

GCxGC-TOFMS of Volatile Organic Compounds in Urban and Rural Air

Jack Cochran, Frank Dorman, and David Shelow
Restek Corporation, Bellefonte, Pennsylvania

Mark Libardoni
LECO Corporation, St. Joseph, Michigan

Note that because of time, I will not show any rural air sample work here, even though that is listed in the title.

I want to note the kind help of my coworkers, especially Dave Shelow, who pulled all of the canister sampling equipment together for me at the last minute, and gave me suggestions on how to use it both for collection and sample introduction.

Outline

- Description of GCxGC-TOFMS
 - Including benefits for air analysis
- Sampling and analysis details
 - Air sample collection and transfer
- Results from analysis
 - Display of GCxGC data
 - » Standard and sample
 - Complex sample analysis
 - Compounds in samples

A simple outline of the presentation is listed here. The description of GCxGC-TOFMS will be brief due to time considerations, but the benefits should be relatively well-explained, especially throughout the presentation.

The sampling and sample introduction are NOT the focus of the presentation at all, as I did not have a preconcentrator, which is typically used for air canister work. The important thing is to note what GCxGC-TOFMS can do for complex samples, like those from urban air mainly.

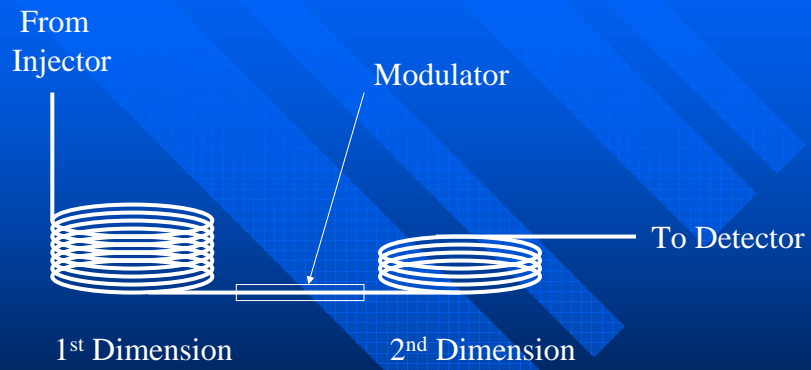
Typical GCxGC Setup

- Primary column (1st dimension)
 - Longer, wider bore, thicker film
 - Non-polar
- Modulator
 - Thermal in nature
 - Focuses effluent from primary column
 - “Injects” this effluent onto secondary column
- Secondary column (2nd dimension)
 - Very short, narrow bore, thinner film
 - Polar or selective
- Fast detector to record 50-500 ms wide peaks
 - TOFMS acquires up to 500 spectra/sec

The typical GCxGC setup is listed in this panel. A longer, wider bore (e.g. 30m x 0.25mm) column is installed in a GC injector. The end of this column is press-fitted to a very short, narrow bore (e.g. 1 m x 0.1mm or other) column that terminates in a detector (in this case, a TOFMS). So... all sample injected passes through both columns. Approximately at the junction of the press-fit connector is a thermal modulator that focuses effluent from the primary column (cold jet), and then quickly injects this effluent (hot jet) to the secondary column. By doing the modulation process rapidly, and having a quick secondary separation, the first column separation is maintained. **I.e. you now have two independent separations occurring for one injection.**

This is not heart-cutting!

GCxGC Schematic



Two independent separation mechanisms

Here is a schematic that shows a comprehensive 2D GC (GCxGC) setup like it was described in the previous slide. The important thing to remember is that **two independent separation mechanisms** are being applied to the whole sample, no splitting.

Why Use GCxGC-TOFMS for Urban and Rural Air Samples?

