turning knowledge into practice

Ion Analysis for the IMPROVE Program
Wood Smoke Investigation Update

IMPROVE Steering Committee Meeting
Wind Cave NP

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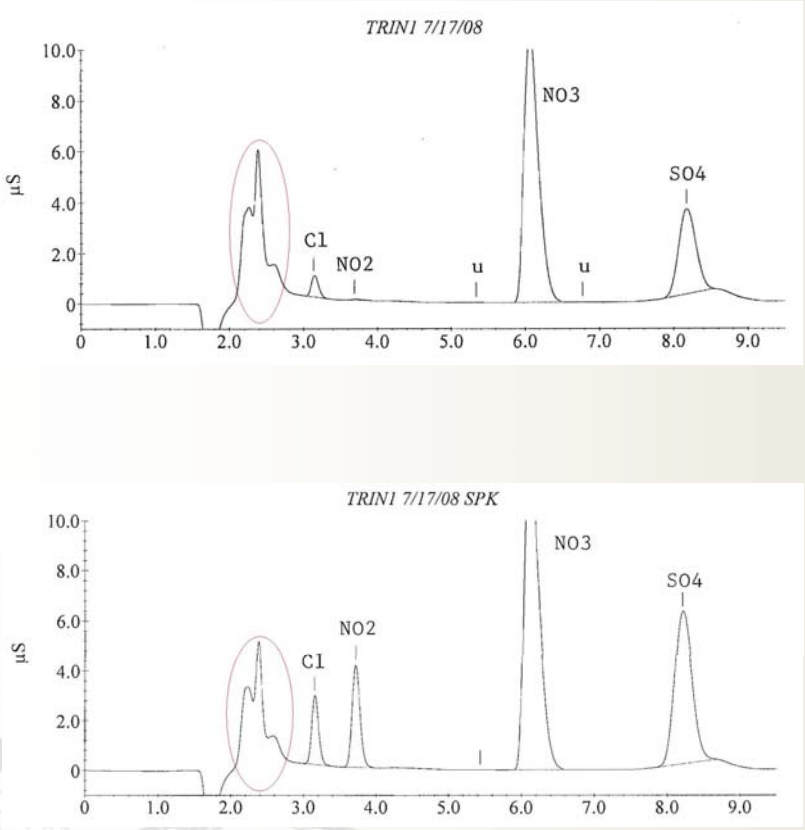
David Hardison

September 22, 2009

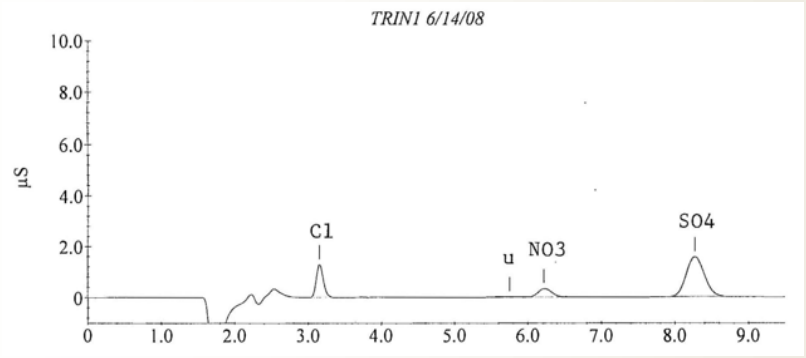
Examination of TRIN Spiked Extract Chromatograms

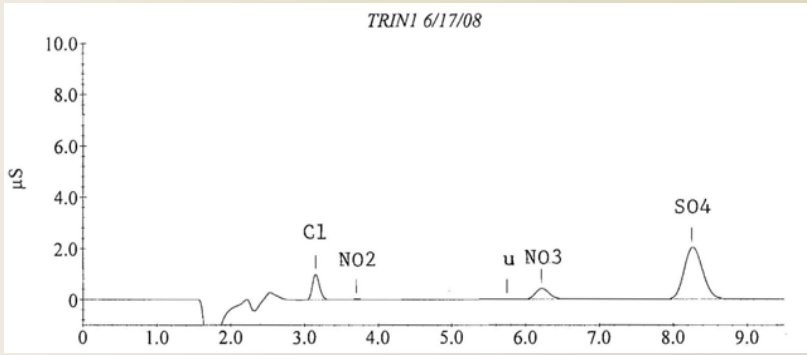


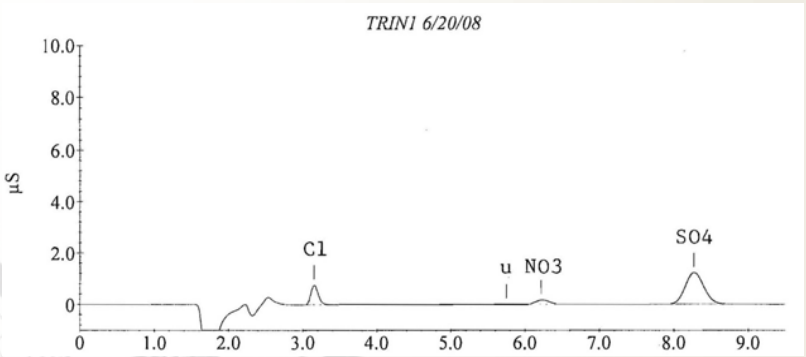
- Unknown peaks are observed in the general area of fluoride, chlorite, bromate, and organic acids (formic, acetic, etc.)
- Small peak is observed after sulfate peak that is unresolved from sulfate and can interfere with sulfate quantitation
- Peaks possibly include an oxidizing agent, since some of the nitrite in the spiked extract appears to have been converted to nitrate

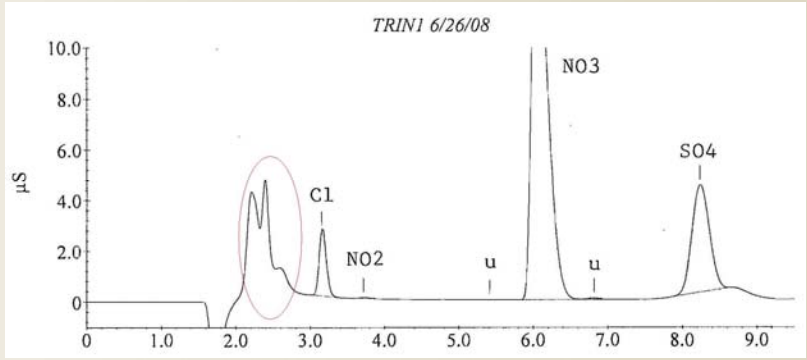
Examination of TRIN1 Chromatograms 6/14/08 thru 6/26/08:

Unknown peaks at RT ~2.2 – 2.6 minutes observed on 6/26/08



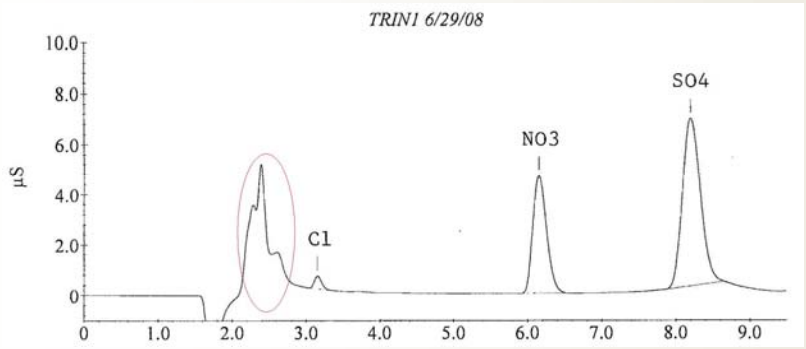


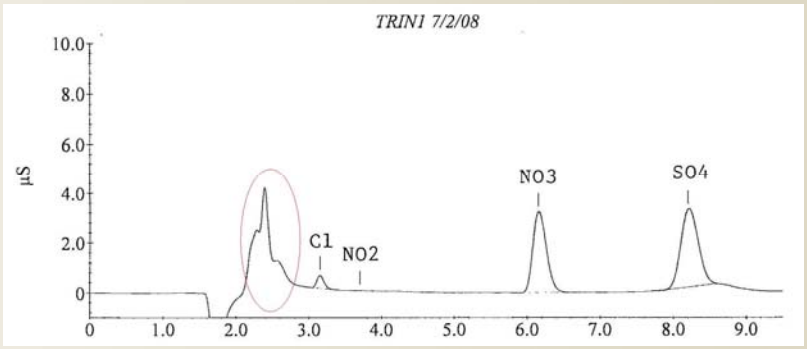


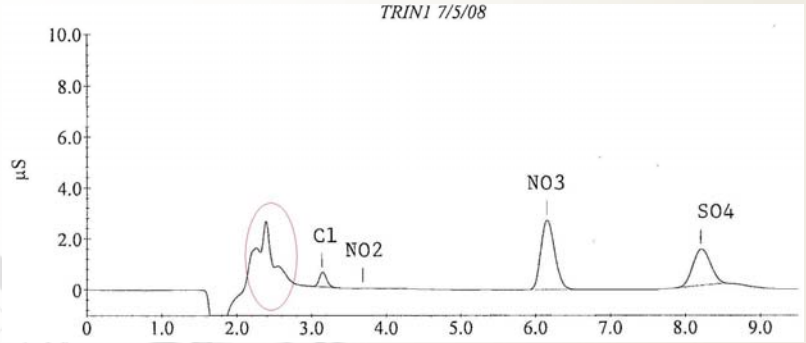


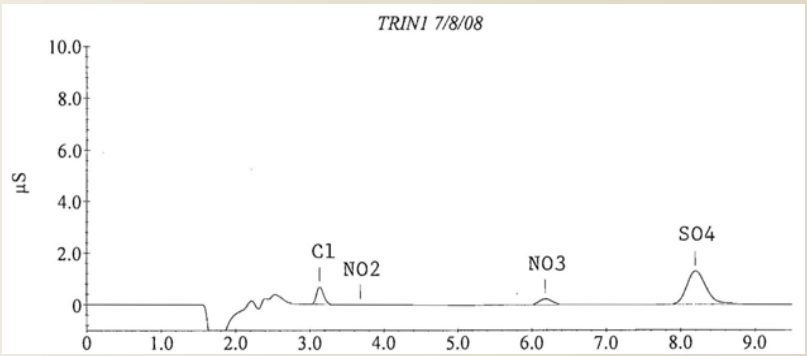
Examination of TRIN1 Chromatograms 6/29/08 thru 7/8/08:

Unknown peaks diminish during this period



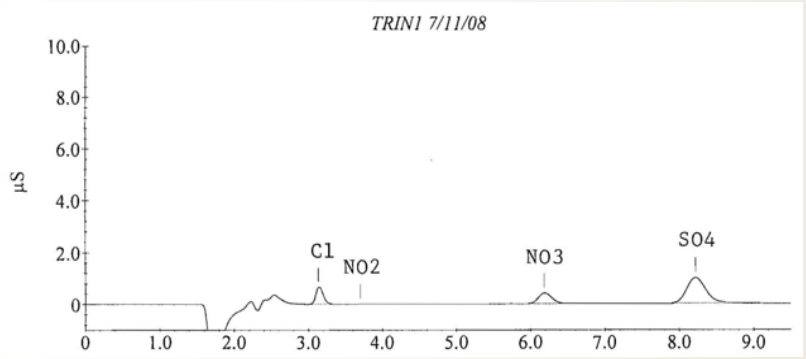


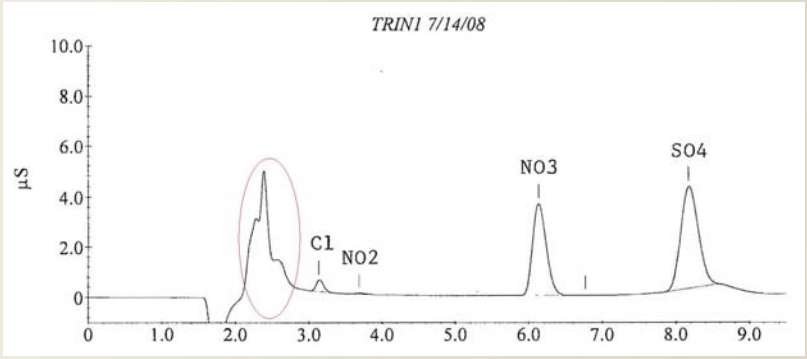


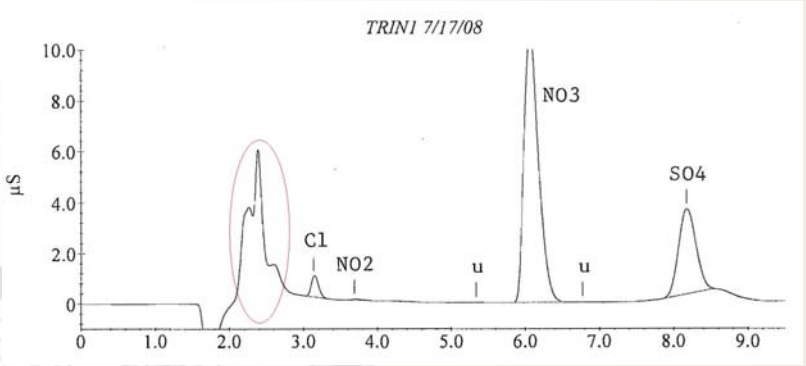


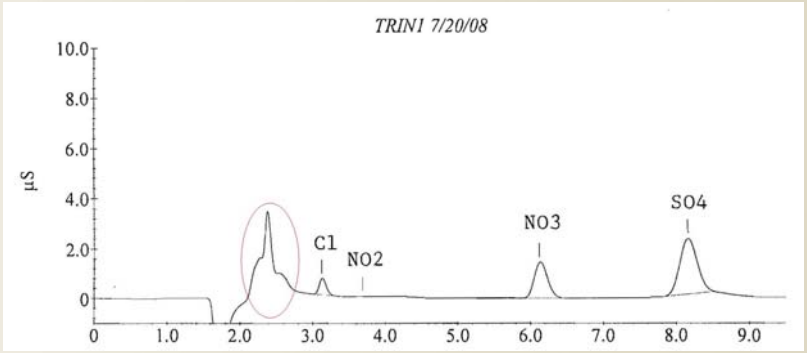
Examination of TRIN1 Chromatograms 7/11/08 thru 7/20/08:

