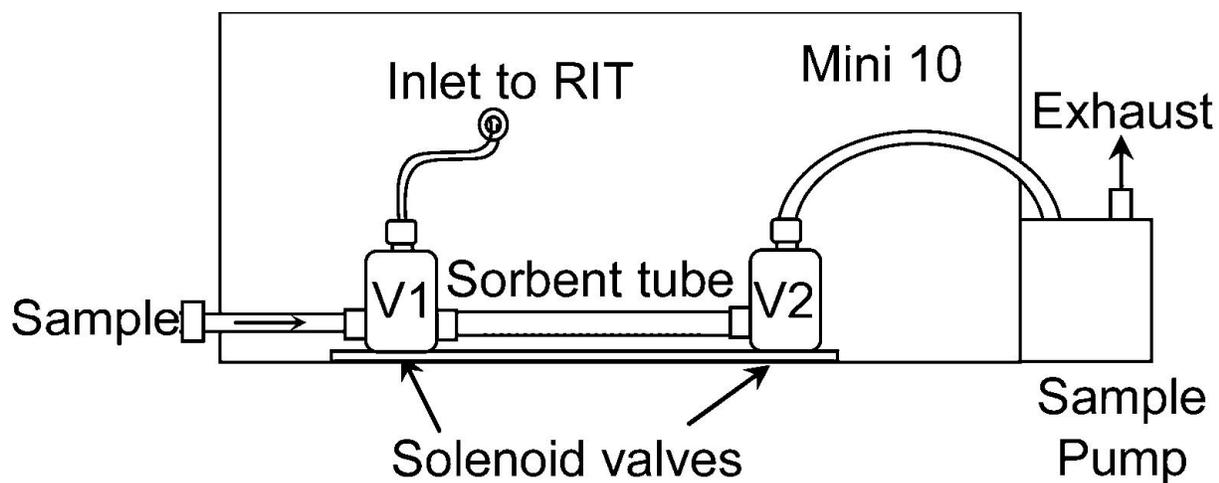


Figure 1: The sorbent trap interface to the Mini 10 uses a sample pump to draw ambient air over the sorbent contained in a tube. When V1 and V2 are opened, sample collects on the sorbent bed as air is pulled by sample pump. V1 is opened to the instrument and V2 is closed to let the sorbent bound analytes outgas into the instrument.



Figure 2: A picture of the lichen commonly referred to as yellow *Acoraspora* growing on lava rock near Cima, CA.

