

Qualitative and Semi-quantitative Analysis Of Semi-volatile Organics from Ambient Air Fine-particulate Matter, $PM_{2.5}$

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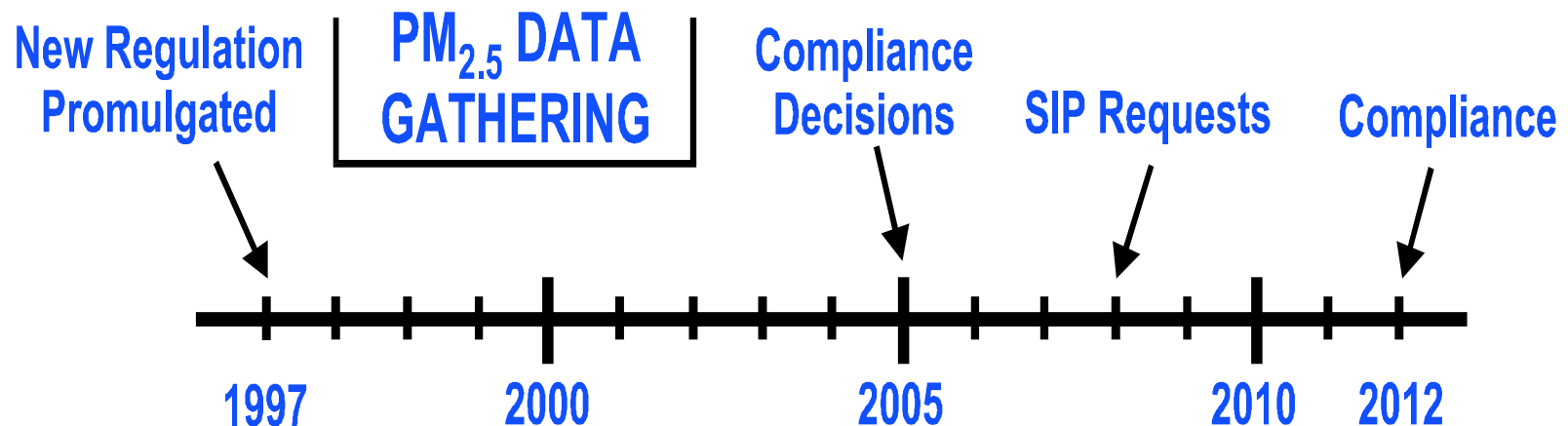
Different Missions

- **EPA – Protect the public health**
- **DOE – Assist the private sector in supplying clean, abundant, and affordable energy**



PM_{2.5} Regulatory Process

- 1997 National Ambient Air Quality Standards (NAAQS) for PM_{2.5} based on “health effects”
 - Mean annual concentration < 15 µg/m³
 - Maximum concentration < 65µg/ m³



PM_{2.5} TIME LINE



Why Is DOE Concerned About PM_{2.5}?

- **Coal-based power systems contribute to PM_{2.5}**
 - Primary particles
 - Ultra-fine fly-ash (Spherical Alumino-silicates, SAS), carbon soot
 - Gaseous precursors
 - SO₂, SO₃, NO_x
 - React with NH₃ in the atmosphere to form ammonium sulfate and ammonium nitrate particles
- **SIPs will likely restrict emissions from coal power plants**



Ambient PM Monitoring and Characterization

Current Project Portfolio

Stuebenville Comprehensive Air Monitoring Project (SCAMP)

NETL-PGH In-house Monitoring Station

CMU/EPA "Supersite"

Upper Ohio River Valley Project (UORVP)

Great Smoky Mountains Project (GSMP)

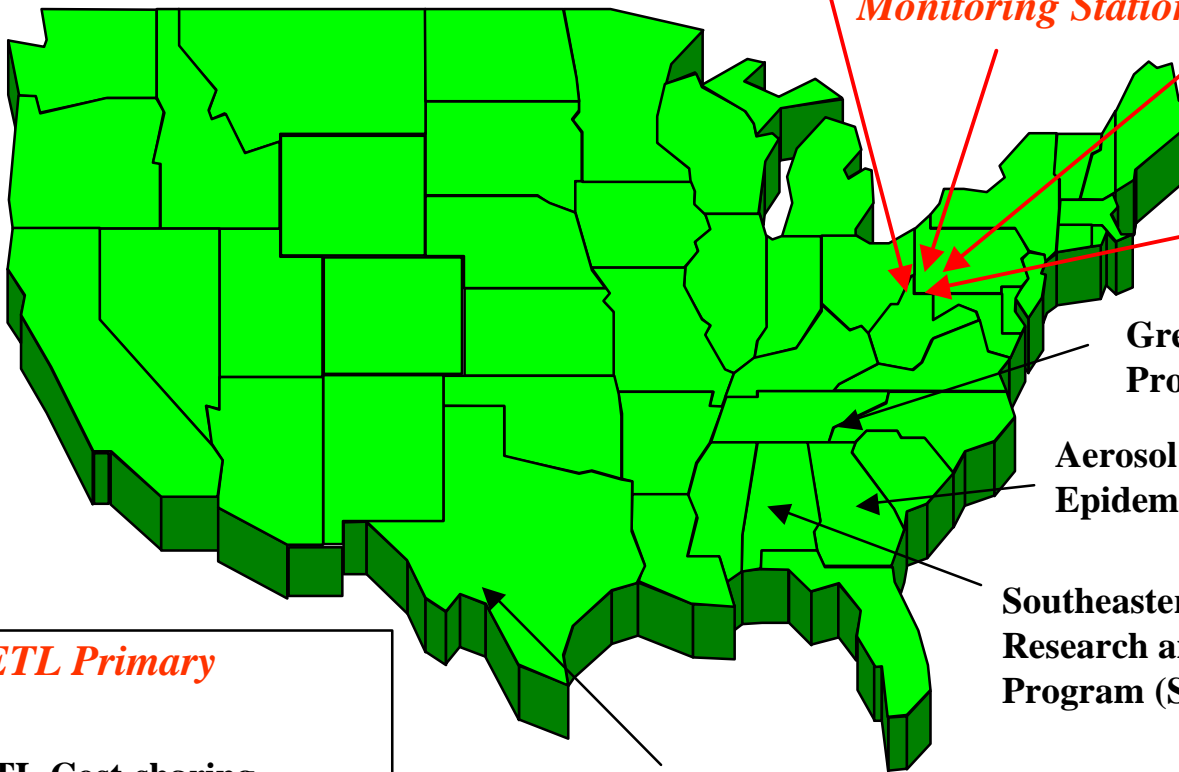
Aerosol Research Inhalation Epidemiology Study (ARIES)

Southeastern Aerosol Research and Characterization Program (SEARCH)