Unknown peaks present 7/14/08, 7/17/08 and 7/20/08



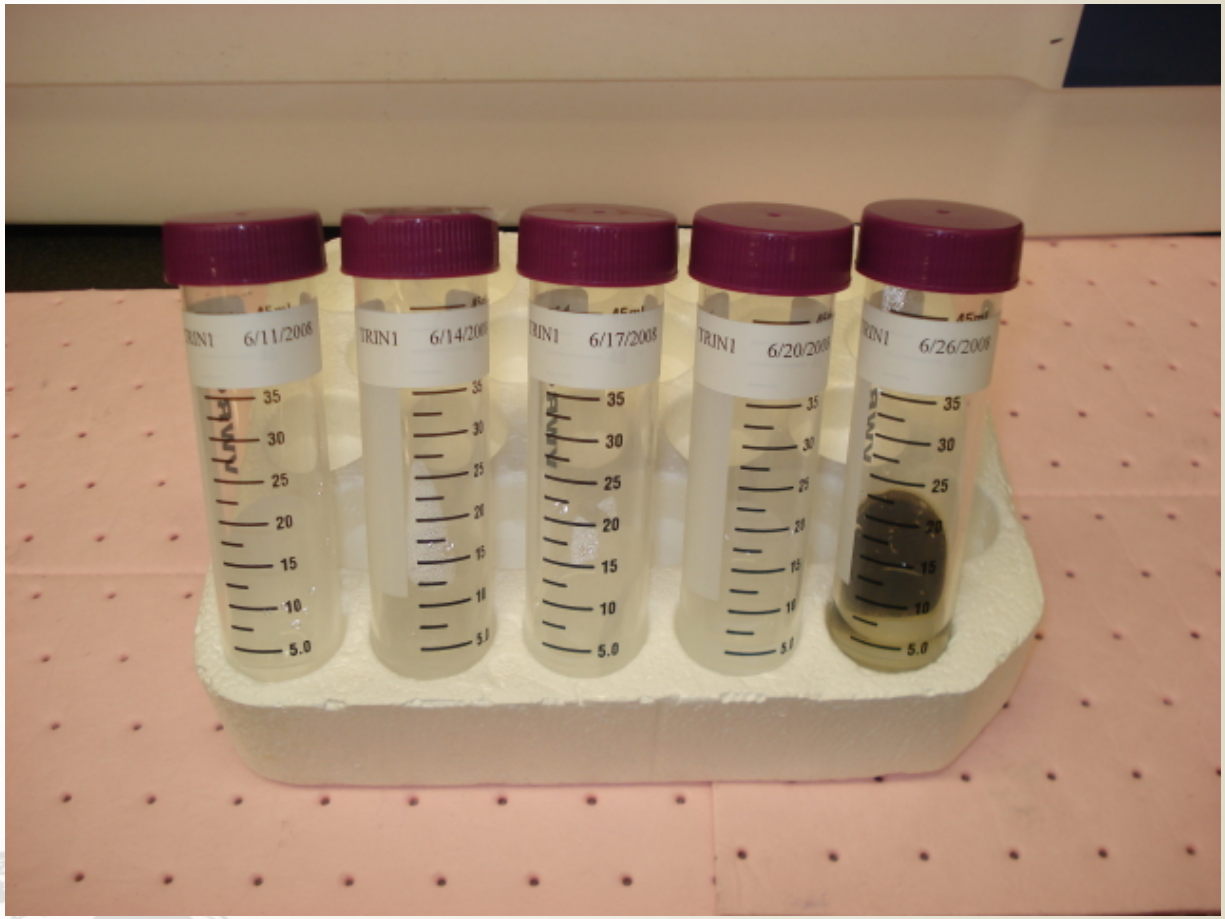






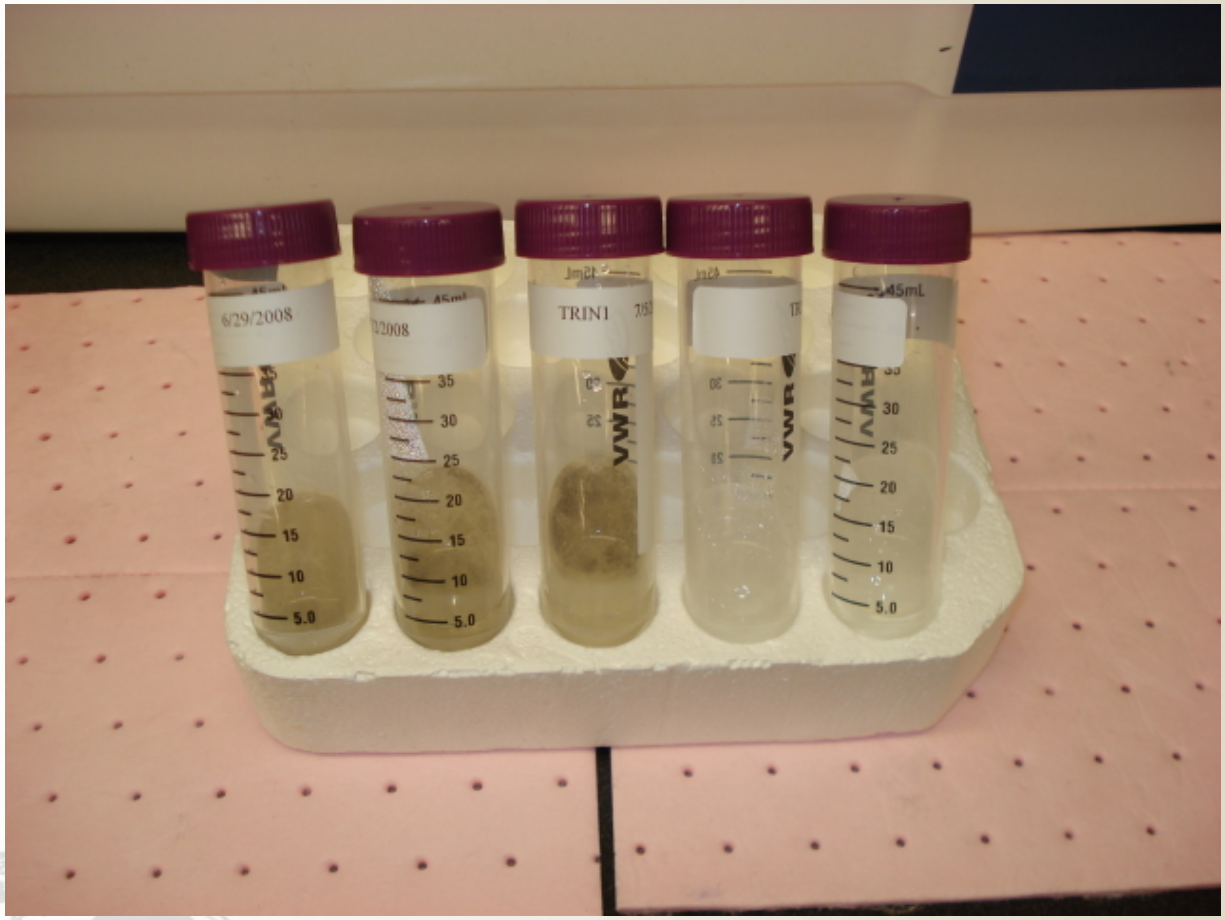
TRIN Extracts

6/11/08, 6/14/08, 6/17/08, 6/20/08, 6/26/08



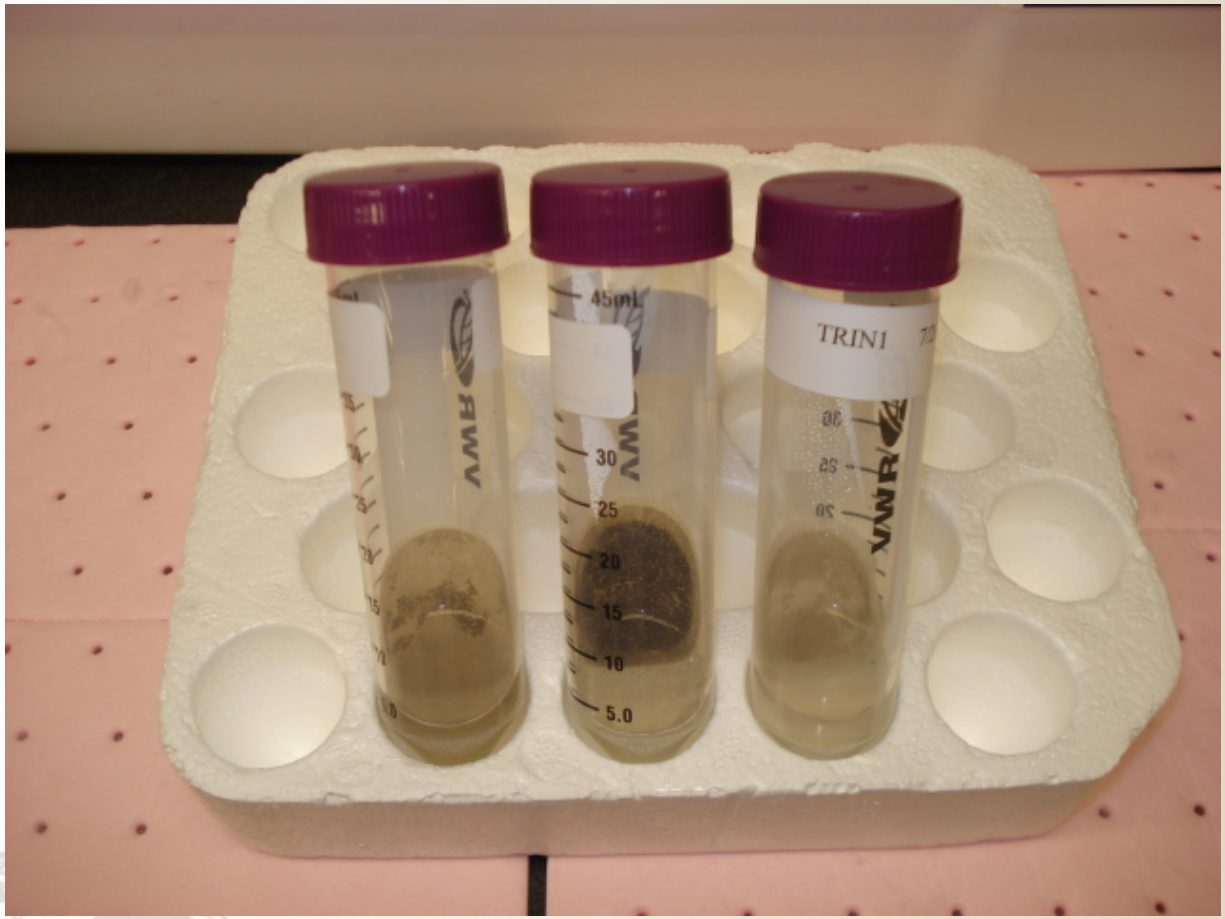
TRIN Extracts

6/29/08, 7/2/08, 7/5/08, 7/8/08, 7/11/08



TRIN Extracts

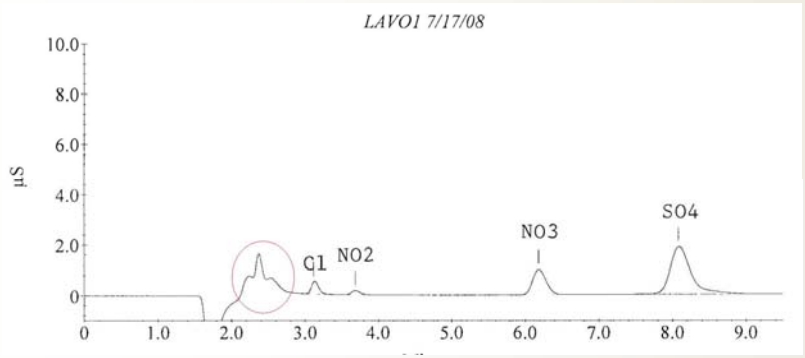
7/14/08, 7/17/08, 7/20/08

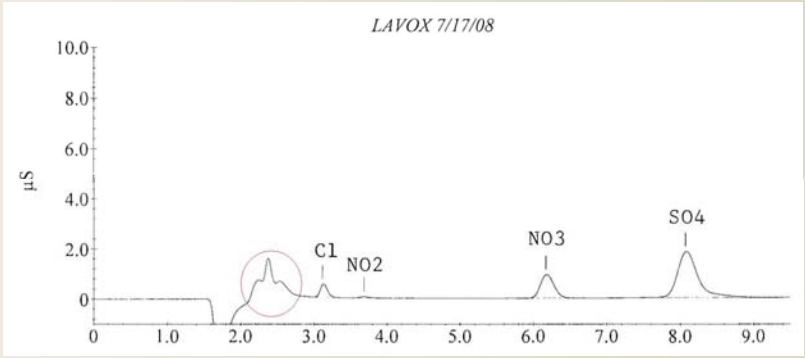


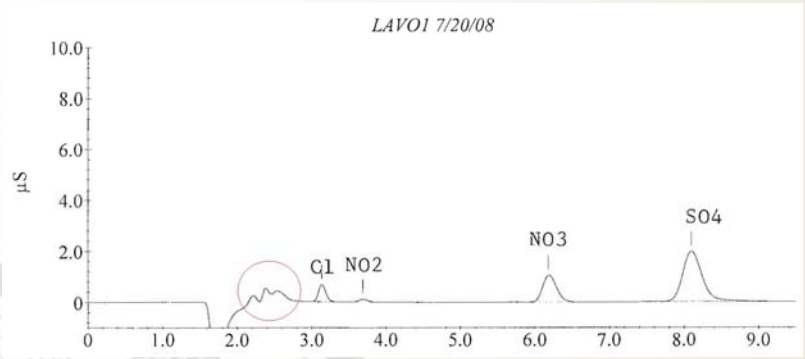
Observations About Unknown Peaks in TRIN1 Samples

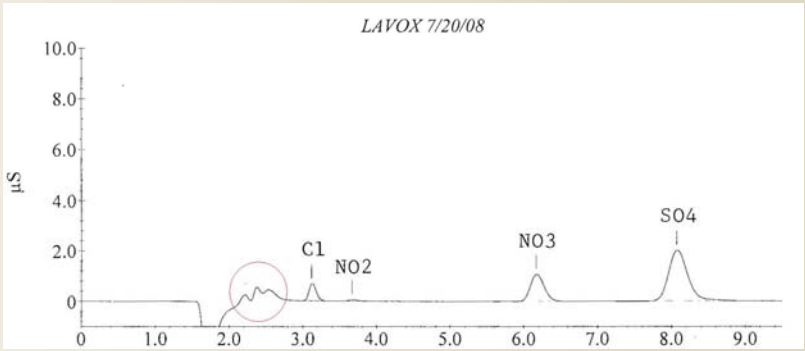
- Unknown peaks are not observed in some samples
- Unknown peaks are in the general area of fluoride, chlorite, bromate, and inorganic acids (formic, acetic, etc.)
- Unknown peaks are of different heights and ratios over time
- Unknown peak sizes generally correlate with filter color/loading (larger peaks for darker color); possible woodsmoke markers?