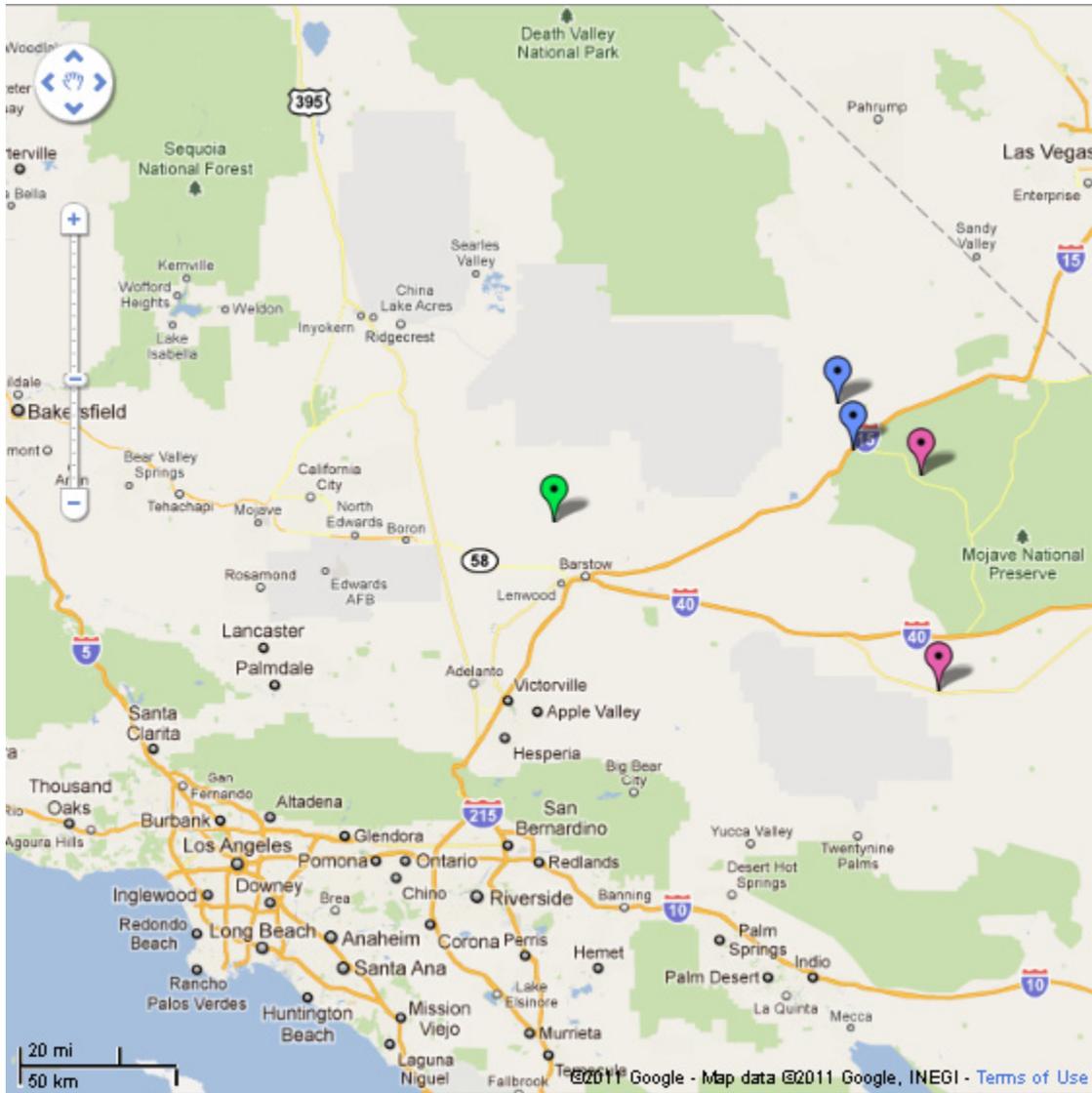


Figure 3: Air sampling was done at these locations throughout the Mojave area. The westernmost marker is Rainbow Basin, the northernmost marker is Salt Creek ACEC, and the marker south of that is Baker, CA on I-15. The two eastern most markers are other sites visited- Cima young lava flow and Amboy crater (not discussed).

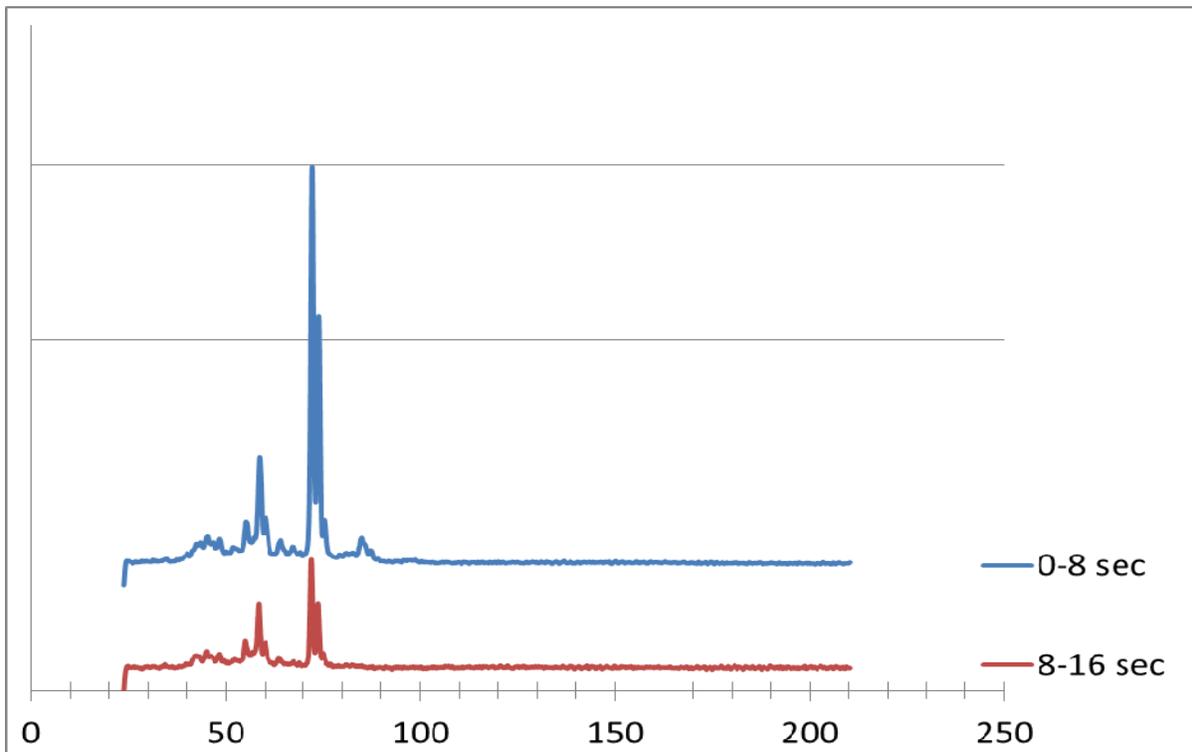


Figure 4a: Mass spectra of air sampled at Rainbow Basin with Hayesep D
Y scale is 500 counts per row