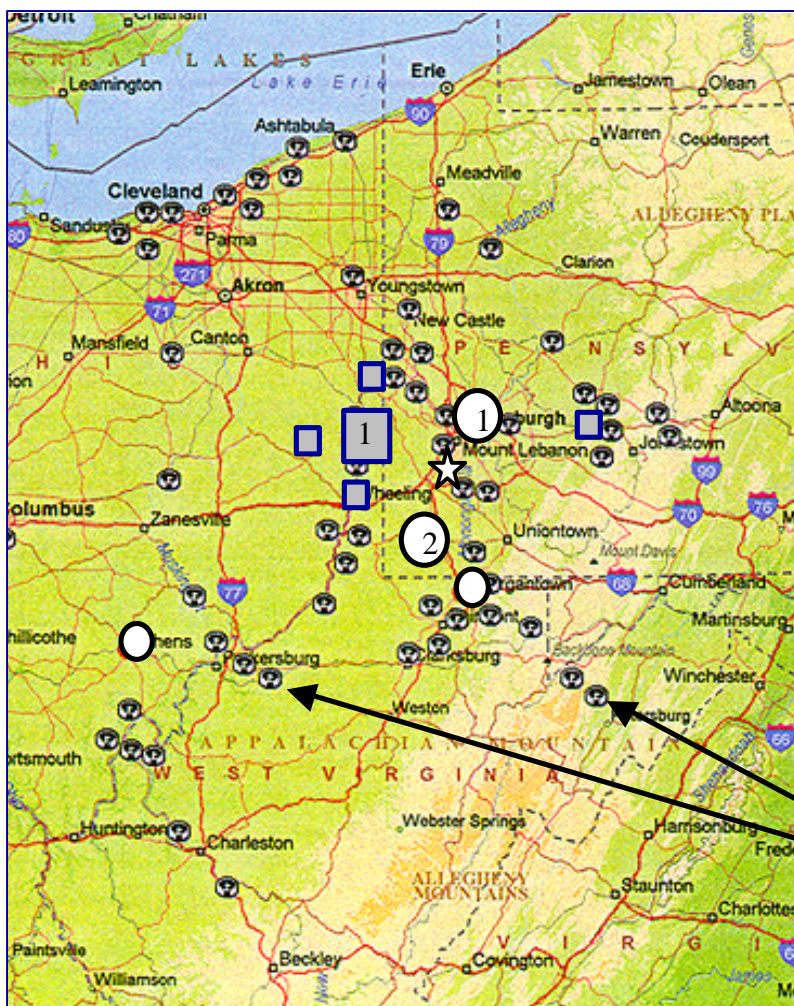
Bravo Project

DOE-NETL Primary Funding

DOE-NETL Cost-sharing



Regional Ambient PM Monitoring Sites



UORVP Sites

- ① - Lawrenceville
- ② - Holbrook
- - Satellites

SCAMP Sites

- ① - Primary
- ② - Satellites

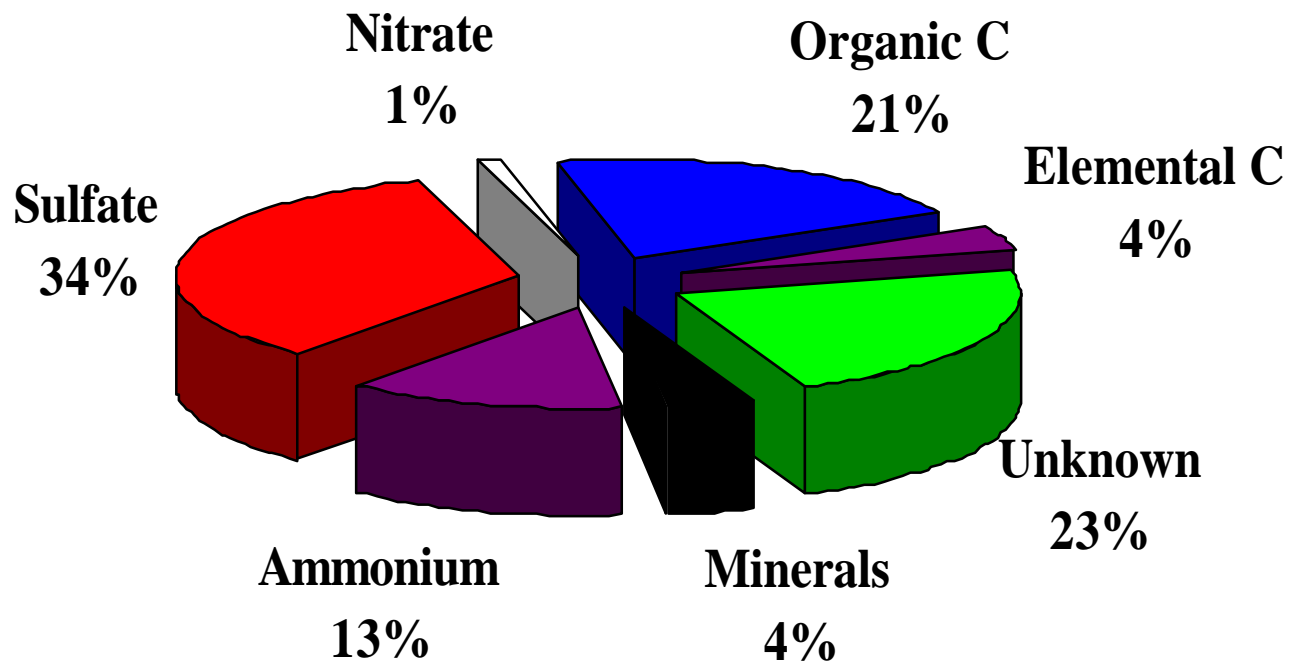
☆ - NETL In-house site

**Coal-fired
power plants**



Eastern PM_{2.5} Mass Apportionment

Current Understanding?



Source: EPA (1996)