LAVO Collocated Samples 7/17/08 and 7/20/08

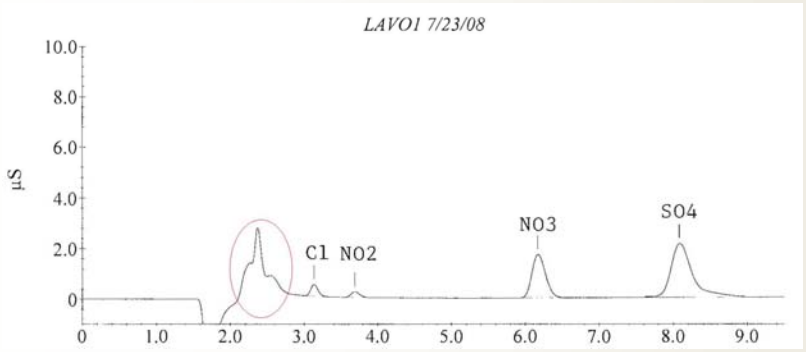


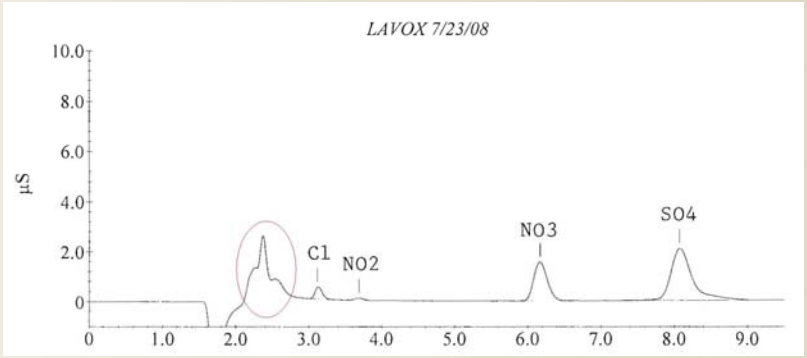


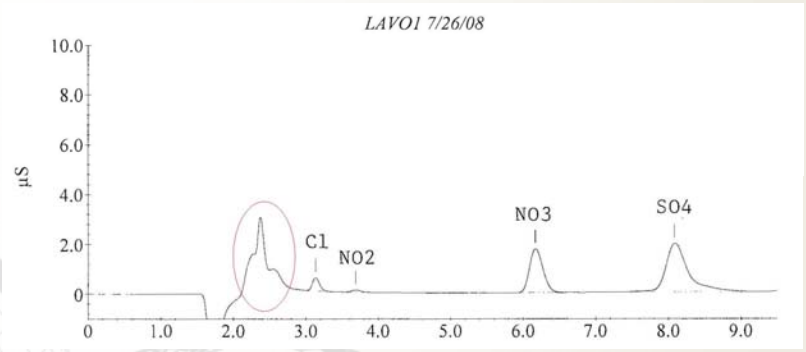


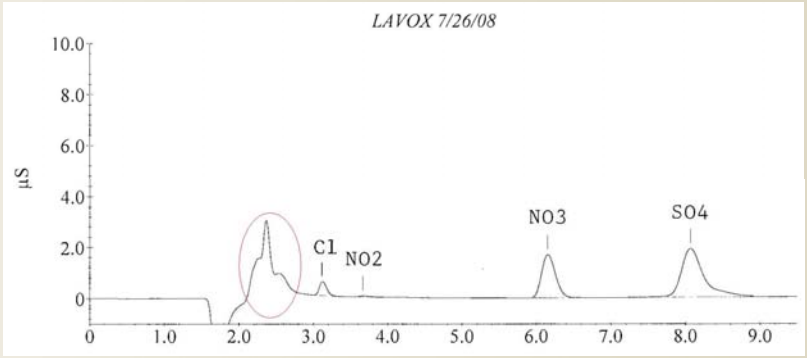


LAVO Collocated Samples 7/23/08 and 7/26/08





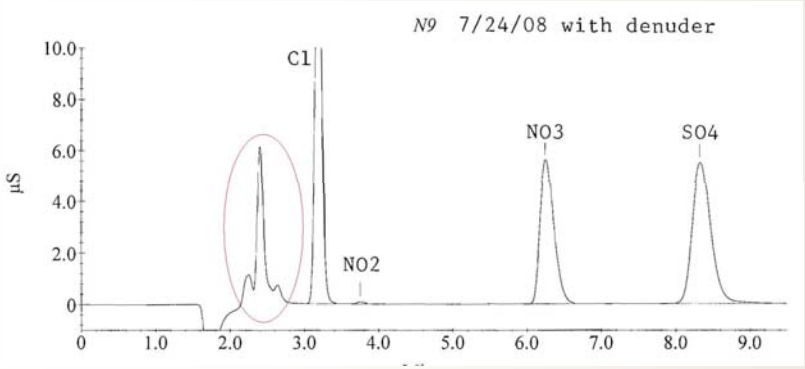


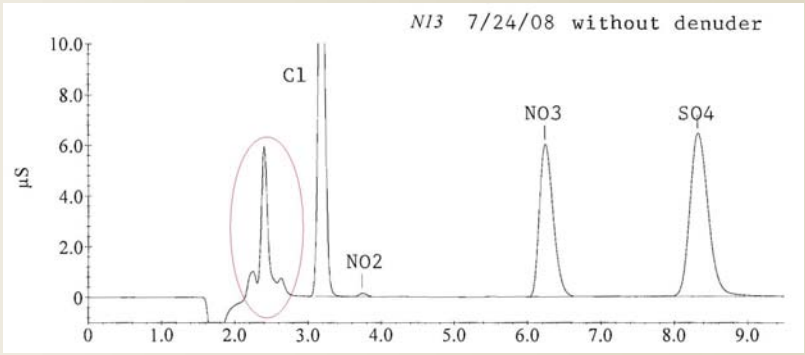


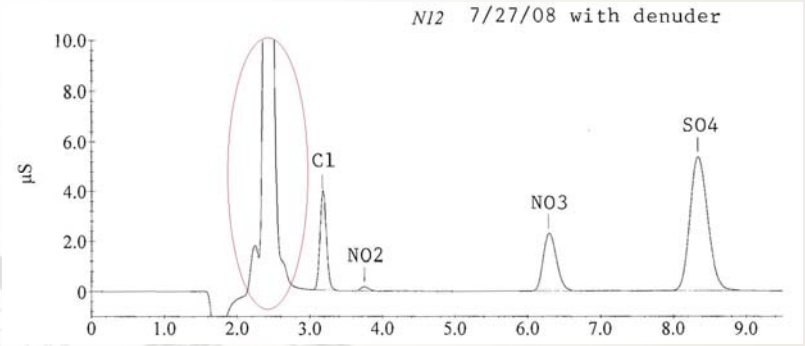
Observations About Unknown Peaks in LAVO Samples

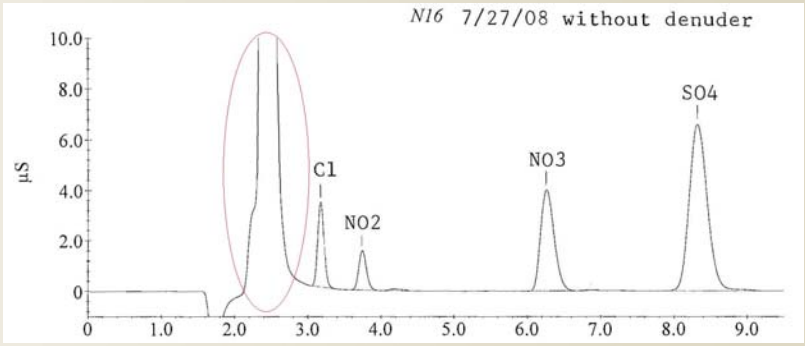
- Unknown peaks in the LAVO samples show the same 3 components as in the TRIN samples
- Unknown peaks are the same shape and size in the collocated samples (LAVO1 and LAVOX) pairs for each sampling day, indicating that they are from atmospheric components (not from sample contamination)
- TRIN and LAVO sites both are in the same general area (Northern California)

QA Samples for UC-Davis









Questions to Answer

- What are the compounds that give rise to the unknown peaks in the ion chromatograms?
- Is one (or more or a combination of) the compounds a potential wood smoke marker?
- If so, does the abundance of the compound(s) correlate with the abundance of levoglucosan?
- Could one of the peaks be methanesulfonate?

RTI IR&D Proposal

- Identify and quantify compounds giving rise to unknown peaks in ion chromatograms of nylon filter extracts (IC; LC/MS)
- Develop capability to analyze for levoglucosan in nylon filter extracts
- Develop capability to analyze for methane sulfonate in nylon filter extracts

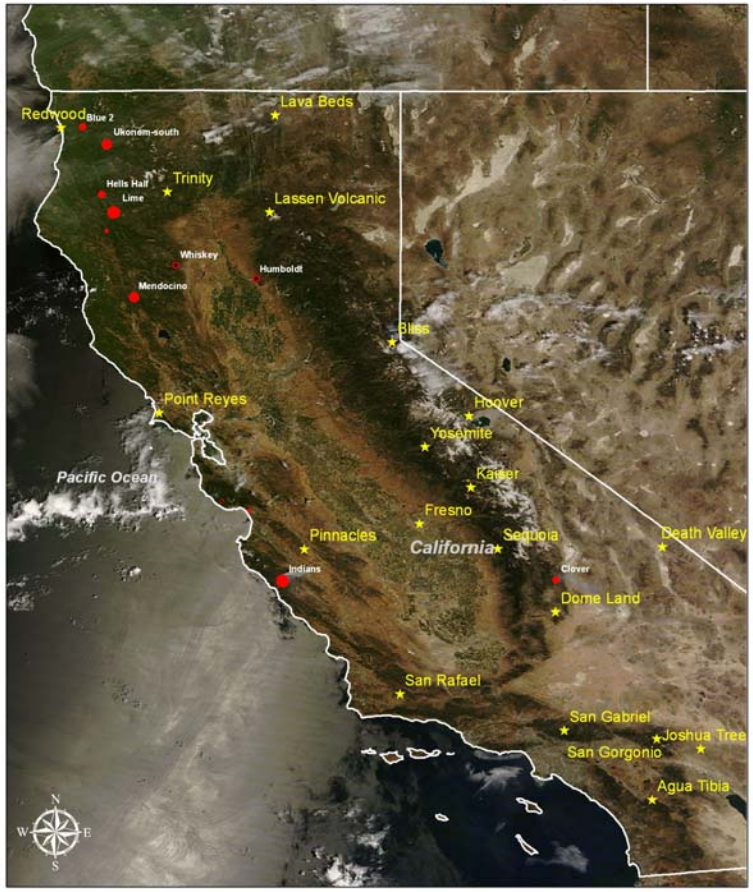
Sites/Dates Impacted by Smoke as Determined by UC-Davis

		Sample Date												
SITE		06/20/08	06/23/08	06/26/08	06/29/08	07/02/08	07/05/08	07/08/08	07/11/08	07/14/08	07/17/08	07/20/08	07/23/08	07/26/08
BLIS1	Impacted by smoke? UCD		Yes	Yes					Yes	Yes		Yes	Yes	Yes
	PM mass, ug/m3	2.85	12.93	44.20	-999.00	-999.00	-999.00	-999.00	79.89	23.24	4.60	8.41	8.48	17.91
DEVA1	Impacted by smoke? UCD		Yes	Yes		Yes	Yes		Yes		Yes			
	PM mass, ug/m3	4.30	10.01	24.95	3.45	19.65	12.20	6.15	17.32	5.84	8.78	5.50	5.26	7.77
HOOV1	Impacted by smoke? UCD		Yes	Yes	Yes	Yes			Yes	Yes				Yes
	PM mass, ug/m3	2.28	25.89	30.33	8.50	11.21	3.00	6.33	53.84	9.63	3.00	6.43	5.07	11.78
PORE1	Impacted by smoke? UCD		Yes	Yes				Yes					Yes	
	PM mass, ug/m3	6.31	11.56	14.62	4.15	1.23	2.41	20.17	7.68	5.72	6.48	4.20	12.44	5.27
SEQU1	Impacted by smoke? UCD	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
	PM mass, ug/m3	8.65	16.54	53.02	25.42	17.68	11.34	25.21	28.66	14.52	16.12	13.03	12.49	18.10
TRIN1	Impacted by smoke? UCD				Yes	Yes		Yes	Yes	Yes		Yes		
	PM mass, ug/m3	2.35	-999.00	-999.00	126.96	116.66	-999.00	8.13	10.03	114.56	-999.00	71.78	-999.00	-999.00
YOSE1	Impacted by smoke? UCD		Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes		Yes	Yes	
	PM mass, ug/m3	4.00	28.75	57.57	25.04	12.59	8.35	14.57	47.03	11.00	5.81	9.16	8.11	-999.00

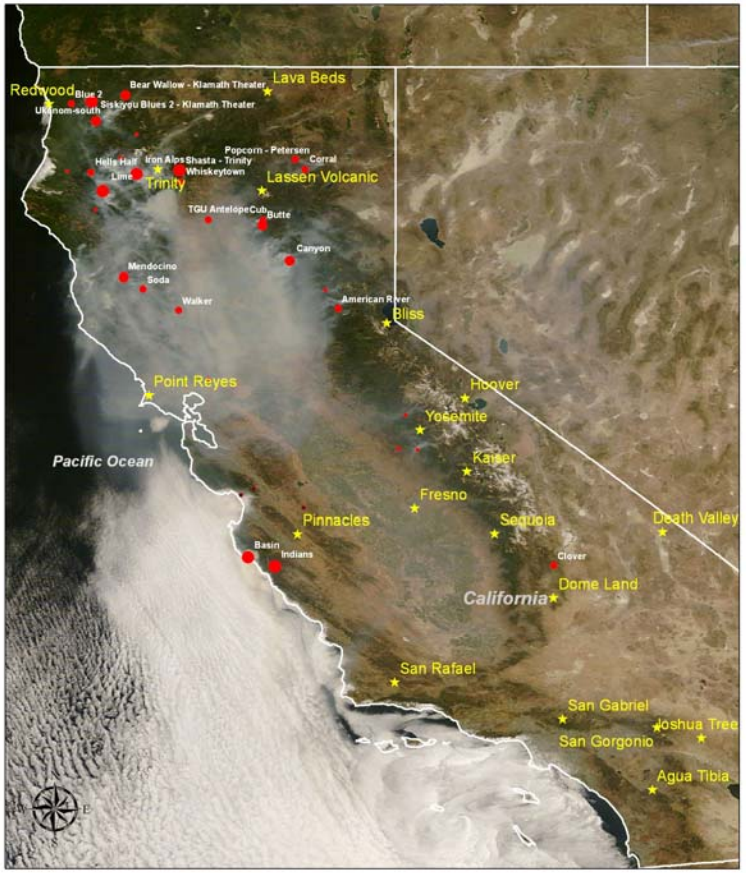
UCD: A site is considered to be impacted by smoke if the PM2.5 concentration is above 8 ug/m3 and/or if the site is shown to be smoky on the satellite map. The average PM2.5 concentration calculated with a standard flow of 22.8 liters per minute is 7.3 ug/m3 for the the sites in California in the Spring quarter of 2008.