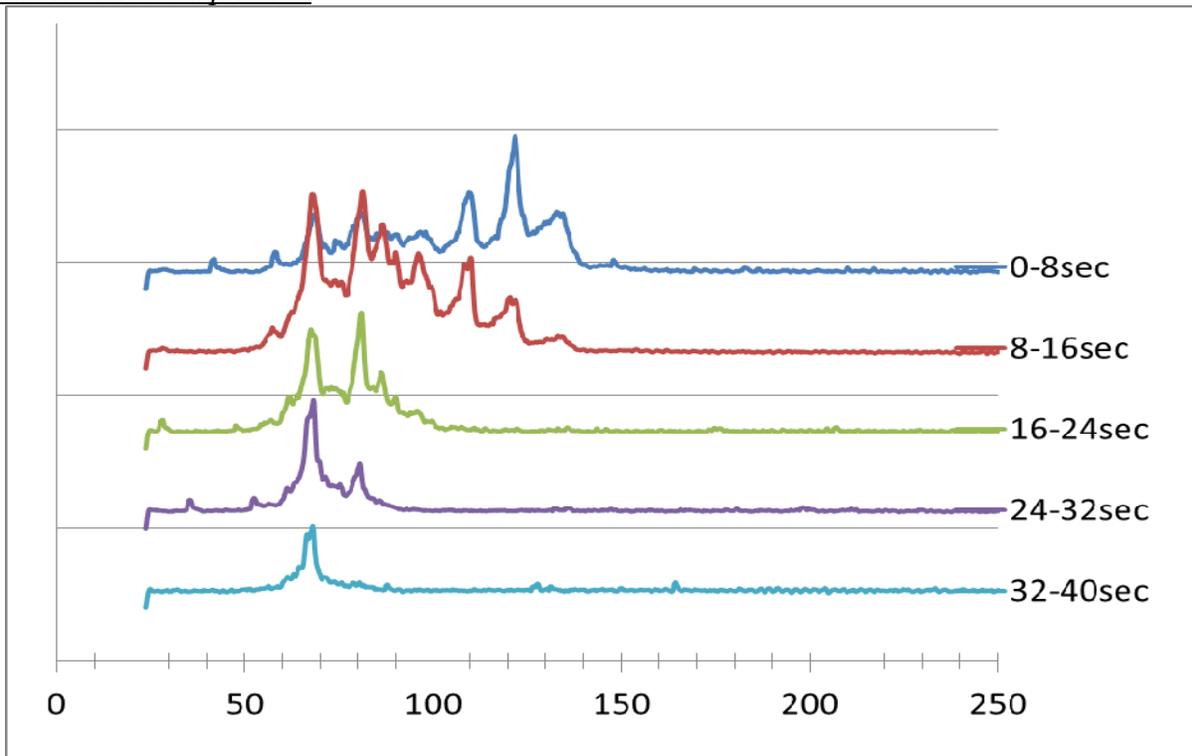


Figure 4b: Mass spectra of air sampled at Rainbow Basin with PoraPak Q.