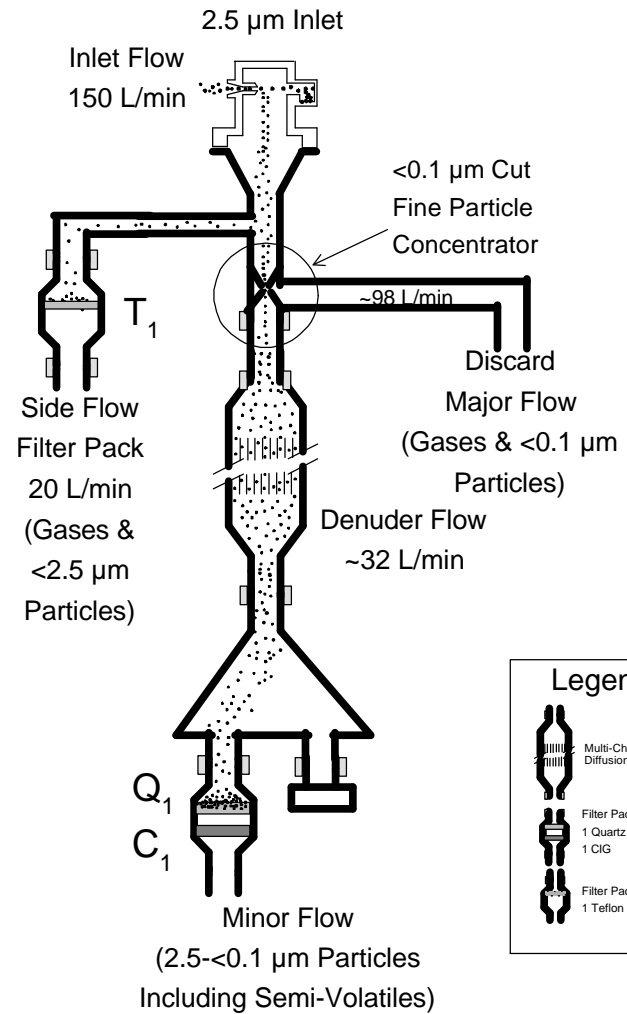


Experimental - Sampling

- **Brigham Young University provided PCBOSS sampler**
 - nominal 2.3 μ m inlet and particle concentrator
 - samples collected on 47mm quartz fiber filters
 - Two flow channels of the PCBOSS were combined to double the flow rate through the filter.
 - Samples were collected from noon to noon.



BYU PC-BOSS

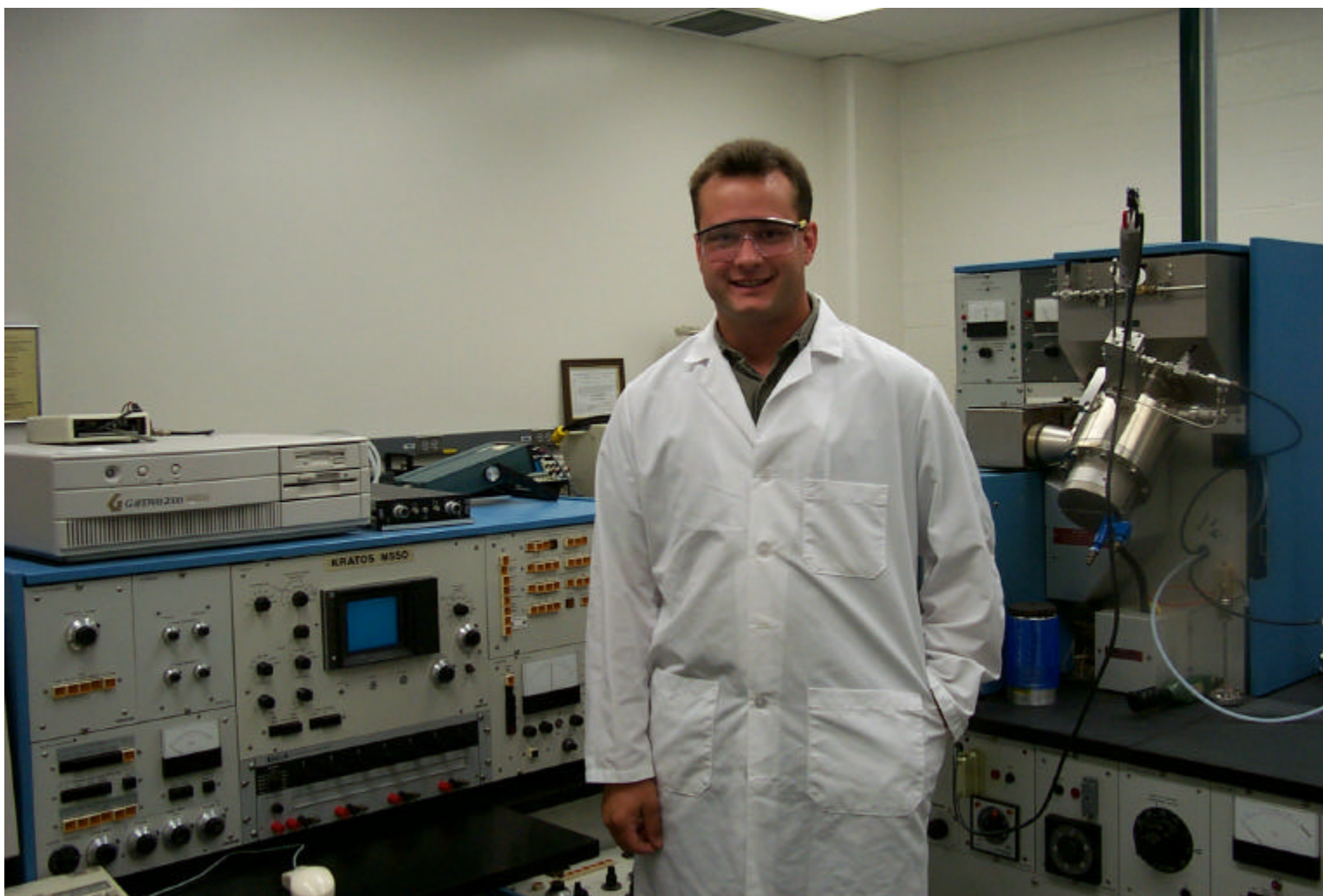


Common Thermal Desorption Steps

- Hewlett Packard (HP) 5890 Series II gas chromatograph equipped with a sequential GERSTEL Thermo-desorption System (TDS 2) and GERSTEL Cooled Injection System (CIS 3)
- An entire 47mm quartz fiber filter was cut into small fragments prior to loading into the TDS 2 desorption tube.
- The sample was heated from 20°C at a rate of 5°/min to 300°C in the TDS 2 with the effluent cold trapped inside the CIS 3 unit at -100°C.



Kratos MS50 High-Resolution Mass Spectrometer



LVHRMS Attributes

- **LVHRMS analysis can serve as a rapid screening tool for particulate matter samples**
 - **gives a comprehensive list of precise masses many of which are molecular ions of all compounds that ionize at 11.5 eV and that are thermally desorbed at temperatures up to 300°C**
 - **In all cases, molecular formulas assigned to a given peak indicates a measured mass within 0.004 amu from the actual molecular mass.**



High-resolution Mass Spectrometry Conditions

- **Low-voltage high-resolution mass spectrometry (LVHRMS) was performed with a Kratos MS-50.**
- **Thermally extracted samples, which were collected on capillary glass tubes within the CIS 3, were introduced to the ion source using a direct insertion probe.**
- **Ionizing voltage was held at 11.5 eV in order to minimize fragmentation and therefore enhance detection of molecular ions.**
- **The mass spectrometer was operated at a resolution of 1 part in 20,000 in order to achieve separation of molecular ions while retaining adequate sensitivity.**