Satellite Maps: Clear Vs. Smoky Day

California Wildfires – Summer 2008
June 19, 11:00 p.m. – June 20, 11:00 p.m.



California Wildfires – Summer 2008
June 26
6:00 a.m. – 6:00 p.m.

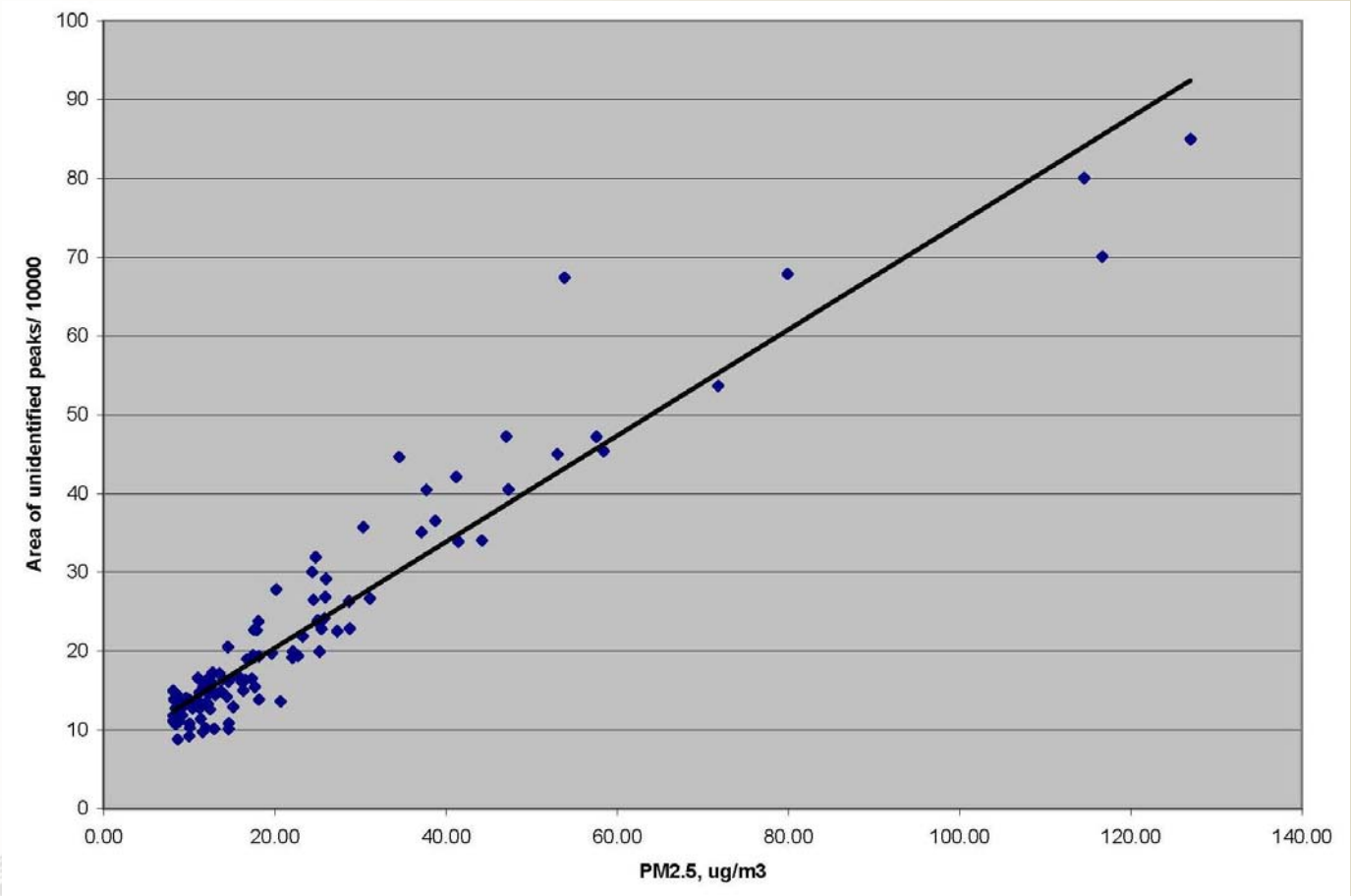


SITE		Sample Date												
		06/20/08	06/23/08	06/26/08	06/29/08	07/02/08	07/05/08	07/08/08	07/11/08	07/14/08	07/17/08	07/20/08	07/23/08	07/26/08
BLIS1	Impacted by smoke? UCD		Yes	Yes					Yes	Yes		Yes	Yes	Yes
	PM mass, ug/m3	2.85	12.93	44.20	-999.00	-999.00	-999.00	-999.00	79.89	23.24	4.60	8.41	8.48	17.91
	Impacted by smoke? RTI		*Yes*	*Yes*					*Yes*	*Yes*	*?*	*Yes*	*Yes*	*Yes*
	Early peaks, area		101463	340423					678679	218991	88091	127721	145712	226406
DEVA1	Impacted by smoke? UCD		Yes	Yes		Yes	Yes		Yes		Yes			
	PM mass, ug/m3	4.30	10.01	24.95	3.45	19.65	12.20	6.15	17.32	5.84	8.78	5.50	5.26	7.77
	Impacted by smoke? RTI	*?*	*Yes*	*Yes*	*?*	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*
	Early peaks, area	25515	92136	236454	48896	197065	132940	97585	165122	89775	110636	76838	90233	98678
HOOV1	Impacted by smoke? UCD		Yes	Yes	Yes	Yes			Yes	Yes				Yes
	PM mass, ug/m3	2.28	25.89	30.33	8.50	11.21	3.00	6.33	53.84	9.63	3.00	6.43	5.07	11.78
	Impacted by smoke? RTI		*Yes*	*Yes*	*Yes*	*Yes*		*?*	*Yes*	*Yes*				*Yes*
	Early peaks, area	63758	268795	357376	128206	147268	76349	122022	673724	140850	67157	74072	89548	133244
PORE1	Impacted by smoke? UCD		Yes	Yes				Yes					Yes	
	PM mass, ug/m3	6.31	11.56	14.62	4.15	1.23	2.41	20.17	7.68	5.72	6.48	4.20	12.44	5.27
	Impacted by smoke? RTI	*Yes*	*Yes*	*Yes*	*Yes*			*Yes*	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*
	Early peaks, area	59212	97314	108569	83065	61991	70438	278004	156769	122333	150802	133908	126062	71545
SEQU1	Impacted by smoke? UCD	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
	PM mass, ug/m3	8.65	16.54	53.02	25.42	17.68	11.34	25.21	28.66	14.52	16.12	13.03	12.49	18.10
	Impacted by smoke? RTI	*?*	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*
	Early peaks, area	87726	163335	449847	228337	154370	114088	199530	263369	141088	161487	144831	161379	237899
TRIN1	Impacted by smoke? UCD				Yes	Yes		Yes	Yes	Yes		Yes		
	PM mass, ug/m3	2.35	-999.00	-999.00	126.96	116.66	-999.00	8.13	10.03	114.56	-999.00	71.78	-999.00	-999.00
	Impacted by smoke? RTI			*Yes*	*Yes*	*Yes*	*Yes*	*?*	*?*	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*
	Early peaks, area	45771		756625	849666	700682	473605	111345	107878	800199	941085	536448	611568	541185
YOSE1	Impacted by smoke? UCD		Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes		Yes	Yes	
	PM mass, ug/m3	4.00	28.75	57.57	25.04	12.59	8.35	14.57	47.03	11.00	5.81	9.16	8.11	-999.00
	Impacted by smoke? RTI		*Yes*	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*	*?*	*Yes*	*Yes*	
	Early peaks, area	74071	228692	471996	239073	151625	107606	161362	472461	137039	99272	118403	149964	

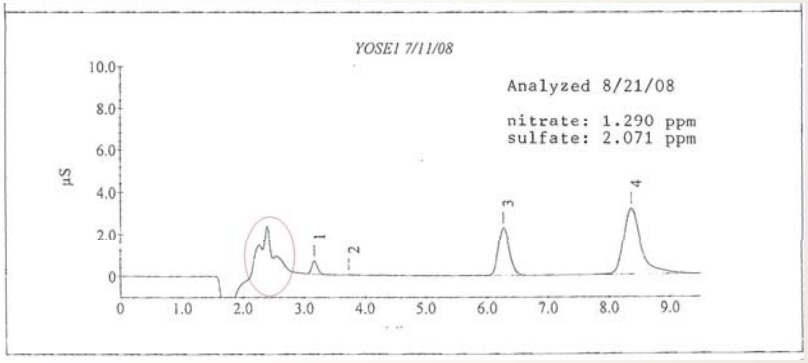
UCD: A site is considered to be impacted by smoke if the PM2.5 concentration is above 8 ug/m3 and/or if the site is shown to be smoky on the satellite map. The average PM2.5 concentration calculated with a standard flow of 22.8 liters per minute is 7.3 ug/m3 for the the sites in California in the Spring quarter of 2008.

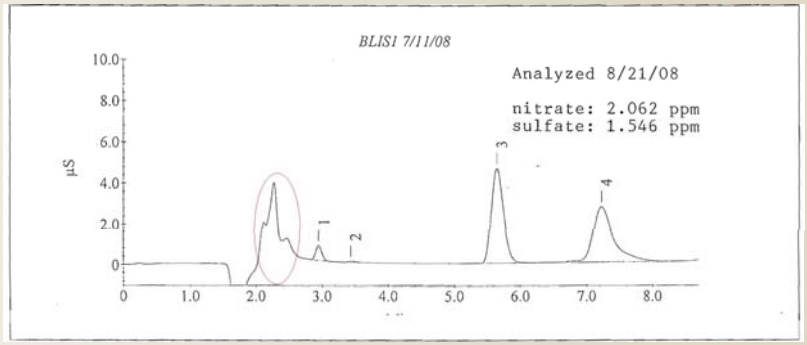
RTI: A site is considered to be impacted by smoke if the ion chromatogram shows two or more peaks between the water dip and the chloride peak.

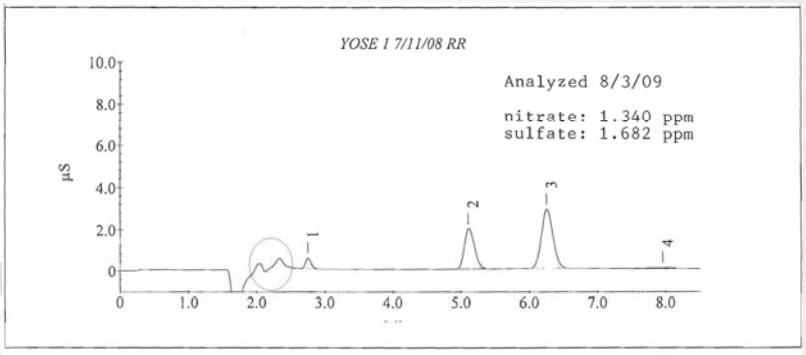
Area of Unknown Peaks vs. PM2.5 Concentration (r = 0.95)

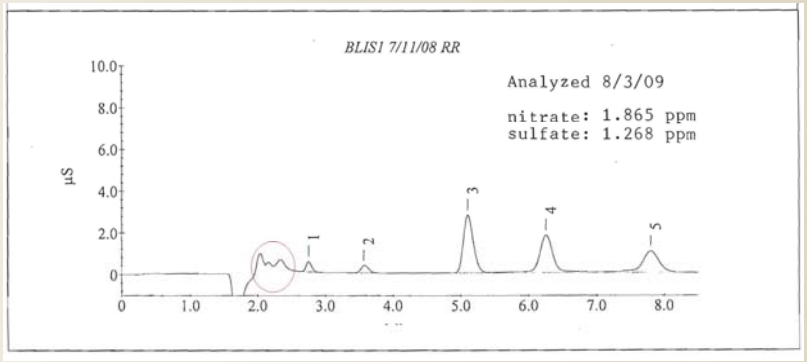


Reanalysis of selected extracts (~ 1 yr after initial analysis)