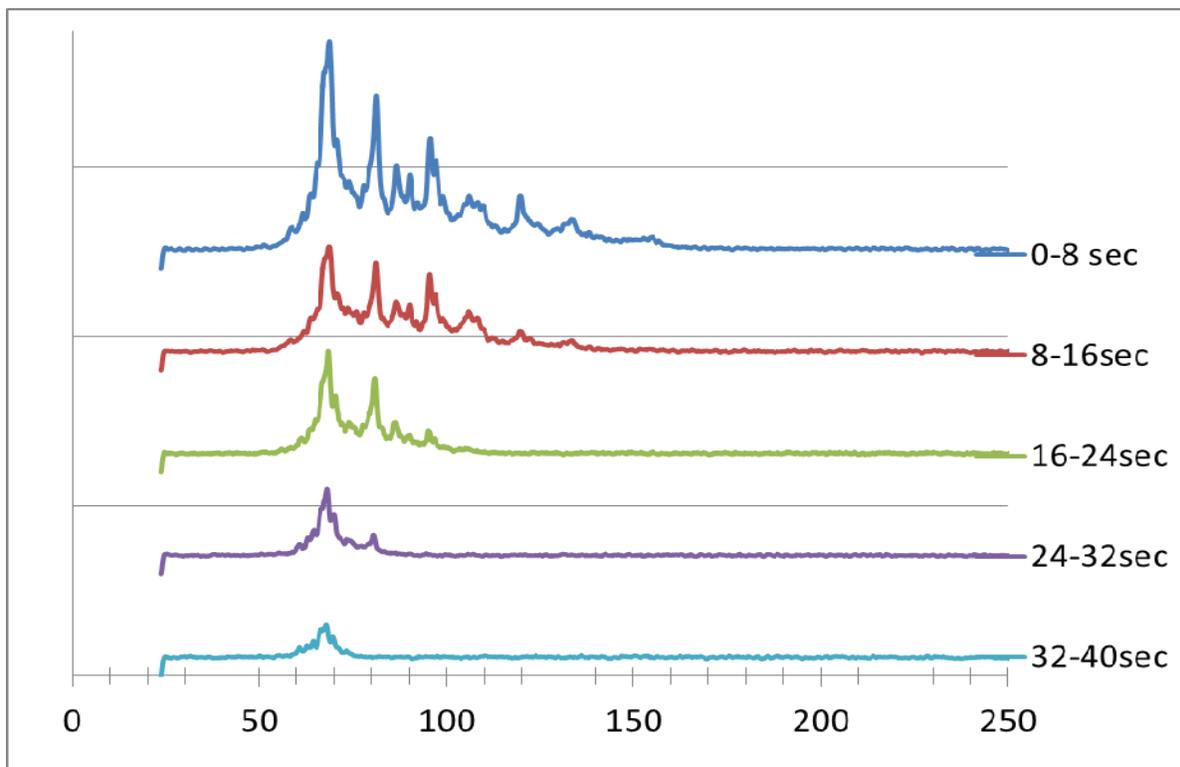


Figure 5a: Mass spectra of air sampled at Salt Creek ACEC with Hayesep D
Y scale is 500 counts per row.