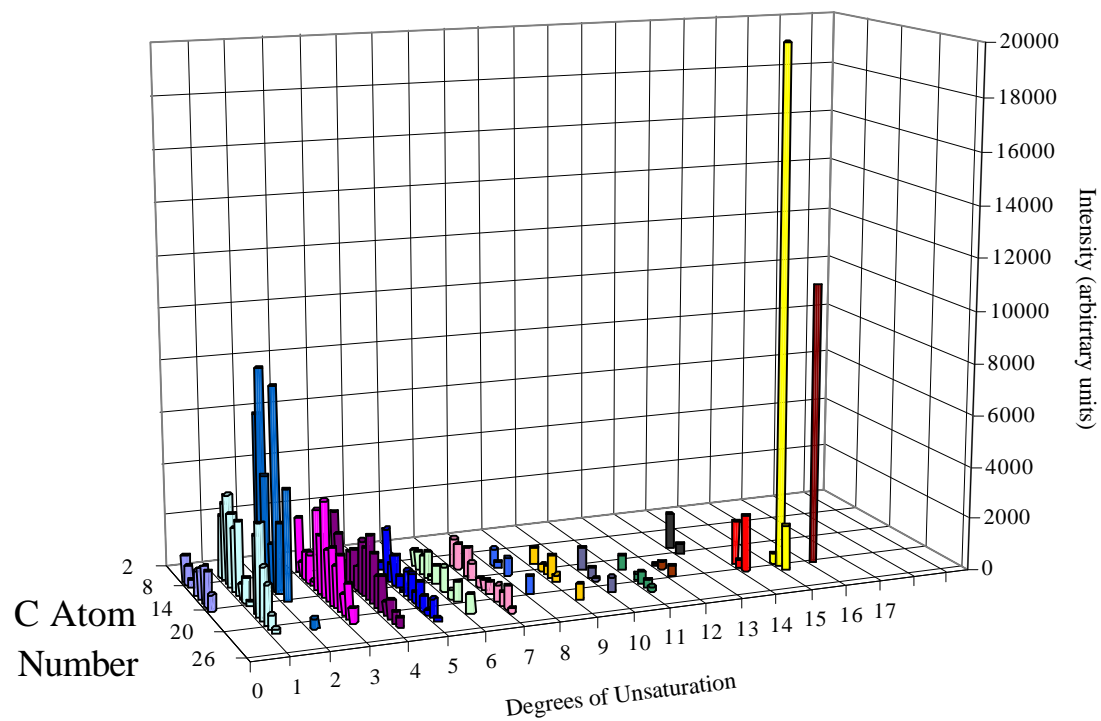


LVHRMS - Results

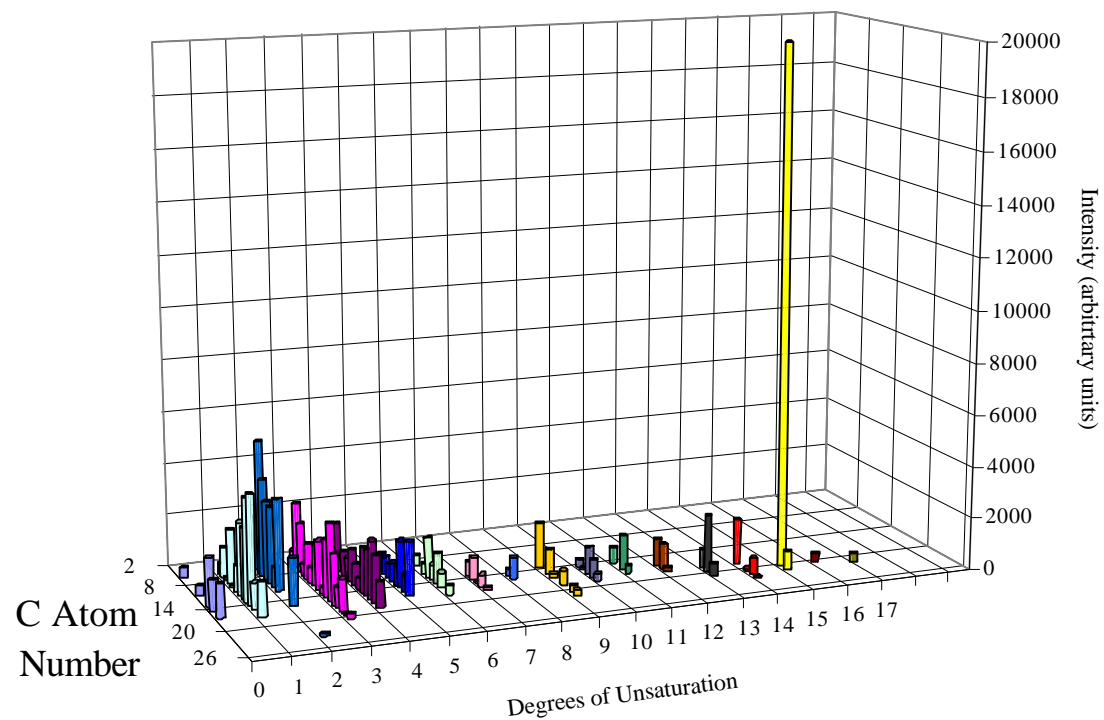
- Four LVHRMS bar graphs showing the relative signal intensity of all of the semi-volatile hydrocarbons present in samples collected over a 24 hour periods from April 30 to May 4 of 2001.
- In each graph the most dominant peak is from mass 252.094, corresponding to a molecular formula of $C_{20}H_{12}$.
 - The dominant peak is from one or more polycyclic aromatic hydrocarbons (PAH) including benzopyrenes, benzofluoranthenes, and perylene.
- Note: largest peak is off-scale in the first three bar graphs in order to show details.