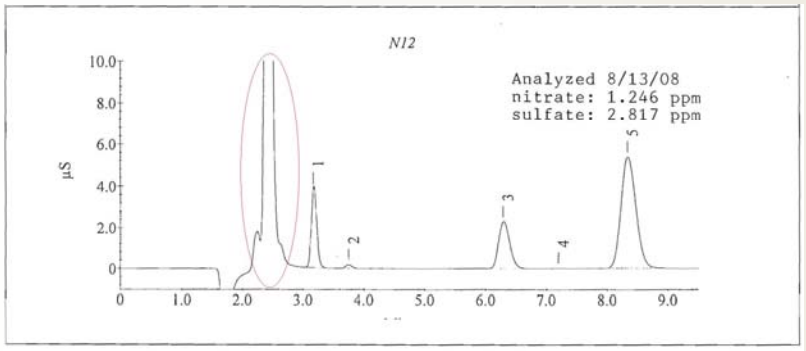


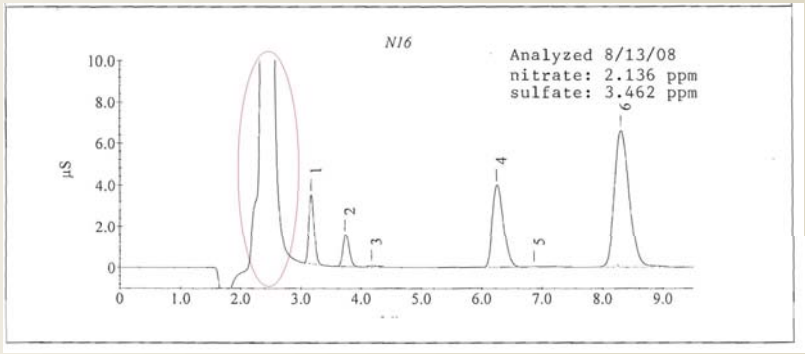


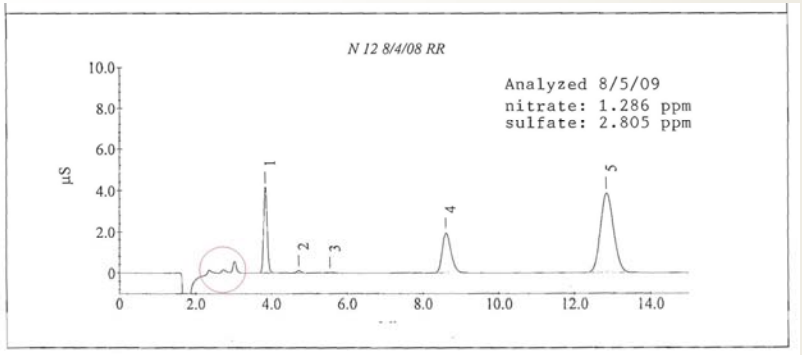


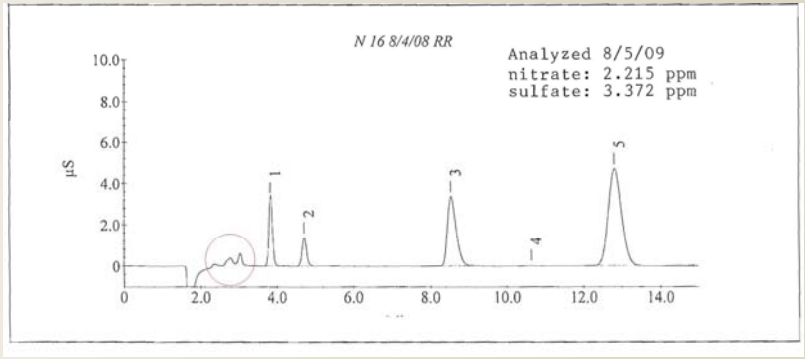


Reanalysis of selected extracts (~ 1 yr after initial analysis), cont'd



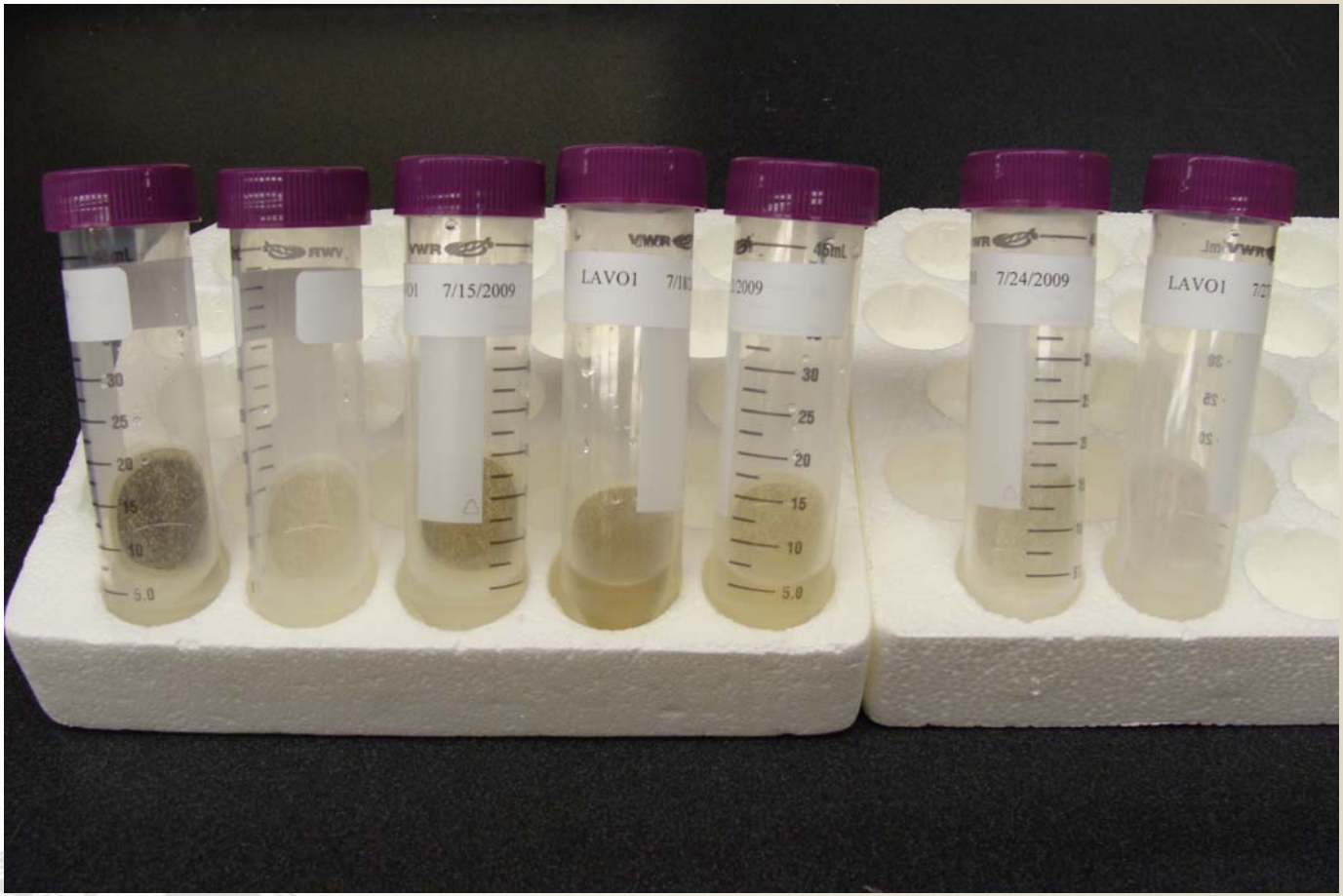




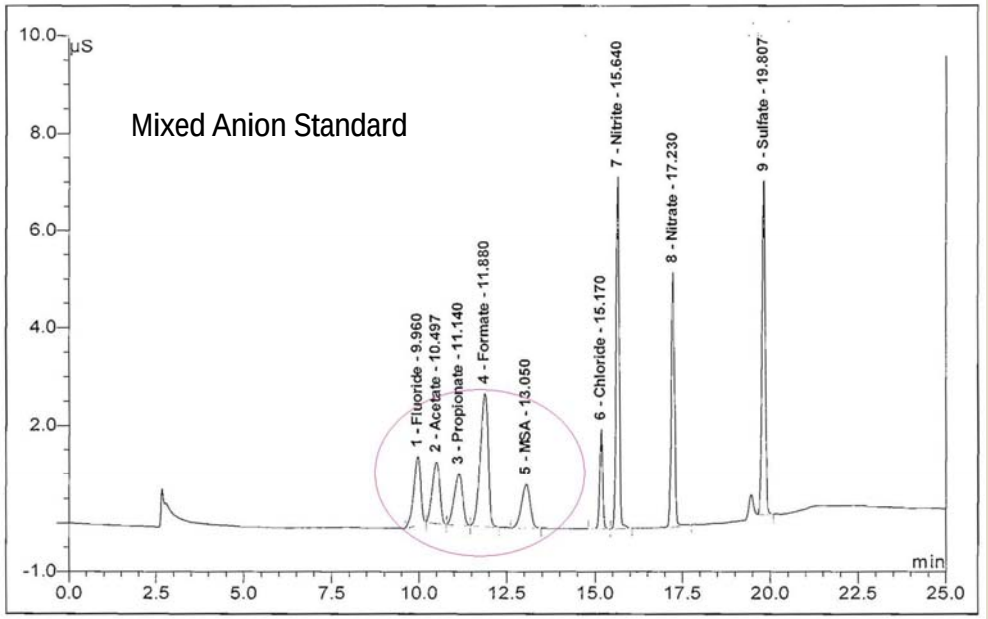


Conclusion: Bugs in the extracts ate our peaks!

Selection of More Recent Extracts with Early Peaks

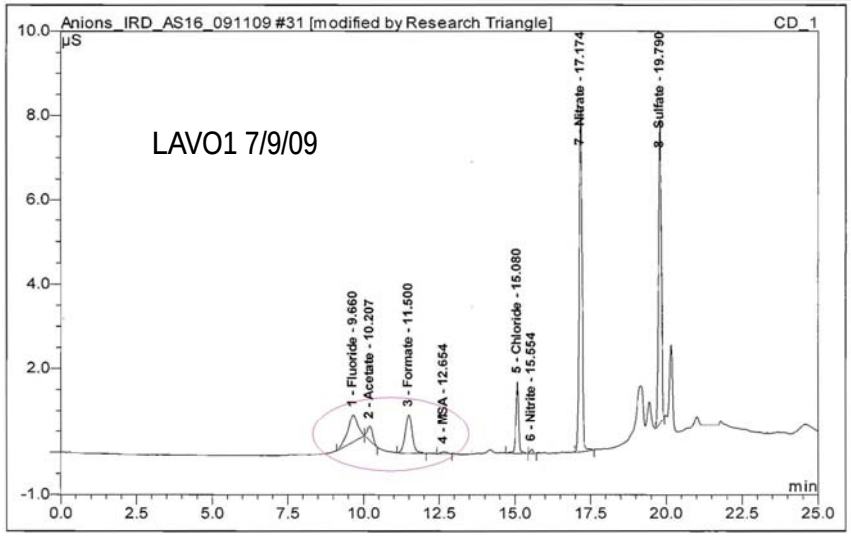


Dionex AS16 Column: 0.2 ppm fluoride, chloride; 1 ppm acetate, formate, MSA, nitrite, nitrate, sulfate

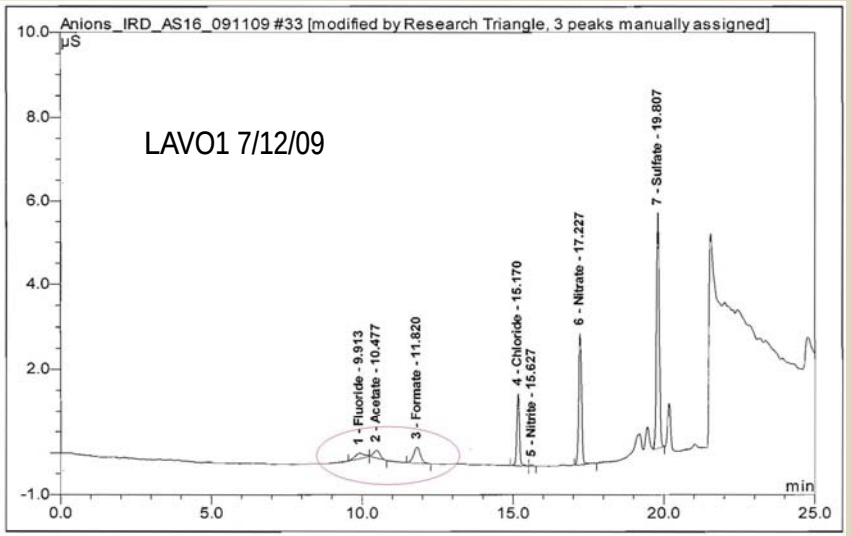


No.	Ret.Time min	Peak Name	Height µS	Area µS*min	Rel.Area %	Amount ppb	Type
1	9.96	Fluoride	1.391	0.321	7.73	200.040	BMb*^
2	10.50	Acetate	1.255	0.312	7.52	1002.869	bMB^
3	11.14	Propionate	1.044	0.289	6.95	1000.509	BMB^
4	11.88	Formate	2.733	0.706	17.00	1000.226	BMB^
5	13.05	MSA	0.891	0.253	6.09	1000.068	BMB^
6	15.17	Chloride	2.037	0.200	4.82	200.065	BMB
7	15.64	Nitrite	7.218	0.751	18.09	999.938	BMB
8	17.23	Nitrate	5.209	0.577	13.88	999.578	BMB
9	19.81	Sulfate	6.856	0.744	17.92	999.644	BMB*
Total:			28.634	4.153	100.00	7402.937	

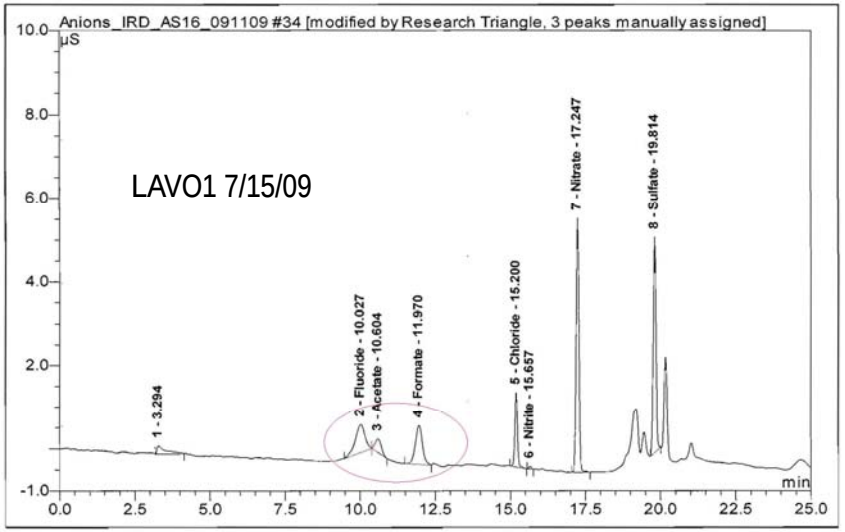
Analysis Using Dionex AS16 Separator Column for Better Separation