- Improved resolving power
 - Increased peak capacity for very complex samples that may contain hundreds to thousands of compounds
- Sensitivity enhancement
 - Focusing through thermal modulation
- Ordered chromatograms
 - Good for aliphatic and aromatic separations when looking at vehicle emissions

The slide is self-explanatory, pretty much. Note that because you are cold focusing close to the detector, you get a peak sharpening that leads to a sensitivity increase, often on the order of 3-10X. An ordered chromatogram, in its simplest description is when the aliphatics elute in a band across the bottom (lower on the Y axis) of a contour plot (a way to display GCxGC data, shown later) and the aromatics elute later in the second dimension (up on the Y axis of the contour plot).

Sampling and Analysis Scheme

- Grab air sample in 6 liter SilcoCan Canister
 - Near McCarran Airport, Las Vegas, Nevada
- Pressurize canister with nitrogen
- Transfer air sample to Tenax trap
 - Average 30 mL/min
 - Approximately 3 liter total
- Desorb trap with Gerstel TDU to CIS4 inlet
- “Inject” CIS4 to GCxGC-TOFMS



Duplicate air samples were “grabbed” near the airport by opening the valve on an evacuated canister to fill.

The canister was pressurized with clean, dry nitrogen to approximately 30 psi in the laboratory.

A Gerstel TDU tube filled with Tenax had a fused silica restrictor on the exit end of it to keep the flow rate to an average of 30 mL/min during the trap sampling. Admittedly, this is far from ideal on canister sampling, but I did not have a preconcentrator in the lab and the focus of the presentation is on how to analyze complex samples with GCxGC-TOFMS. Also, it is realized that Tenax is not the best sorbent, as it will not trap things like the most volatile Freons and vinyl chloride quantitatively, but that is all I had in the lab at the time.

The Tenax trap was desorbed to a Gerstel CIS4 inlet (liner packed with small volume of Tenax and cooled during sampling) which was then rapidly heated to desorb volatiles to the GCxGC system.

GCxGC Columns

- 30 m x 0.25 mm x 1.0 μm Rtx-1
- 1 m x 0.18 mm x 0.40 μm Rtx-50
- Corrected constant flow He at 0.7 mL/min

The GCxGC column setup is described here. The columns were joined with a press fit, after inserting the second column (Rtx-50) through the modulator and into the secondary oven of the 2D GC system.

The column films were thicker to support the analysis of volatile organic compounds.

GCxGC Conditions

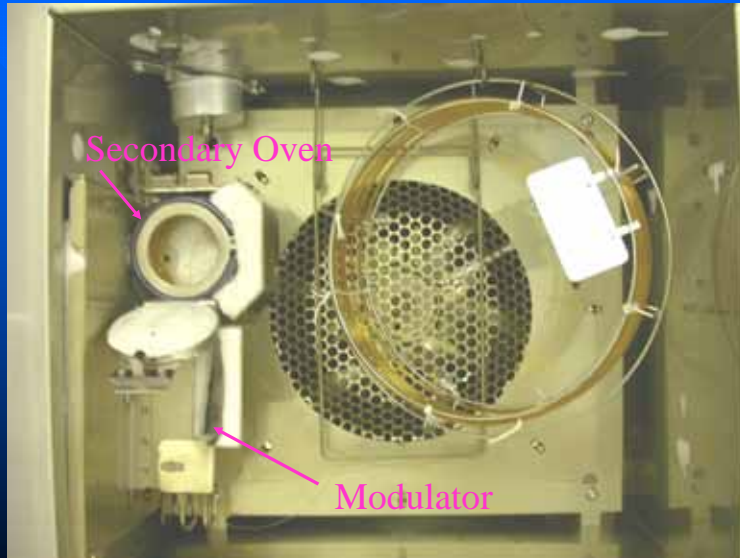
- Primary oven
 - 30°C (1 min), 3°/min to 210°
- Modulator (quad-jet, dual-stage)*
 - Temperature offset: 20°C
 - Modulation time: 3 sec
- Secondary oven
 - Offset of +5°C from primary oven