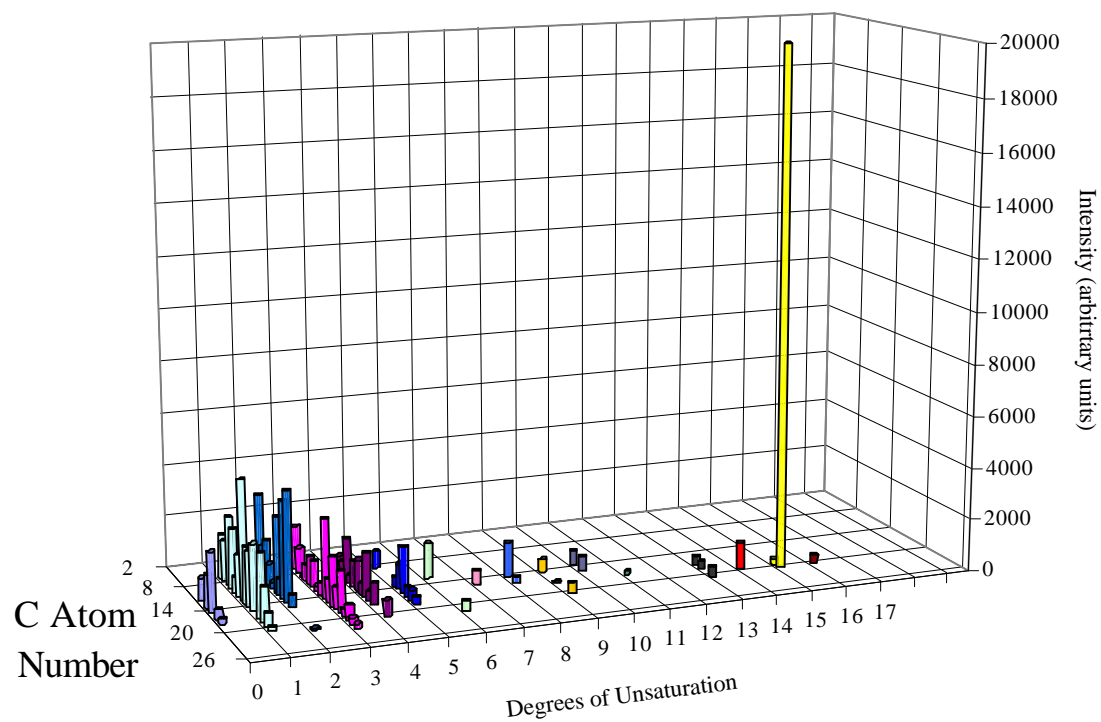
LVHRMS Analysis April 30 – May 1, 2001



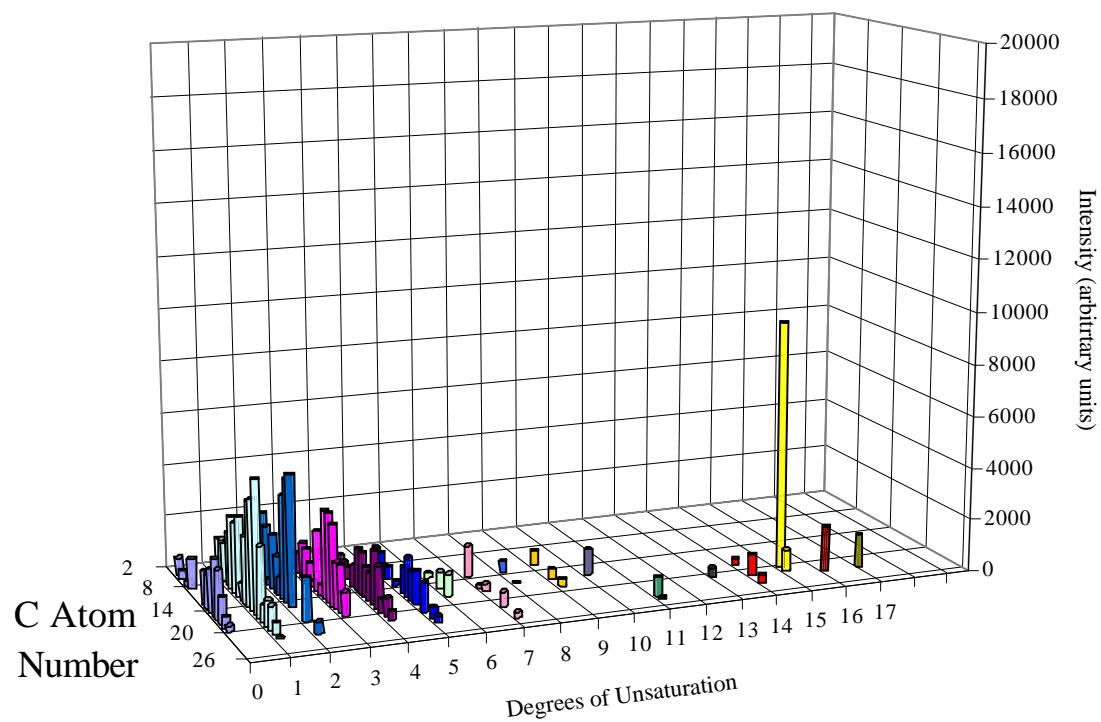
LVHRMS Analysis May 1 – May 2, 2001



LVHRMS Analysis May 2 – May 3, 2001



LVHRMS Analysis May 3 – May 4, 2001



LVHRMS – Results Continued

- **The mass spectra obtained from LVHRMS experiments were compared to a list of known source tracer molecules in order to evaluate the technique as a tool in source apportionment modeling.**
- **The detected masses that were exact matches within (0.004 amu) with known source tracer molecules are contained in the next table along with the absolute intensity of each in arbitrary units.**



Source Tracers

Source Tracers	formula	Calc. mass	signal intensity			
			4/30-5/1	5/1-5/2	5/2-5/3	5/3-5/4
Wood smoke:						
guaiacol	C ₇ H ₈ O ₂	124.05	1557	1679	188	1158
4-methylguaiacol	C ₈ H ₁₀ O ₂	138.06	269	1369		
formylguaiacol	C ₈ H ₈ O ₃	152.04	498		707	417
4-ethylguaiacol	C ₉ H ₁₂ O ₂	152.08	587	2977	936	271
syringol	C ₈ H ₁₀ O ₃	154.06		368	40	
acetylguaiacol	C ₉ H ₁₀ O ₃	166.06	391			1043
4-propylguaiacol	C ₁₀ H ₁₄ O	166.09	85	568	321	
methylsyringol	C ₉ H ₁₂ O ₃	168.07	611	655	163	
propenylsyringol	C ₁₁ H ₁₄ O	194.09		391		
acetylsyringol	C ₁₀ H ₁₂ O	196.07	531		224	
propylsyringol	C ₁₁ H ₁₆ O	196.11			516	
retene	C ₁₈ H ₁₈	234.14	101	296	596	
Auto exhaust:						
cyclopenta(cd)pyrene	C ₁₈ H ₁₀	226.07	1691	1728	1710	235
benzo(b)fluoranthene	C ₂₀ H ₁₂	252.09	29662	21963	21829	9565
benzo(k)fluoranthene	C ₂₀ H ₁₂	252.09	29662	21963	21829	9565
benzo(ghi)perylene	C ₂₂ H ₁₂	276.09				1279
indeno(1,2,3-cd)pyrene	C ₂₂ H ₁₂	276.09				1279
dibenzanthracene	C ₂₂ H ₁₄	278.11				1724



Source Traces - Continued

Source Tracers	formula	Calc. mass	signal intensity			
			4/30-5/1	5/1-5/2	5/2-5/3	5/3-5/4
Auto brakes:						
triethylene glycol-monomethyl	C ₇ H ₁₆ O ₄	164.10	272	315	392	
triethylene glycol-monoethyl	C ₈ H ₁₈ O ₄	178.12	82	197		
Meat cooking:						
nonanal	C ₉ H ₁₈ O	142.13		1062		
decanone	C ₁₀ H ₂₀ O	156.15	116			290
myristic acid	C ₁₄ H ₂₈ O	228.20	353	402		
palmitic acid	C ₁₆ H ₃₂ O	256.24	1634	4893	6949	1048
oleic acid	C ₁₈ H ₃₄ O	282.25	179			
stearic acid	C ₁₈ H ₃₆ O	284.27	5870	1658	1895	8518
Coal Combustion:						
benzo(b)naphtho(2,1-d)thiophene	C ₁₆ H ₁₄ S	238.08			220	
picene	C ₂₂ H ₁₄	278.11				1724
Tobacco smoke:						
nicotine	C ₁₀ H ₁₄ N	162.11	343			
Statistics:						
range of error (mmu)		-3.60 4.0	avg relative error (ppm)		7.8	
avg absolute error (mmu)		1.4	std dev relative error (ppm)		6.5	
std dev absolute error (mmu)		1.0	range of relative error (ppm)		0.0 31.4	