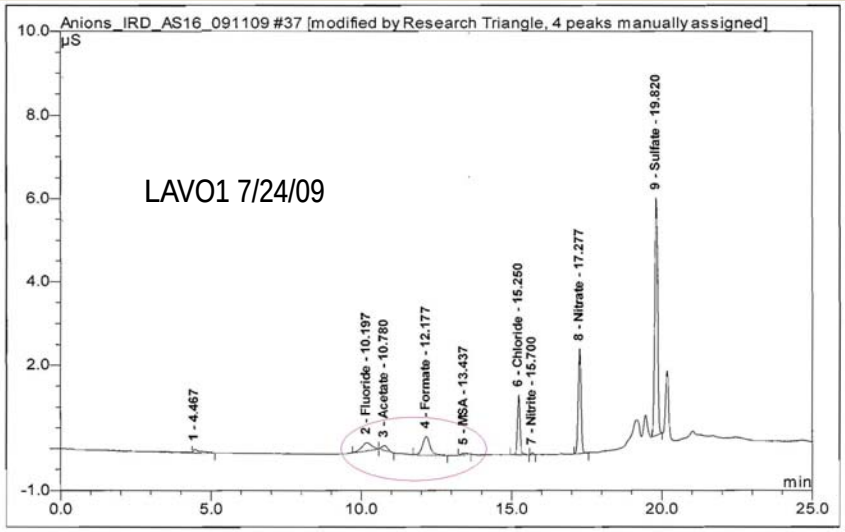
No.	Ret.Time min	Peak Name	Height µS	Area µS*min	Rel.Area %	Amount ppb	Type
1	9.66	Fluoride	0.632	0.237	9.81	154.750	BMb
2	10.21	Acetate	0.328	0.068	2.81	189.327	bMB
n.a.	n.a.	Propionate	n.a.	n.a.	n.a.	n.a.	n.a.
3	11.50	Formate	0.913	0.241	9.95	351.921	BMB
4	12.65	MSA	0.029	0.007	0.27	29.345	BMB*
5	15.08	Chloride	1.708	0.180	7.44	180.752	BMB
6	15.55	Nitrite	0.084	0.009	0.36	13.017	BMB*
7	17.17	Nitrate	8.159	0.911	37.64	1500.140	BMB
8	19.79	Sulfate	7.203	0.767	31.72	1027.582	BMB
Total:			19.057	2.419	100.00	3446.835	



No.	Ret.Time min	Peak Name	Height µS	Area µS*min	Rel.Area %	Amount ppb	Type
1	9.91	Fluoride	0.115	0.039	3.00	29.254	BMb^
2	10.48	Acetate	0.174	0.043	3.28	117.749	bMB^
n.a.	n.a.	Propionate	n.a.	n.a.	n.a.	n.a.	n.a.
3	11.82	Formate	0.375	0.098	7.53	144.954	BMB^
n.a.	n.a.	MSA	n.a.	n.a.	n.a.	n.a.	n.a.
4	15.17	Chloride	1.718	0.172	13.21	173.315	BMB
5	15.63	Nitrite	0.026	0.003	0.19	3.750	BMB*
6	17.23	Nitrate	3.132	0.344	26.40	620.842	BMB
7	19.81	Sulfate	5.600	0.605	46.39	827.661	BMB
Total:			11.140	1.303	100.00	1917.526	

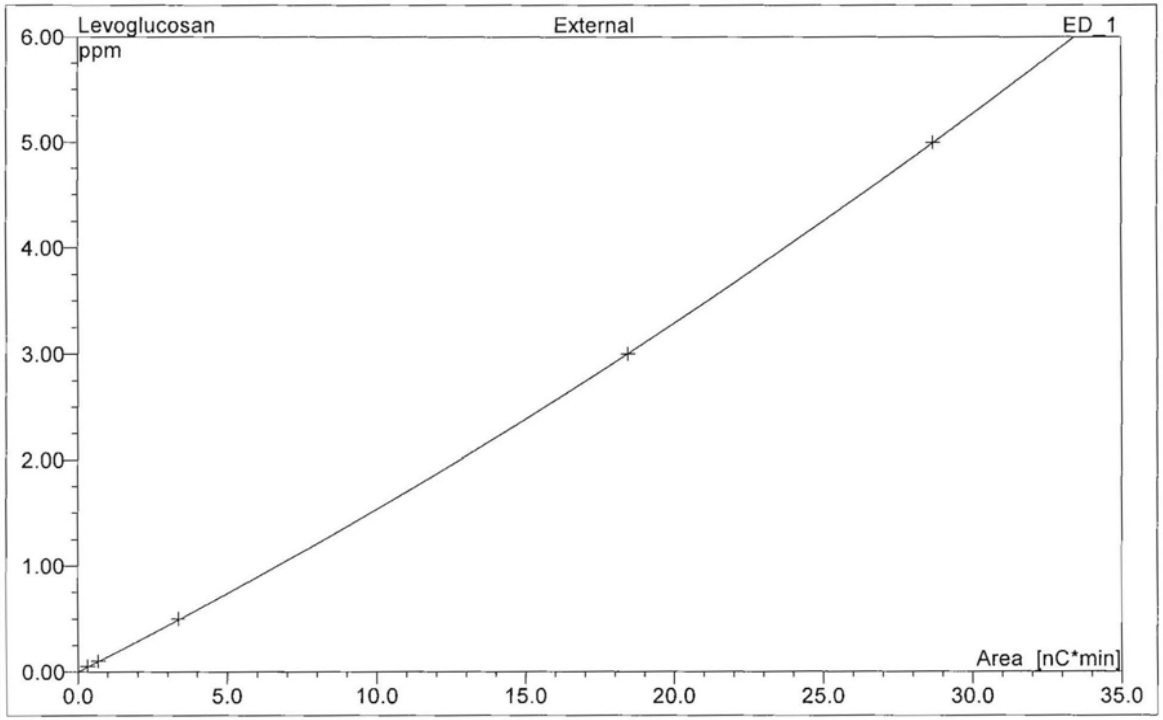


No.	Ret.Time min	Peak Name	Height µS	Area µS*min	Rel.Area %	Amount ppb	Type
2	10.03	Fluoride	0.659	0.241	11.81	157.029	BMb^
3	10.60	Acetate	0.324	0.076	3.74	213.403	bMB^
n.a.	n.a.	Propionate	n.a.	n.a.	n.a.	n.a.	n.a.
4	11.97	Formate	0.929	0.251	12.30	367.347	BMB^
n.a.	n.a.	MSA	n.a.	n.a.	n.a.	n.a.	n.a.
5	15.20	Chloride	1.786	0.181	8.85	181.774	BMB
6	15.66	Nitrite	0.065	0.006	0.29	8.908	BMB*
7	17.25	Nitrate	6.080	0.673	32.93	1148.781	BMB
8	19.81	Sulfate	5.133	0.555	27.14	764.718	BMB
Total:			14.977	1.984	97.05	2841.959	



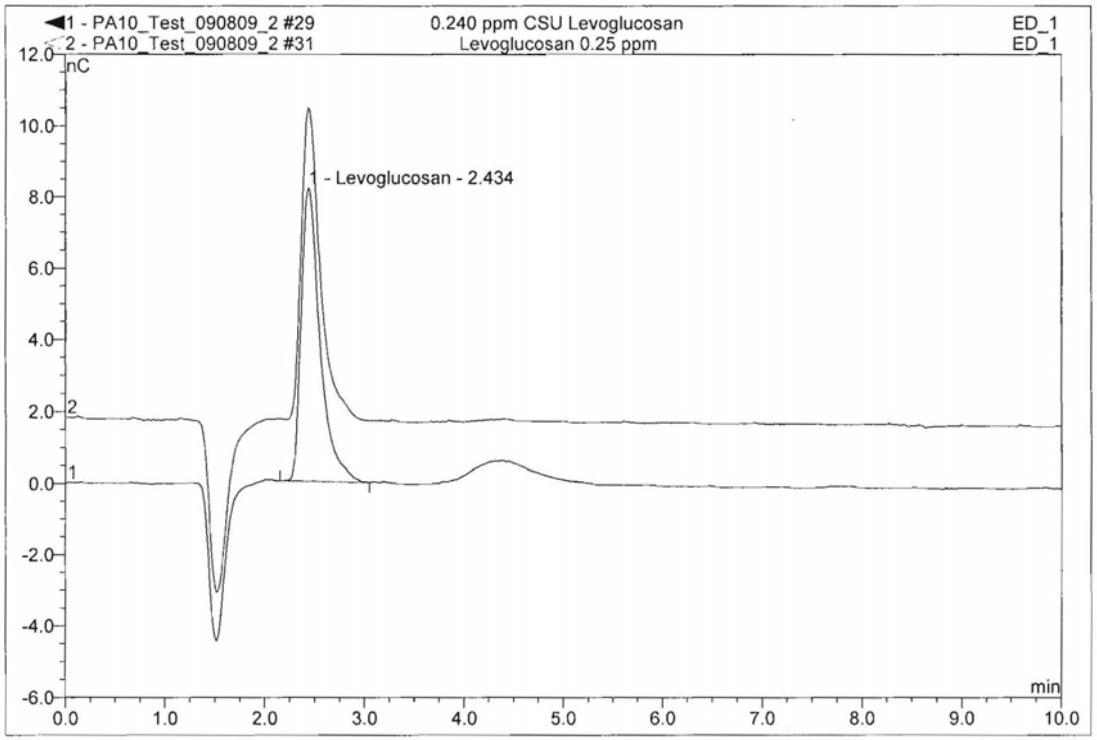
No.	Ret.Time min	Peak Name	Height µS	Area µS*min	Rel.Area %	Amount ppb	Type
2	10.20	Fluoride	0.184	0.069	5.34	50.265	BMb^
3	10.78	Acetate	0.109	0.025	1.92	67.352	bMB^
n.a.	n.a.	Propionate	n.a.	n.a.	n.a.	n.a.	n.a.
4	12.18	Formate	0.437	0.128	9.90	188.147	BMB^
5	13.44	MSA	0.031	0.007	0.55	31.608	BMB*^
6	15.25	Chloride	1.439	0.144	11.16	145.834	BMB
7	15.70	Nitrite	0.046	0.004	0.33	6.349	BMB*
8	17.28	Nitrate	2.510	0.275	21.38	503.370	BMB
9	19.82	Sulfate	5.703	0.617	47.88	843.000	BMB
Total:			10.460	1.268	98.45	1835.925	

Calibration Curve for Levoglucosan

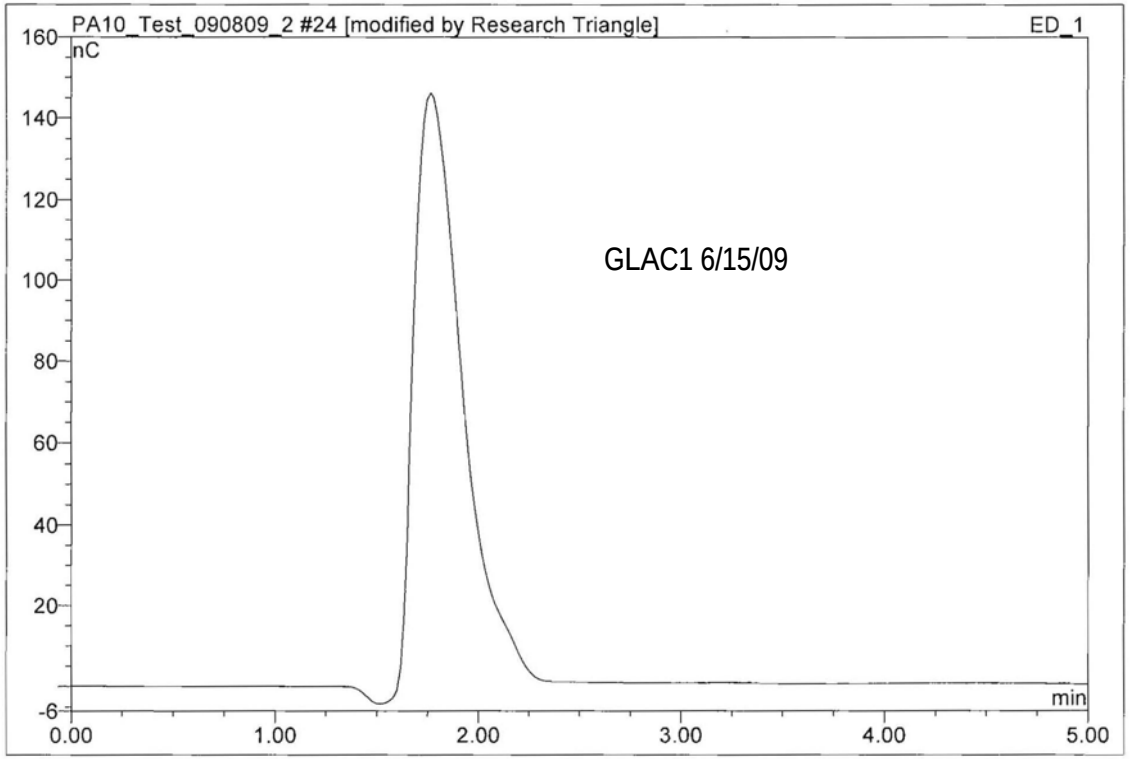


No.	Ret.Time min	Peak Name	Cal.Type	Points	Coeff.Det. %	Offset	Slope	Curve
1	2.42	Levoglucosan	Quad	5	99.9994	0.0000	0.1423	0.0011
Average:					99.9994	0.0000	0.1423	0.0011

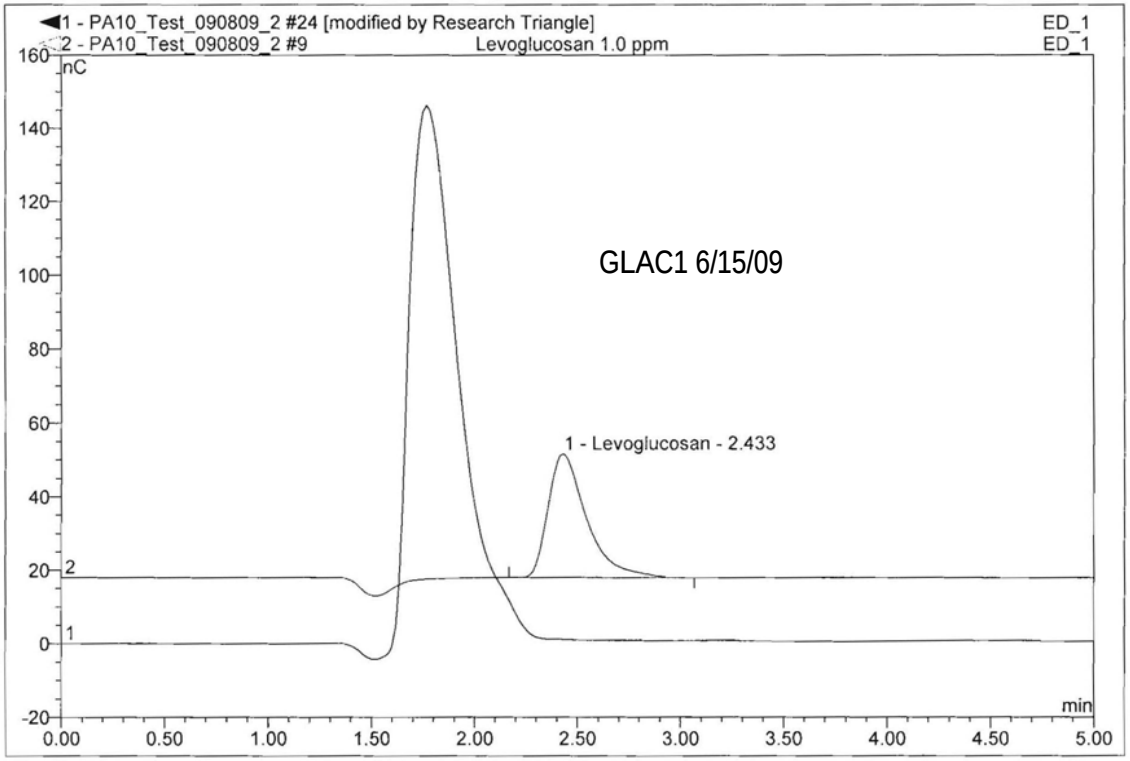
Comparison of RTI and CSU Levoglucosan Standards