Run time = 61 min

*Built by LECO under license from Zoex Corporation

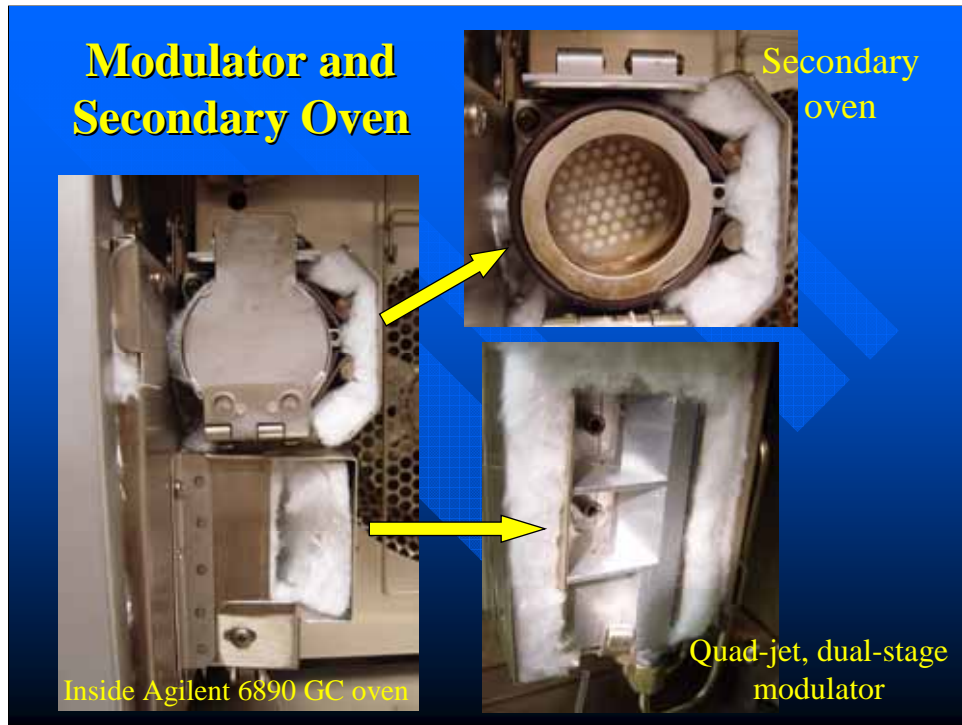
Here are the operational conditions for GCxGC. These were not optimized really in any form, except that the start temperature was kept relatively low to better “focus” early eluting volatiles during the CIS4 “injection”.

Modulator and Secondary Oven



Here is a picture of the modulator and secondary oven as they sit inside an Agilent 6890 GC oven. The primary column is seen on the right. The secondary column travels through the thermal modulator and sits inside of its own oven that can be temperature programmed independently of the primary oven (the Agilent 6890 GC oven). The picture shows the secondary oven open, but during analysis, the cover would be closed.

The transfer line to the MS (not shown here) is just to the left of the secondary oven.



The modulator and secondary oven in a “zoom” shot. The modulator cold jets are visible as tubes pointing out towards the audience in the lower-right shot where the cover of the modulator has been removed for the photograph. Liquid nitrogen-cooled nitrogen gas is how the cold focusing works. The hot jets, which are visible (with close inspection in the same lower-right photo) as slits to the right of the tubes, use heated air or nitrogen to desorb analytes from the modulation zone so that the secondary separation can proceed.

The secondary oven (and column inside) can be temperature programmed independently of the primary oven.

Modulation time (which can also be thought of as secondary column separation time) is usually on the order of a few seconds.