Systematic “Oxygen” Error derived from LVHRMS data

	4/30/01	5/1/01	5/2/01	5/3/01	average
Weight percent C	76.70	74.94	70.75	76.02	74.60
Weight percent H	8.76	8.58	8.29	9.22	8.71
Weight percent N	2.93	2.27	5.56	3.56	3.58
Weight percent O	8.38	11.99	10.87	8.79	10.01
Weight percent S	3.06	2.04	4.30	2.19	2.90
number of compounds	613	523	586	644	591.5
total organic/carbon	1.30	1.33	1.41	1.32	1.34
C+O/carbon	1.11	1.16	1.15	1.12	1.13



GC-MS Analysis Conditions

- Qualitative analysis of the thermally extracted samples was performed using a Hewlett Packard (HP) 5988A gas chromatograph/mass spectrometer system employing 70-eV ionizing voltages and a quadrupole mass filter.
- A bonded-phase fused silica capillary column was used to perform the separation for product identification. The low-polar column was a 30 m X 0.20 mm i.d. fused silica capillary coated with a 0.3 μm film of 5%phenyl substituted cross-linked polydimethylsiloxane (known commercially as SPB®-5).
- Helium was used as the carrier gas with the head pressure adjusted for each column to obtain an average linear velocity of ~35 cm/s at the initial analysis temperature.

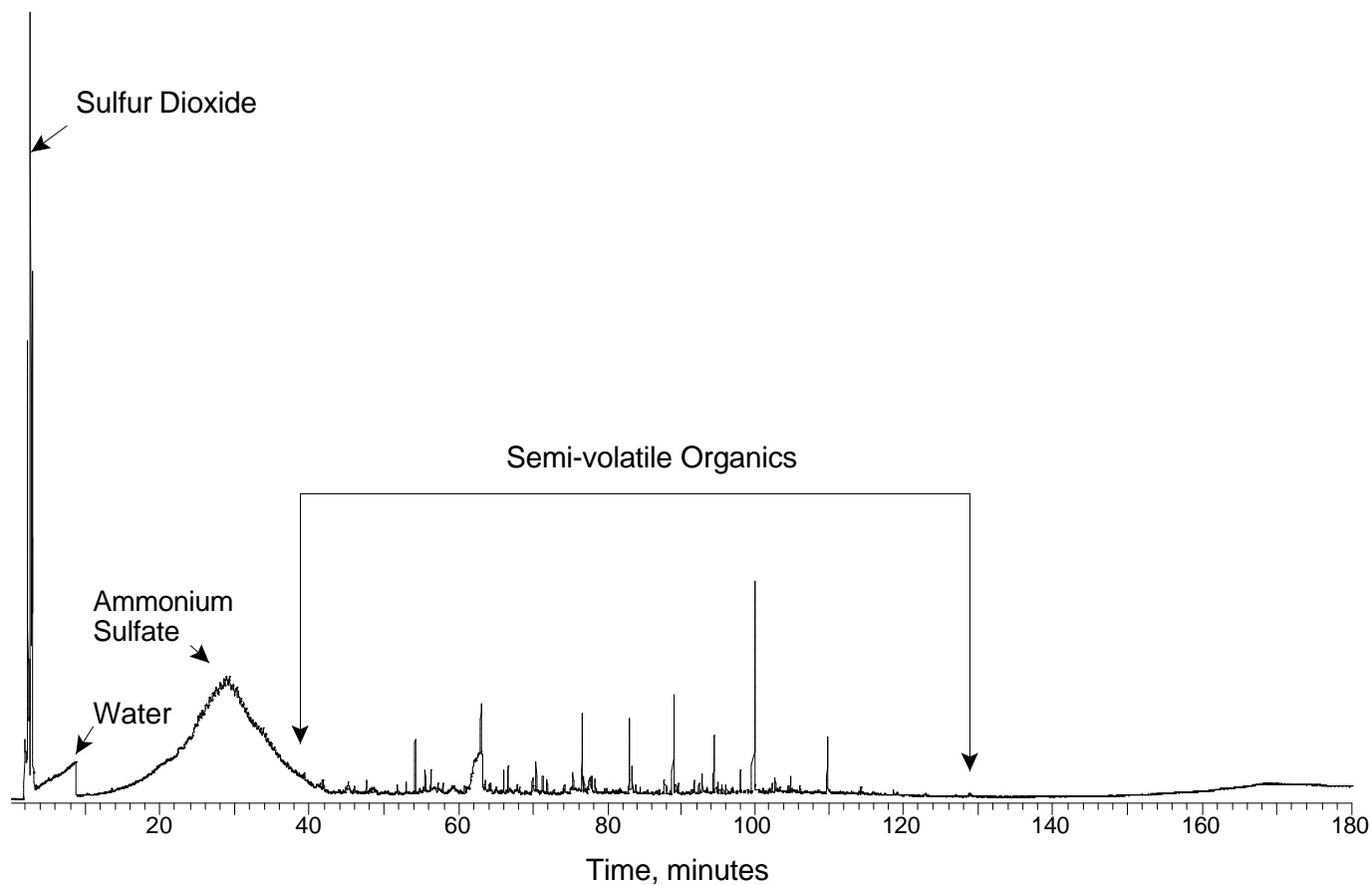


GC-MS Analysis Conditions Continued

- The splitless injector was equipped with a backpressure regulator capable of controlling the column head pressure to 170 kPa.
- A second rapid thermal desorption, -100 to 300°C at 12°C/min with a 30s hold, was performed with the CIS 3 in splitless mode to introduce the semi-volatile components onto the gas chromatographic column.
- The column was then temperature programmed from -10°C for 2min to 320°C at 2°C/min, with a 15min hold, while the mass spectrometer was scanned from 10 to 400 amu every 2.4s.