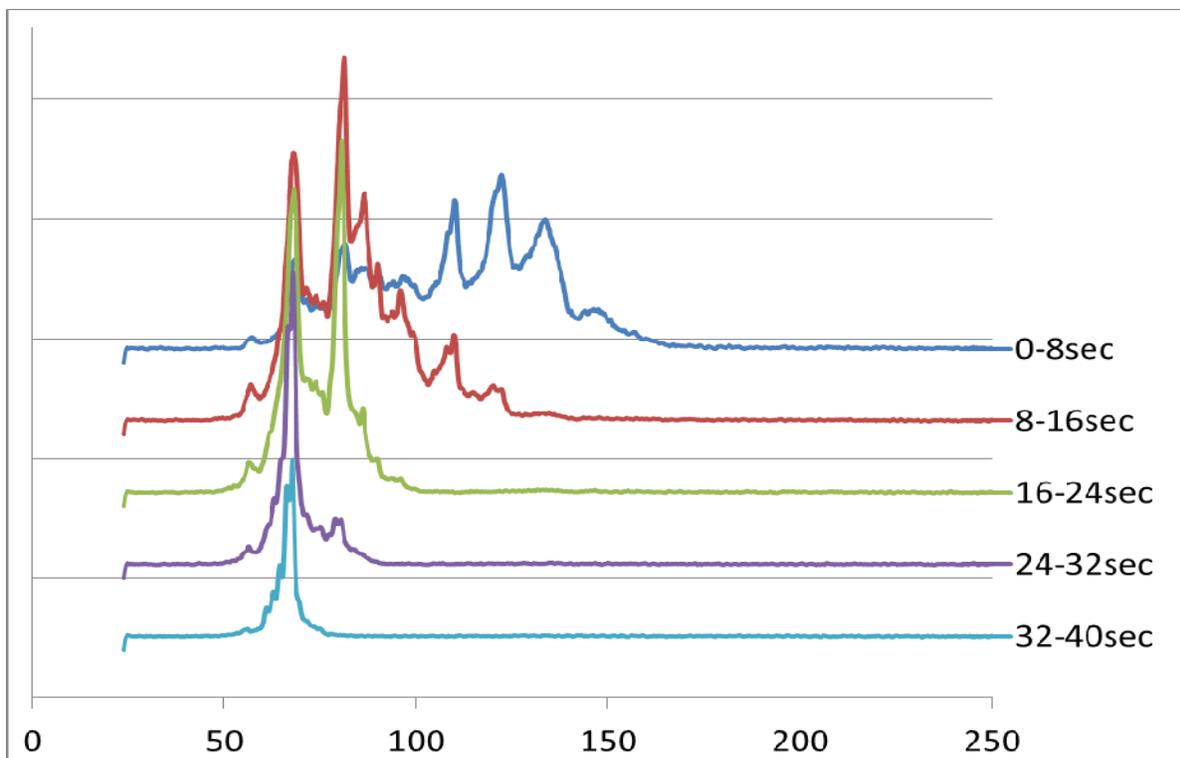


Figure 5b: Mass spectra of air sampled at Salt Creek ACEC with PoraPak Q

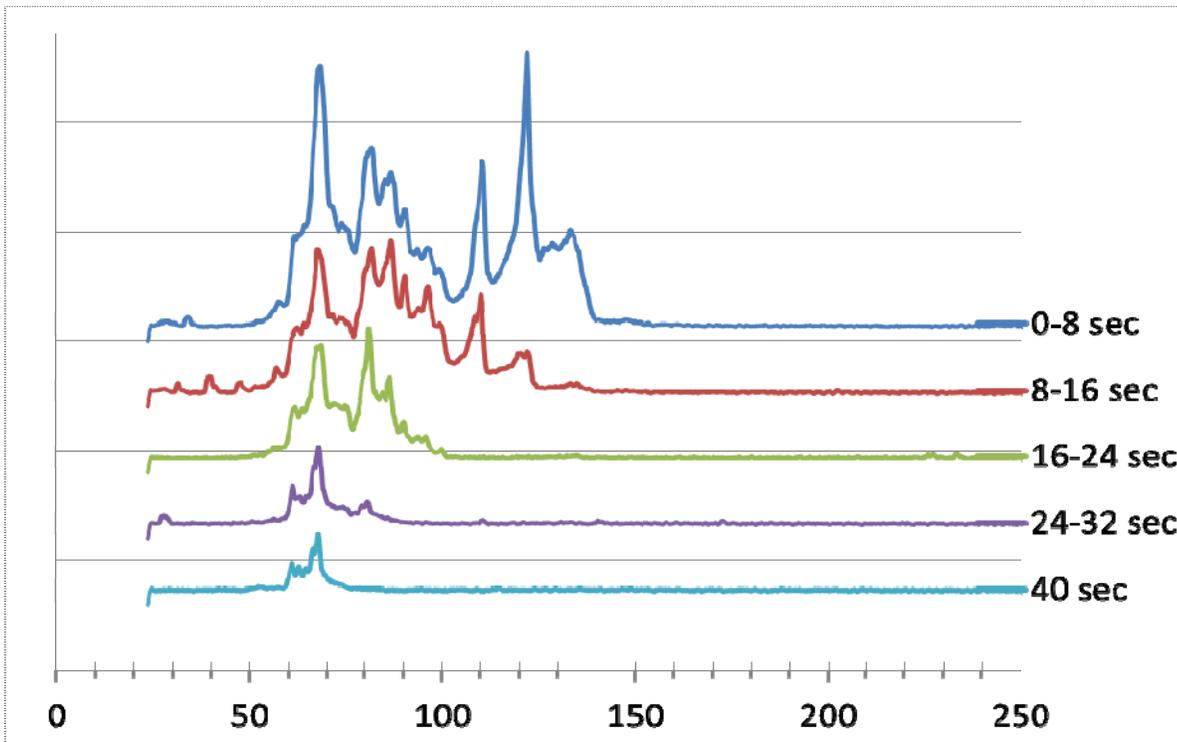


Figure 6a: Mass spectra of air sampled at Baker, CA with Hayesep D

Y scale is 500 arbitrary units per row.