TOFMS Conditions LECO Pegasus 4D

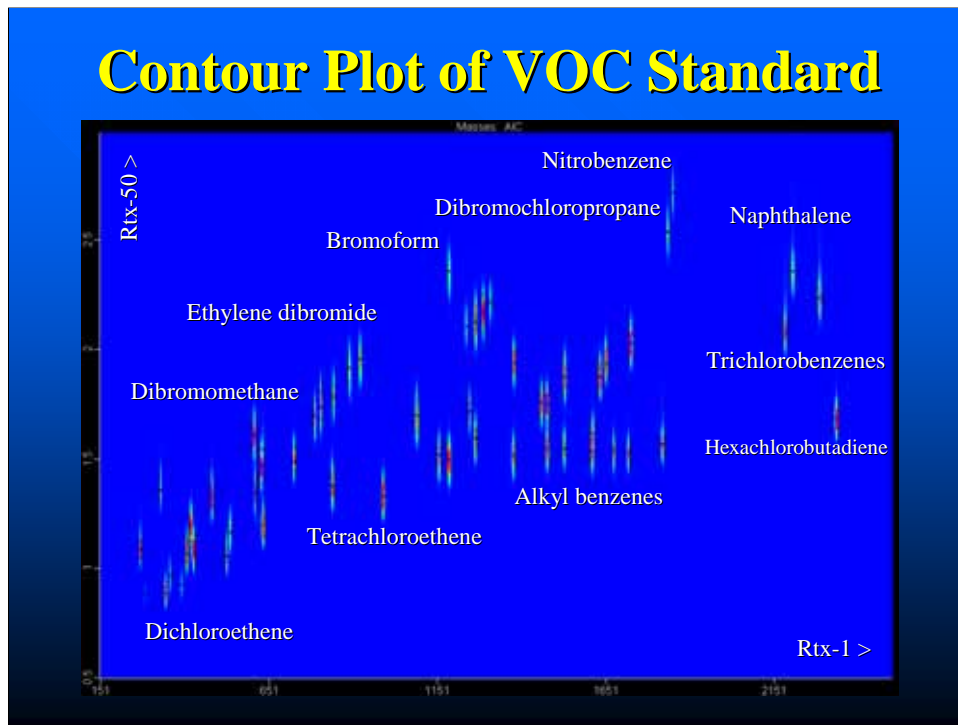
- Source temperature: 180°C
- Electron ionization: 70 eV
- Stored mass range: 35 to 350 u
- Acquisition rate: 100 spectra/sec



The TOFMS conditions. Notice the acquisition rate, extremely fast (if you're comparing it to a quadrupole or magnetic sector), and relatively fast for TOFMS (500 spectra/sec being the fastest for the Pegasus). Modulation, focusing and re-injecting, produces peaks that are about 200ms wide at the base in this work, and you need a fast MS to handle peak definition.

Magnetic sector and quadrupoles can't acquire data this fast.