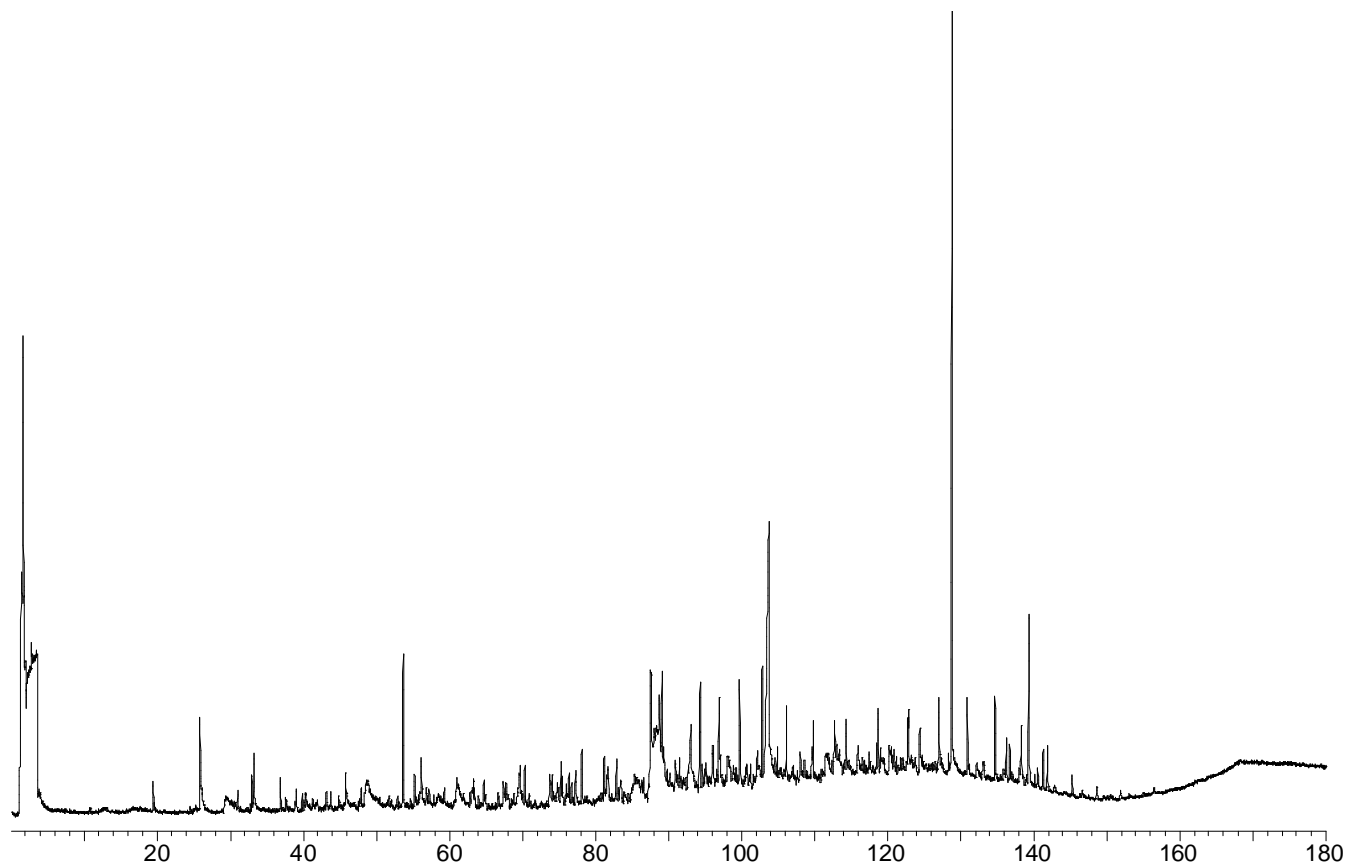


GC-MS Preliminary Results – Total Ion Chromatogram (TIC)

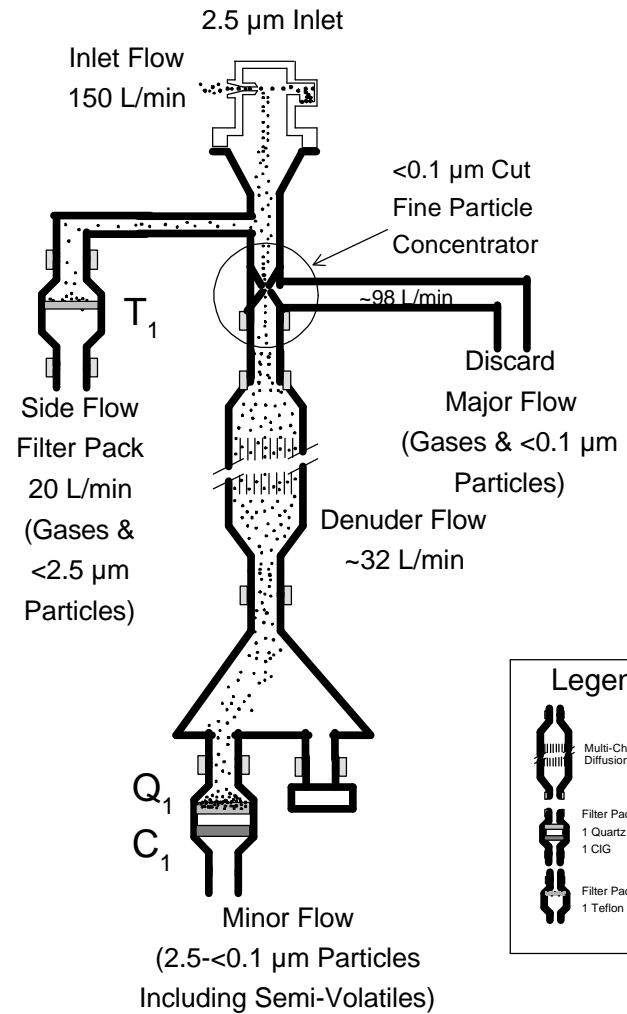


GC-MS TIC Sample Blank?