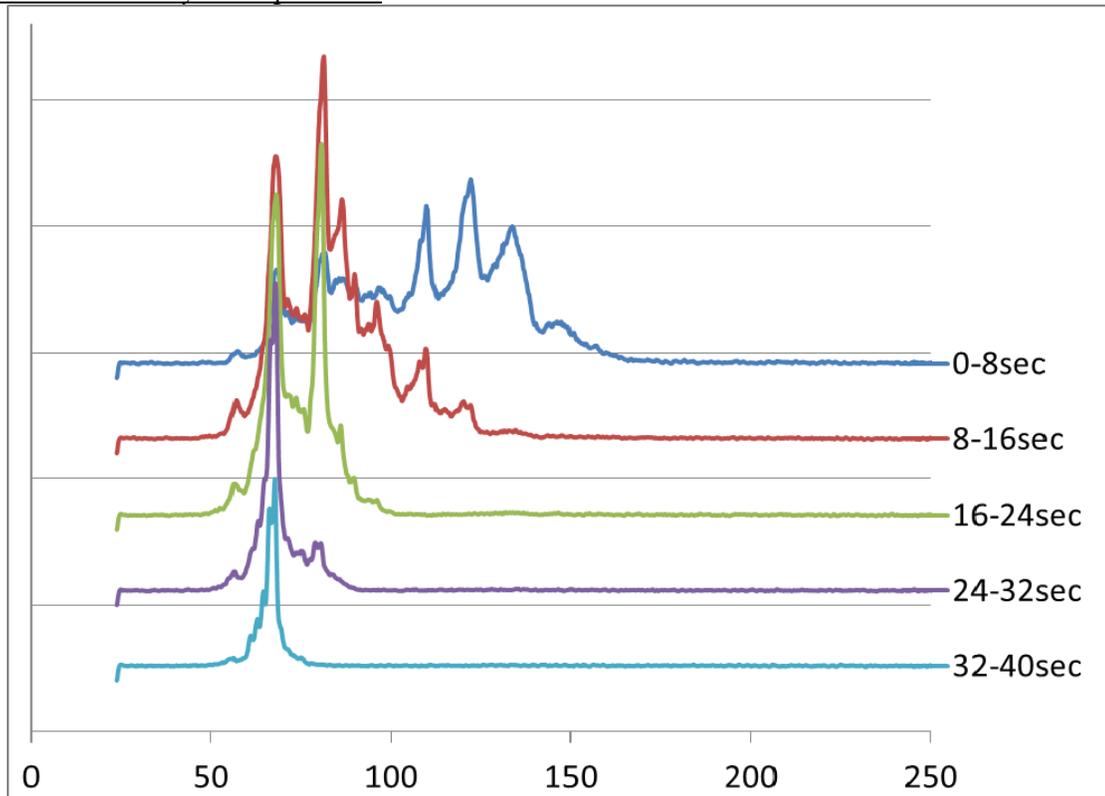


Figure 6b: Mass spectra of air sampled at Baker, CA with PoraPak Q

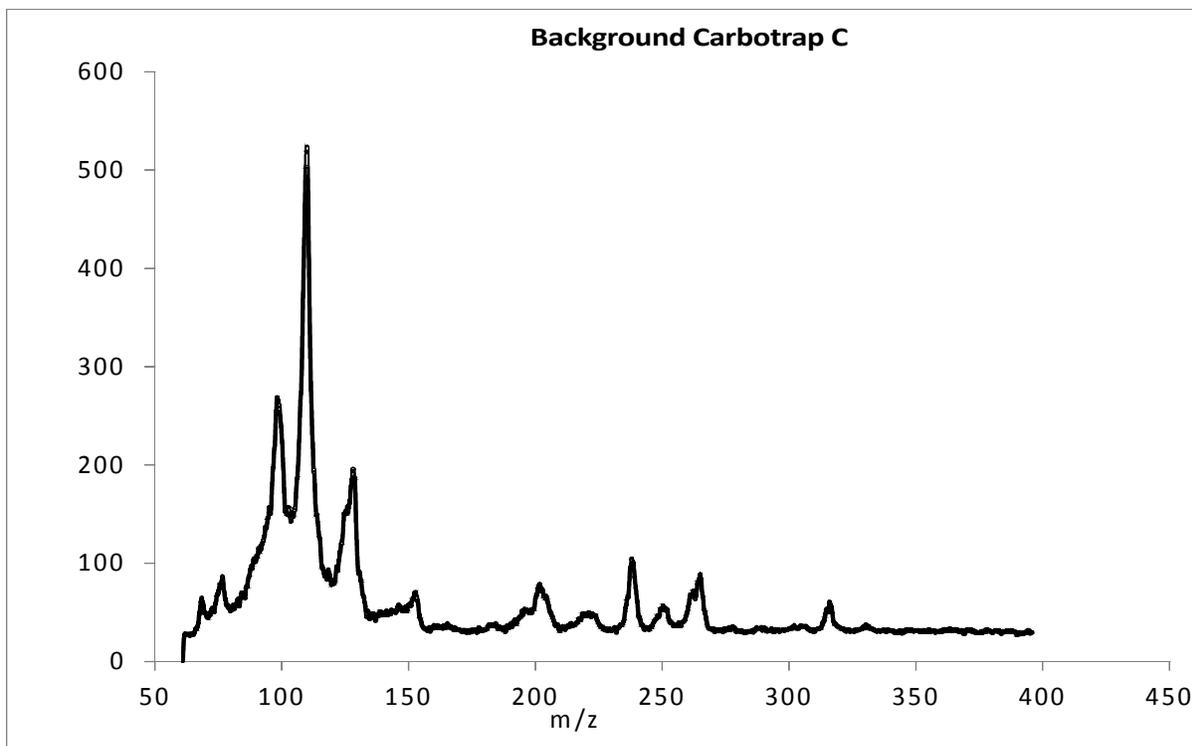


Figure 7: Background signal from blank Carbopak C tube.