No.	Ret.Time min	Peak Name	Height nC	Area nC*min	Rel.Area %	Amount ppm	Type
1	2.43	Levoglucosan	8.192	1.795	100.00	0.225	BMB
Total:			8.192	1.795	100.00	0.225	

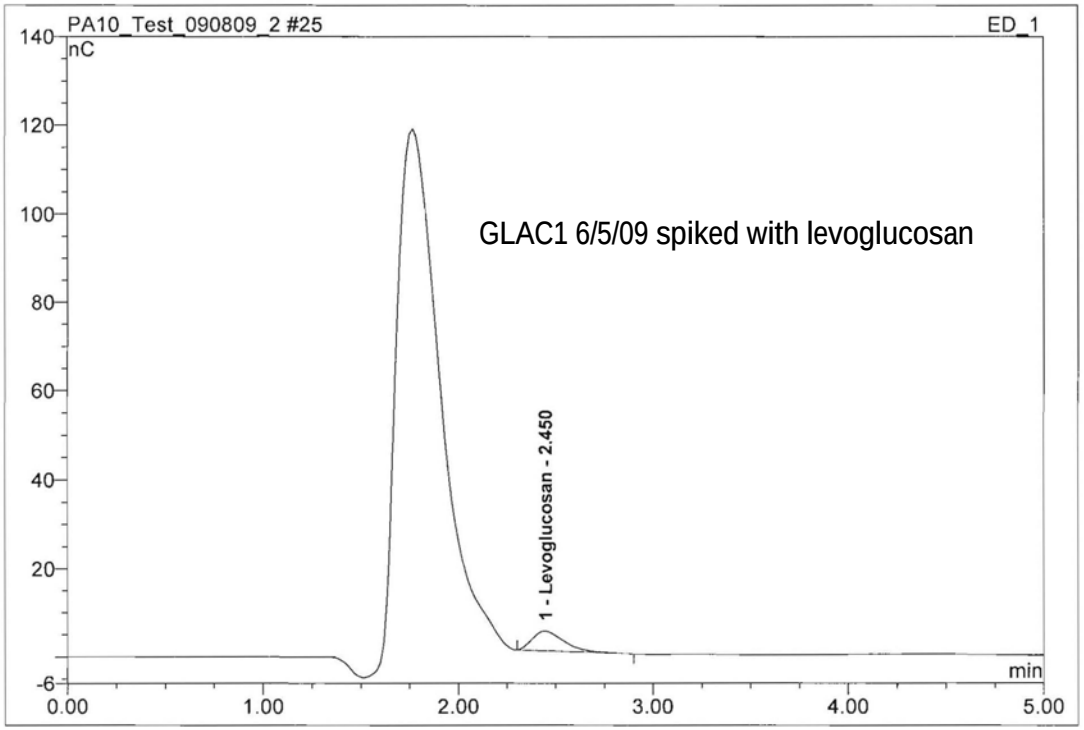


No.	Ret.Time min	Peak Name	Height nC	Area nC*min	Rel.Area %	Amount ppm	Type
Total:			0.000	0.000	0.00	0.000	



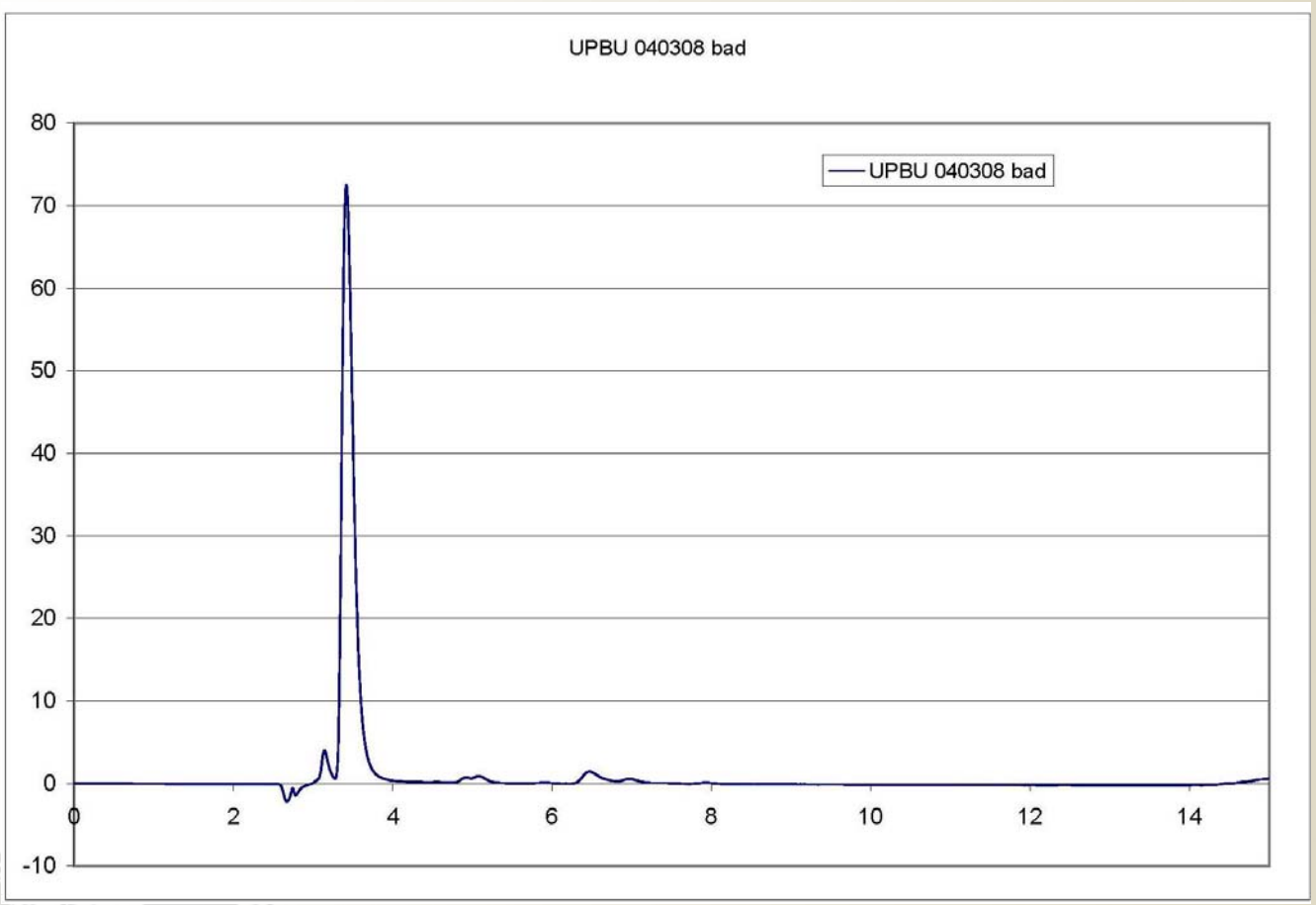
GLAC1 6/15/09

No.	Ret.Time min	Peak Name	Height nC	Area nC*min	Rel.Area %	Amount ppm	Type
Total:			0.000	0.000	0.00	0.000	

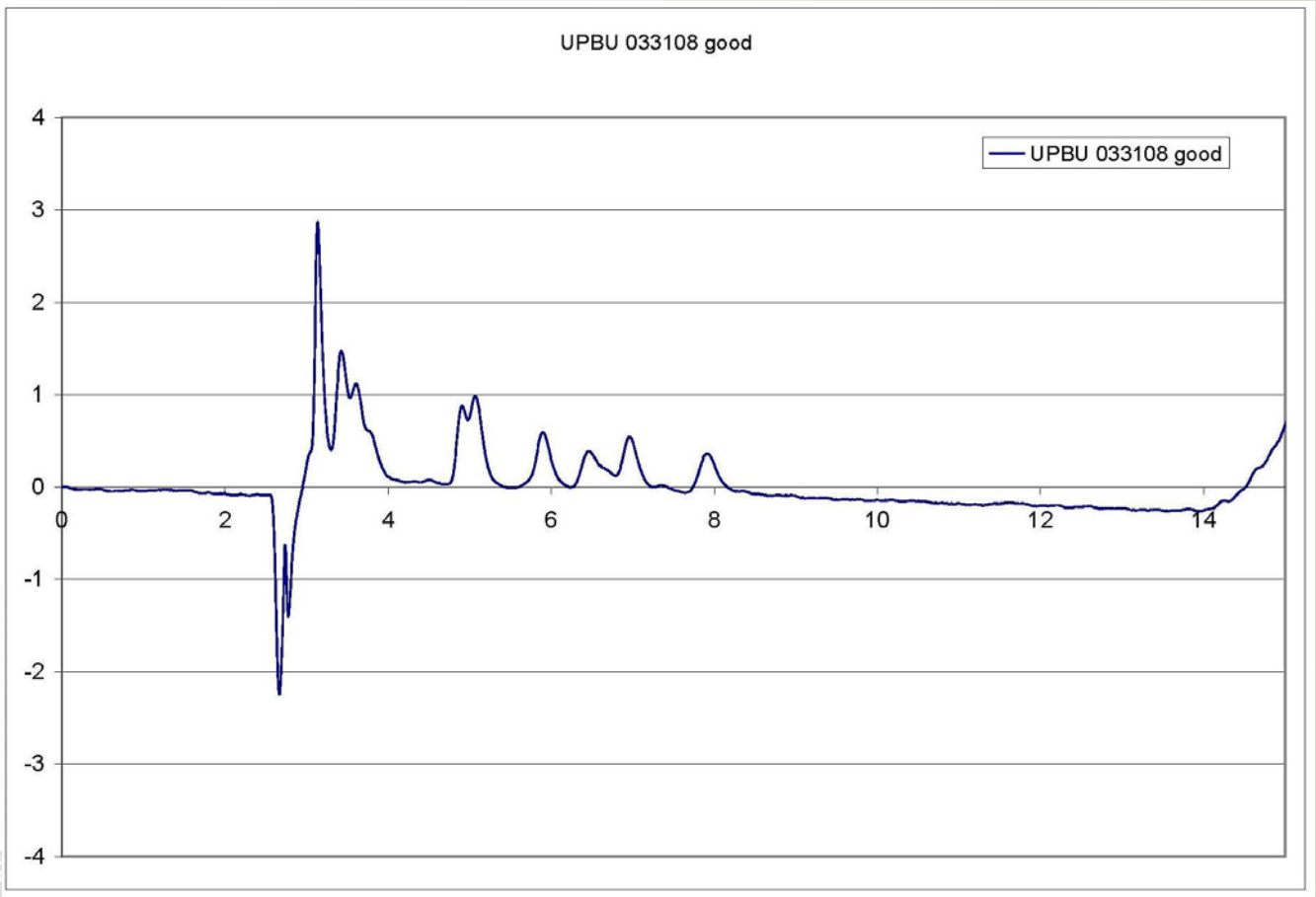


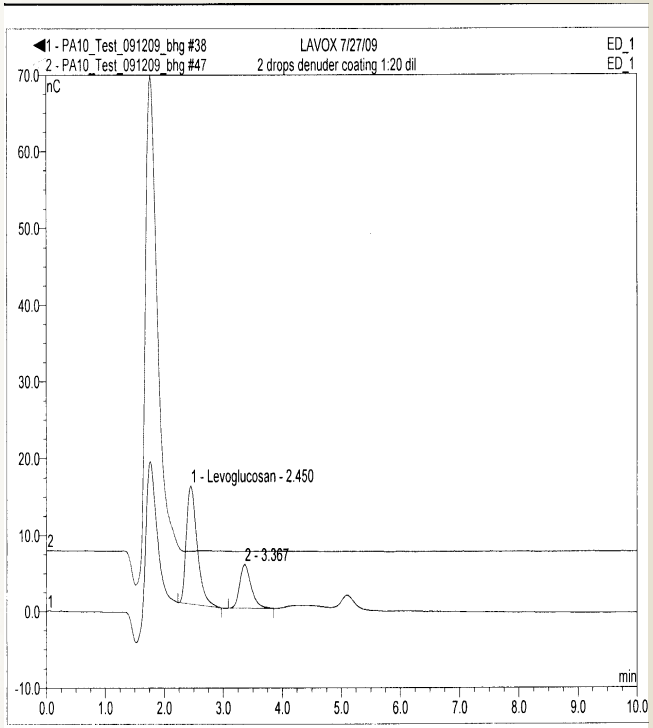
No.	Ret.Time min	Peak Name	Height nC	Area nC*min	Rel.Area %	Amount ppm	Type
1	2.45	Levoglucosan	4.501	0.859	100.00	0.107	BMB
Total:			4.501	0.859	100.00	0.107	