Full Scale = ~2,000,000

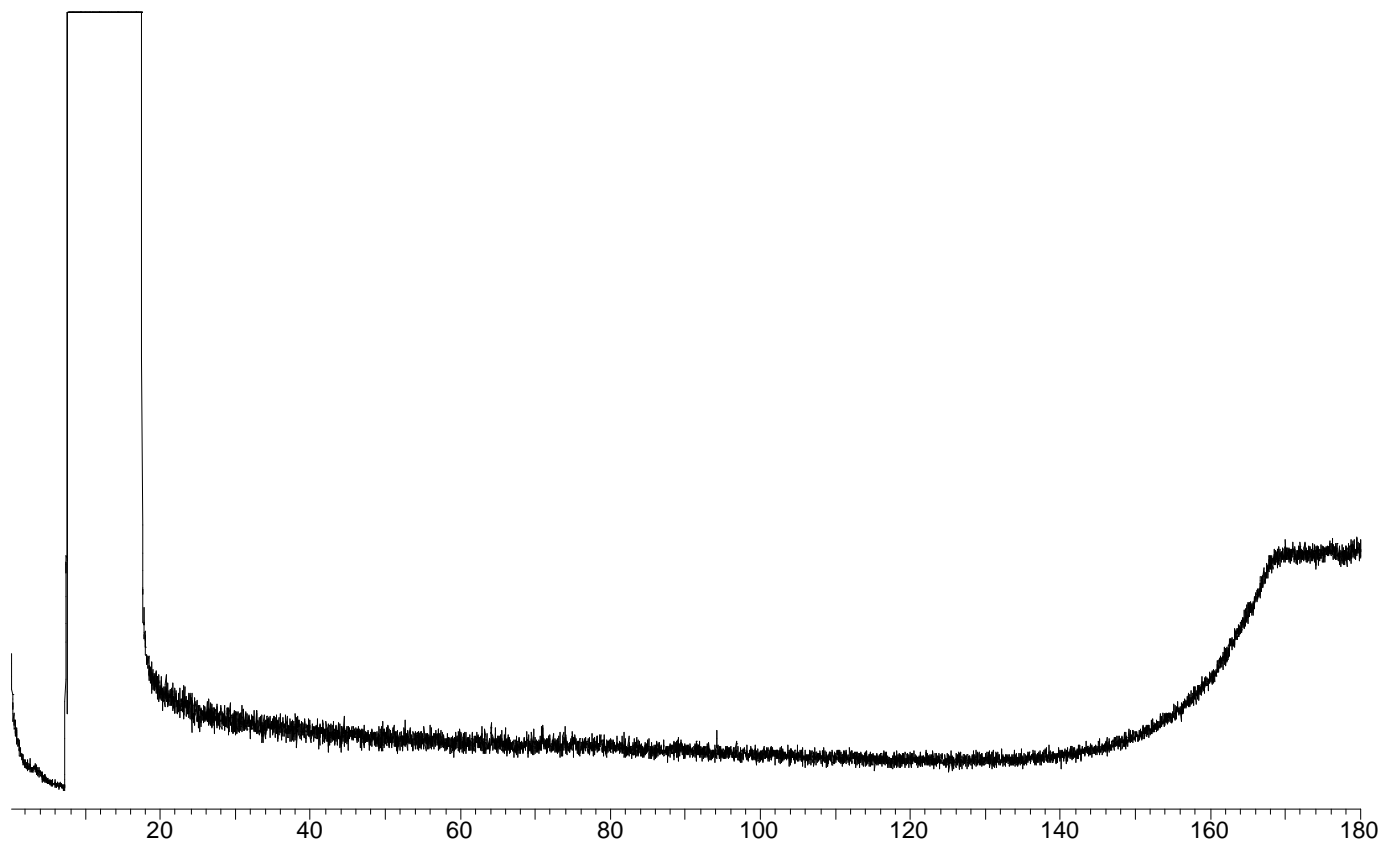


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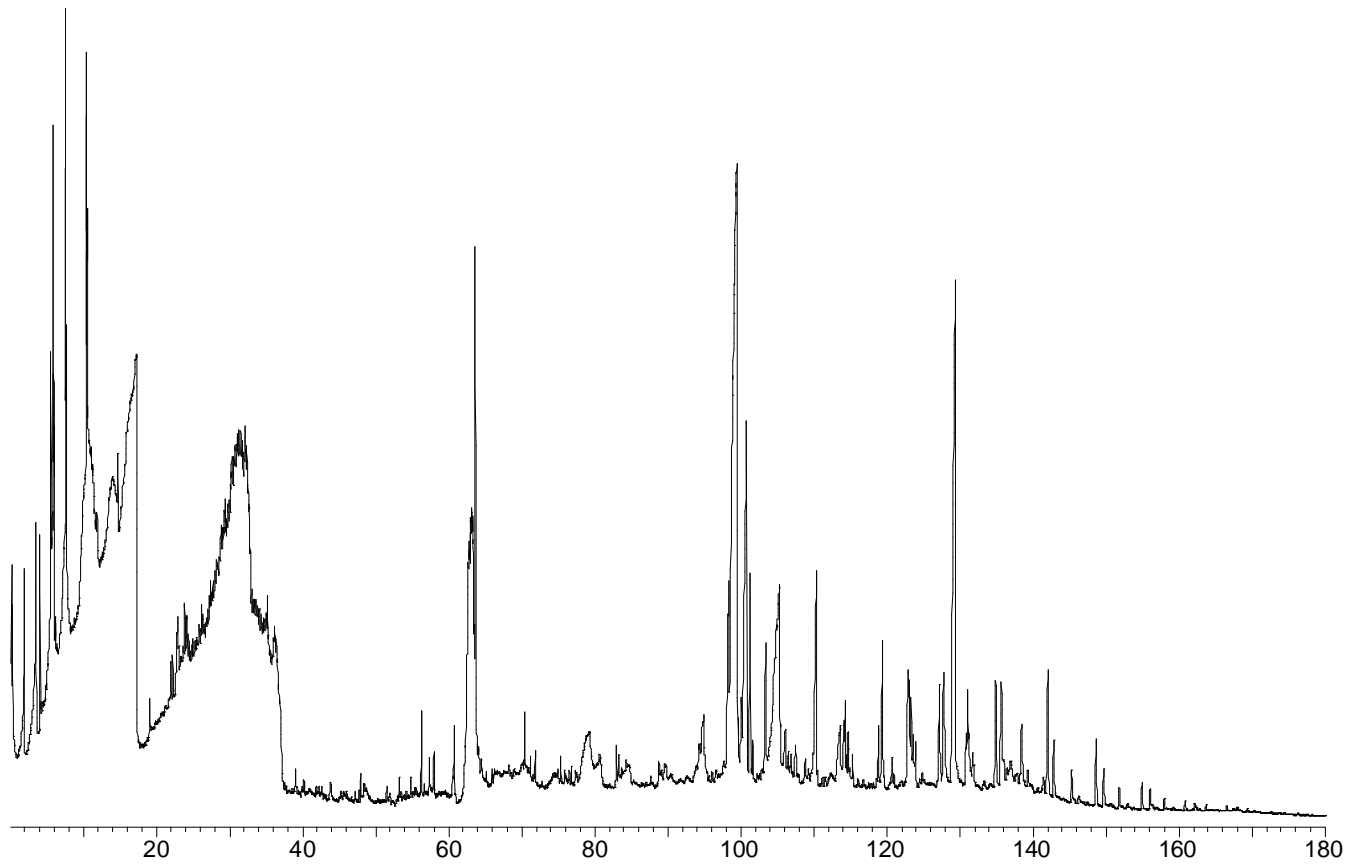


GC-MS TIC Second “Sampled” Quartz Filter

Full Scale = 100,000



GC-MS TIC Top Sampled Filter



Conclusions

- Thermal desorption of 47mm filters provides sufficient semi-volatile material to perform LVHRMS and GC-MS analysis.
- These preliminary results indicate that LVHRMS of thermally desorbed ambient samples can be a fast and effective tool for source characterization of PM_{2.5}.



Future Work

- **Apply LVHRMS and GC-MS techniques to a much larger set of samples in order to determine source and transport properties of particle associated semi-volatile organics.**
- **GC-MS analysis with 100m columns at lower GC oven heating rates to improve peak resolution.**
- **Many of the peaks tentatively identified as semi-volatile organics will be further identified based on both mass spectra and retention index comparison to authentic standards.**



Acknowledgments

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