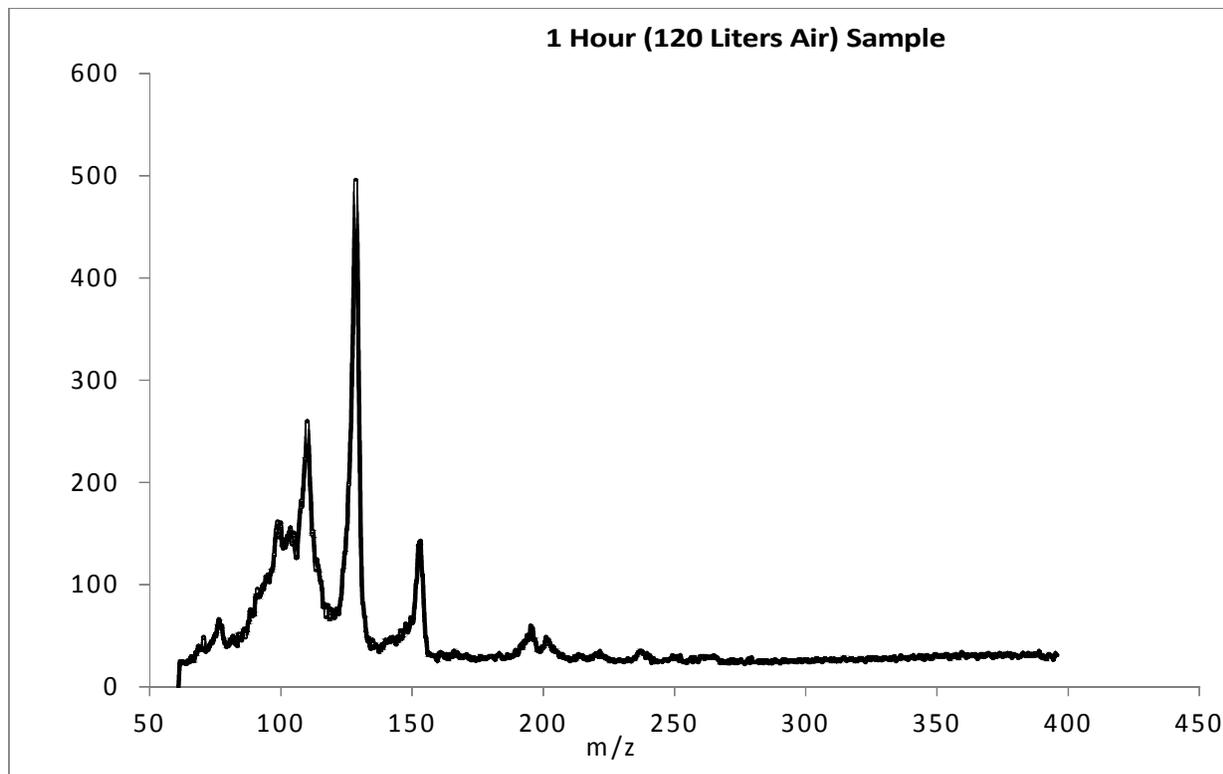


Figure 8: Raw signal from a sampling of 120 L of air next to the freeway.

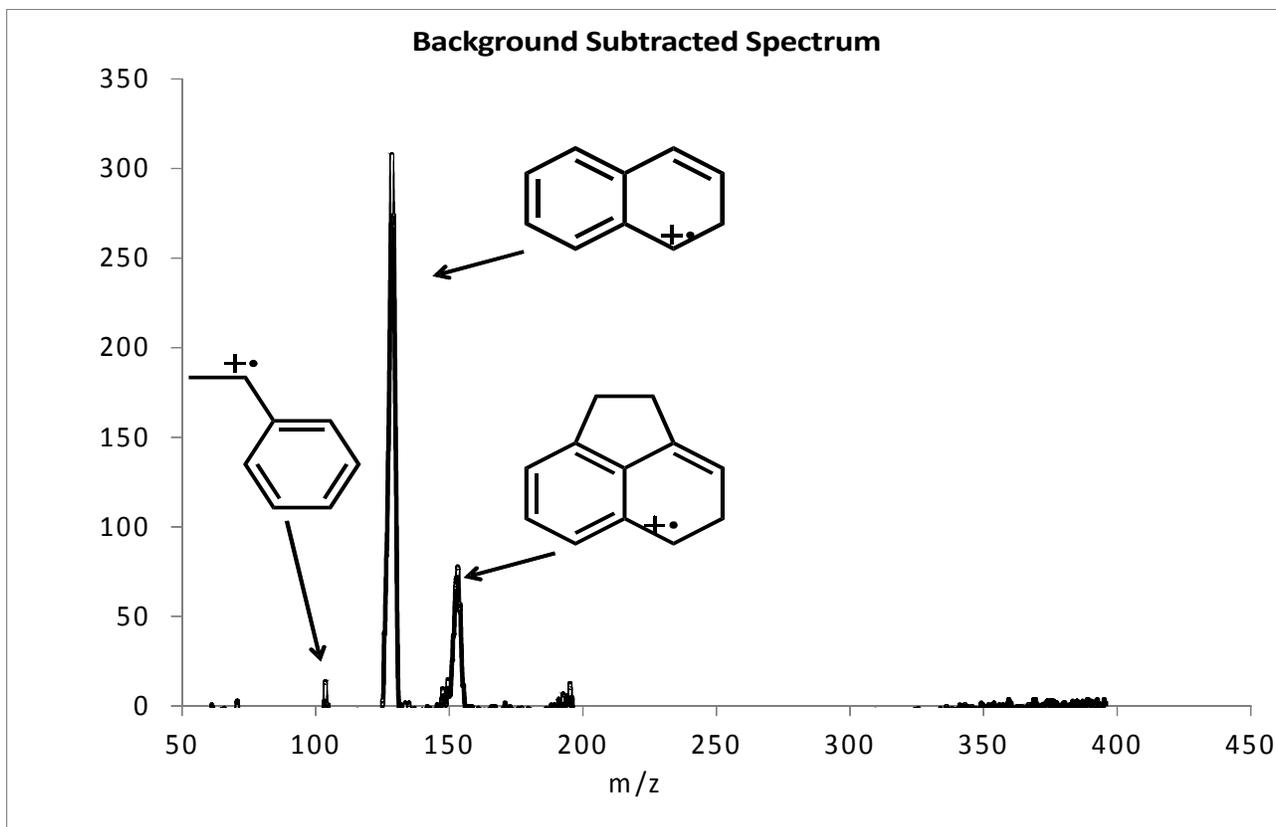


Figure 10: The background subtracted spectrum shows three peaks corresponding to aromatic hydrocarbons commonly found in diesel exhaust; naphthalene, acenaphthene, and styrene.