CSU Analysis for Levoglucosan: “Bad” Sample Extract from RTI

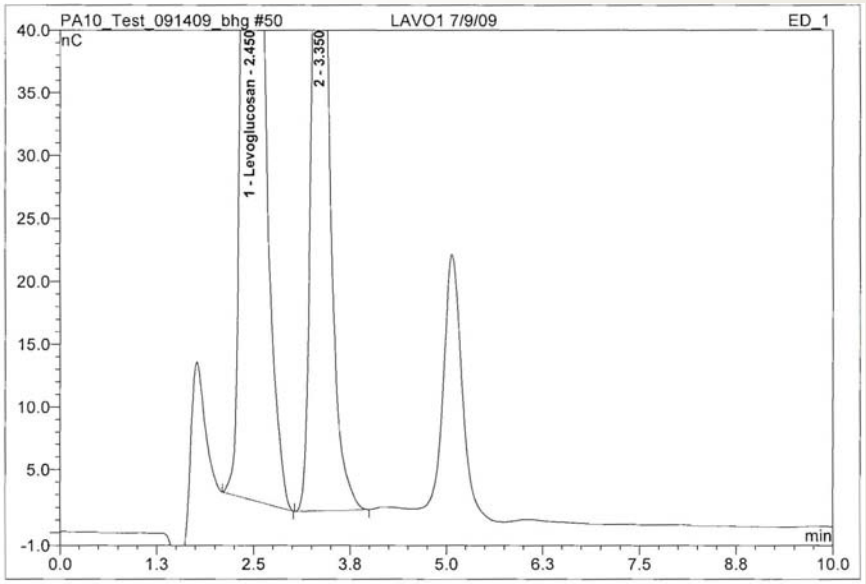


CSU Analysis for Levoglucosan: “Good” Sample Extract from RTI

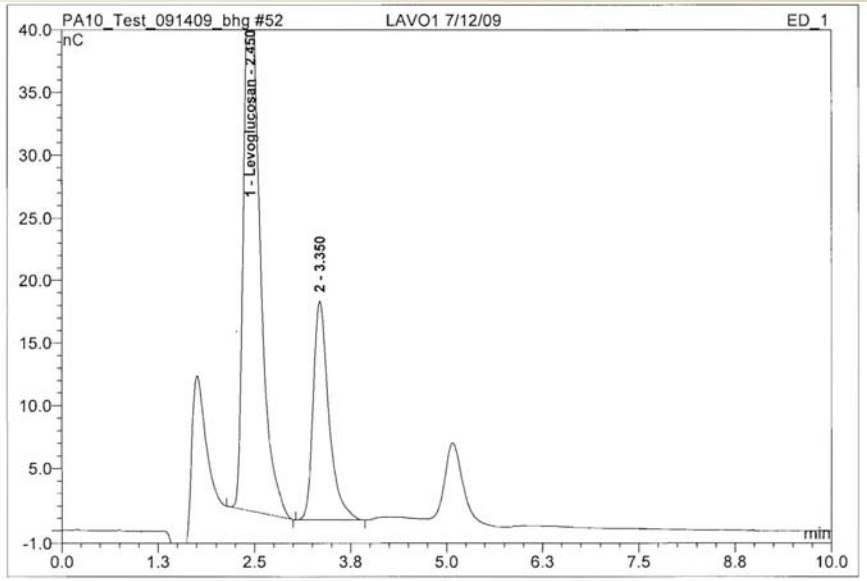




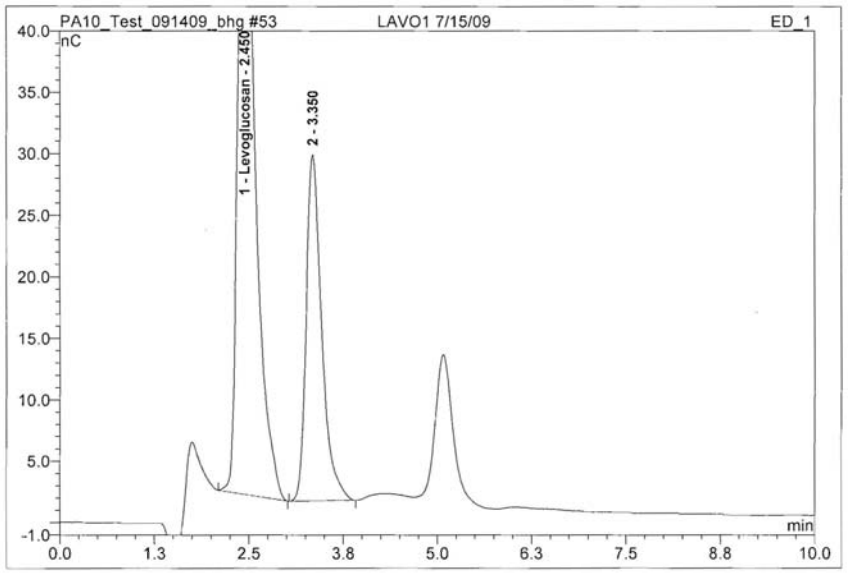
No.	Ret.Time min	Peak Name	Height nC	Area nC*min	Rel.Area %	Amount ppm	Type
1	2.45	Levoglucosan	15.478	3.315	71.84	0.475	BMB
2	3.37	n.a.	5.790	1.299	28.16	n.a.	BMB
Total:			21.269	4.614	100.00	0.475	



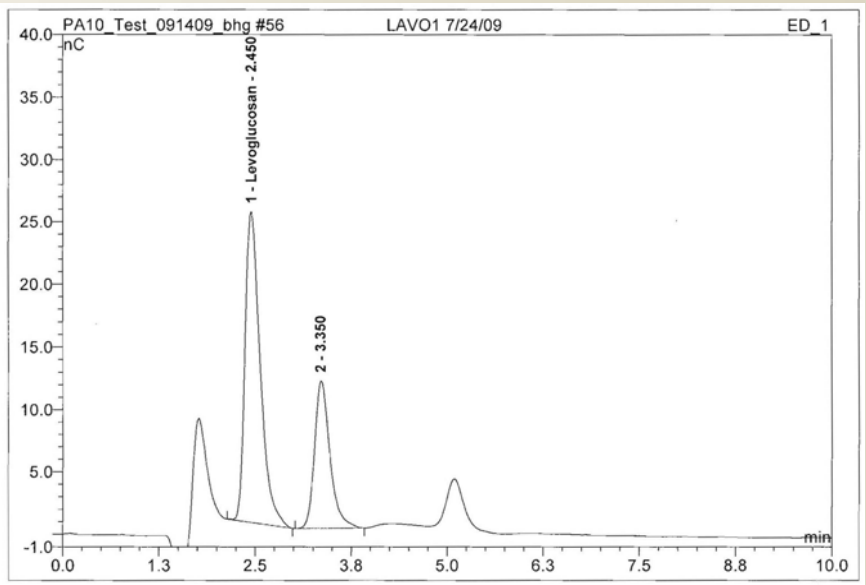
No.	Ret.Time min	Peak Name	Height nC	Area nC*min	Rel.Area %	Amount ppm	Type
1	2.45	Levoglucosan	114.485	31.322	65.01	5.551	BMB
2	3.35	n.a.	71.053	16.858	34.99	n.a.	BMB
Total:			185.539	48.180	100.00	5.551	



No.	Ret.Time min	Peak Name	Height nC	Area nC*min	Rel.Area %	Amount ppm	Type
1	2.45	Levoglucosan	45.260	10.752	72.19	1.655	BMB
2	3.35	n.a.	17.515	4.142	27.81	n.a.	BMB
Total:			62.775	14.894	100.00	1.655	



No.	Ret.Time min	Peak Name	Height nC	Area nC*min	Rel.Area %	Amount ppm	Type
1	2.45	Levoglucosan	55.303	14.736	68.68	2.334	BMB
2	3.35	n.a.	28.161	6.721	31.32	n.a.	BMB
Total:			83.464	21.457	100.00	2.334	



No.	Ret.Time min	Peak Name	Height nC	Area nC*min	Rel.Area %	Amount ppm	Type
1	2.45	Levoglucosan	24.876	5.692	67.38	0.843	BMB
2	3.35	n.a.	11.830	2.756	32.62	n.a.	BMB
Total:			36.706	8.448	100.00	0.843	

Sample ID	Total Area Early Peaks	Levoglucosan, µg/mL	Potassium Ion, µg/mL
LAVO1 7/9/09	275027	5.551	0.289
LAVO1 7/12/09	114227	1.655	0.058
LAVO1 7/15/09	278675	2.334	0.132
LAVO1 7/18/09	313540	1.593	0.162
LAVO1 7/21/09	220868	1.389	0.065
LAVO1 7/24/09	125003	0.843	0.061
LAVO1 7/27/09	118597	0.497	0.043

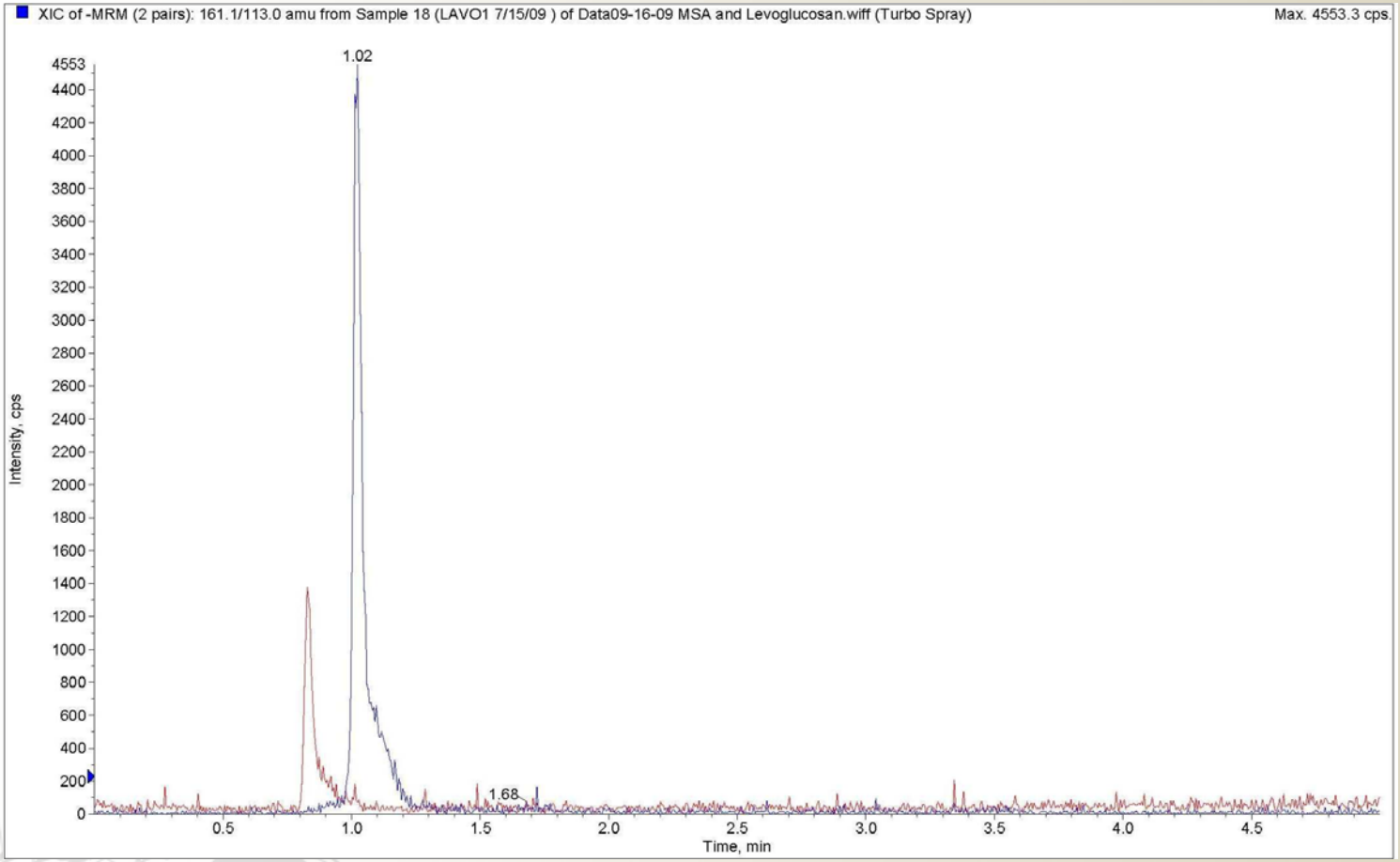
UPLC/MS Investigations

- C_{18} reversed phase ultra-performance LC (UPLC, Waters Acquity) with MS/MS (Applied Biosystems 4000 Q-trap)
- Turbo Ion Spray (Elestrospray) in the negative ion mode
- Detectable compounds eluted within 3 minutes
- Initial MS screen suggested acetate (mobile phase constituent), sulfate, levoglucosan

UPLC/MS Investigations, continued

- Using standards, determination of levoglucosan and methansulfonate by this method was shown to be feasible.
- An MS/MS method was established, the MDLs were estimated, and the method was used to quantify these analytes in selected extracts.

HPLC/MS figure



UPLC/MS Conclusions

- Through comparisons of retention times and selective detector responses (conductivity, PAD, MS/MS) the presence of methanesulfonate and levoglucosan in sample extracts was confirmed.
- UPLC/MS/MS can augment/simplify other analytical methods, e.g., GC for sacharides, and provide greater selectivity for confirmation of chemical identities.
- UPLC/MS/MS will be a valuable tool for the study of water-soluble fraction of PM.

Study Conclusions

- The appearance of measurable peaks early in the ion chromatograms of nylon filter extracts can indicate smoke or other significant events.
- Additional experiments are needed to identify the large peak prior to levoglucosan (glycerol?).
- If glycerol is present, it could indicate carryover from the denuder.

Michael Tolocka

Contribution of organosulfur compounds to organic aerosol mass

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(1) Louisiana State University and A&M College (2) Rutgers University

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Preference: No preference
Working Group: Carbonaceous Aerosols in the Atmosphere

Abstract
Organosulfates have been proposed as products of secondary organic aerosol formation. While organosulfates have been identified in ambient aerosol samples, a question remains as to the magnitude of their contribution to particulate organic mass. At the same time, discrepancies have been observed between total particulate sulfur measured by XRF and sulfur present as inorganic sulfate measured by ion chromatography in fine particulate matter. These differences could be attributed to measurement bias and/or the contribution of other sulfur compounds, including organosulfates. Using the National Park Service IMPROVE PM2.5 database, we examined the disparity between the sulfur and sulfate measurements at 12 sites across the United States to provide upper-bound estimates for the annual average contributions of organosulfates to organic mass. The data set consists of over 150,000 measurements. The 12 sites include Brigantine, NJ, Cape Cod, MA, Washington, DC, Chassahowitzka, FL, Great Smoky Mountains National Park, TN, Okefenokee, FL, Bondville, IL, Mingo, MO, Phoenix, AZ, San Gabriel, CA, Crater Lake National Park, OR, and Spokane, WA. These sites are representative of the different regions of the country: Northeast, Southeast, Midwest, Southwest and Northwest. We estimate that organosulfur compounds could comprise as much as 5-10% of the organic mass at these sites. The contribution varies by season and location and appears to be higher during temperate months when photochemical oxidation chemistry is most active. It should be noted that these compounds are a more substantial contributor to particulate organic matter than they are to particulate sulfur.