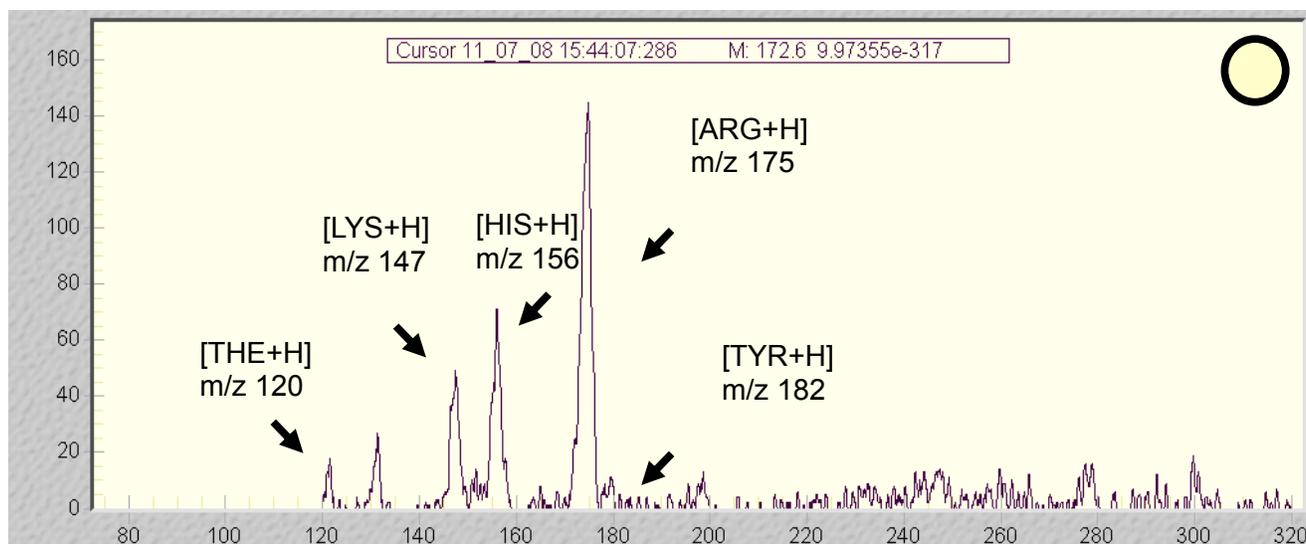


Figure 11: Full spectrum 100 scan average of the simulated eluant obtained nanoESI - MS shows 4 apparent protonated amino acid peaks $[\text{THE}+\text{H}]^+$, $[\text{LYS}+\text{H}]^+$, $[\text{HIS}+\text{H}]^+$, $[\text{ARG}+\text{H}]^+$. The $[\text{TYR}+\text{H}]^+$ peak seen in individual scans is buried.

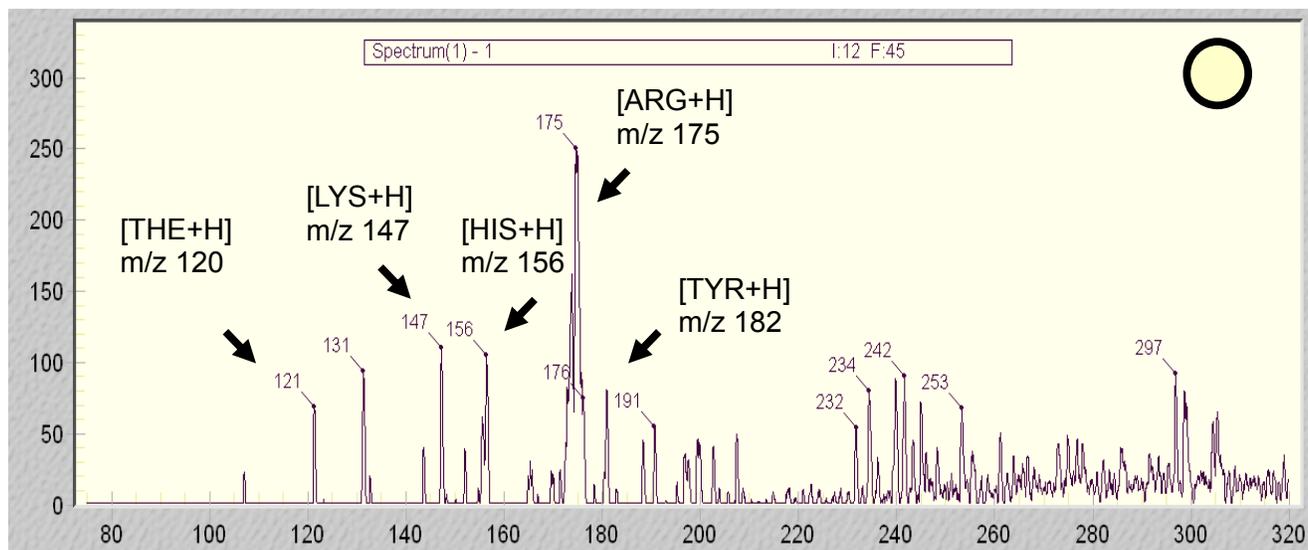


Figure 12: Individual scans regularly showed all five amino acids including TYR.