Contour Plot of VOC Standard

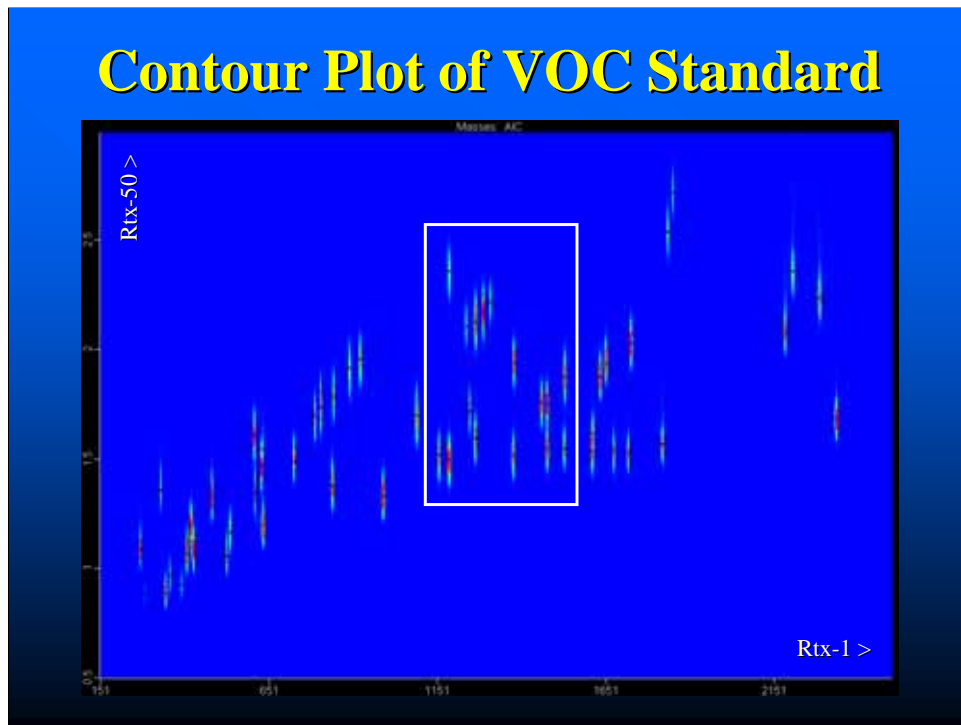


This is one way how GCxGC data can be displayed, the **Contour Plot**, and here we have a chromatogram of a standard of volatile organic compounds (VOCs) from a standard. Each “spot” represents a VOC and the black dashes in the middle of the spot are Peak Markers. The intensity of the peak is represented on a scale of blue (low) to red (high). The TIC is being plotted.

Note how the separations are occurring in two dimensions, the first being the Rtx-1 (x axis retention time; longer time scale) and the second being the Rtx-50 (y axis retention time; very short, on the order of seconds time scale).

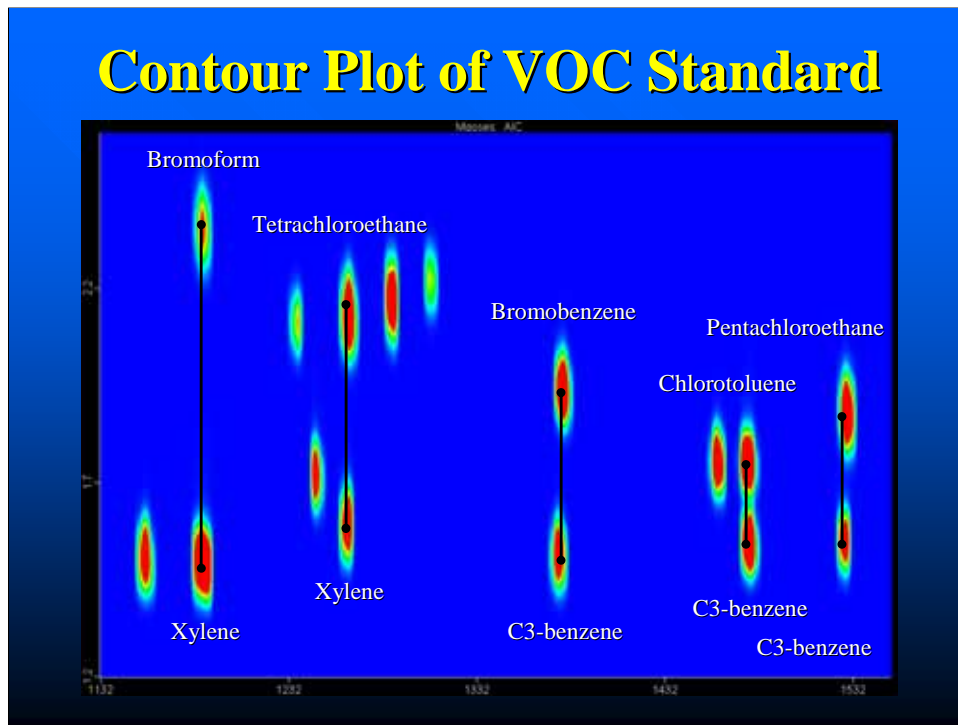
The reason we can attach names to them (in addition to being a known standard) is that we have a mass spectrometer and can take spectra and library search.

Contour Plot of VOC Standard



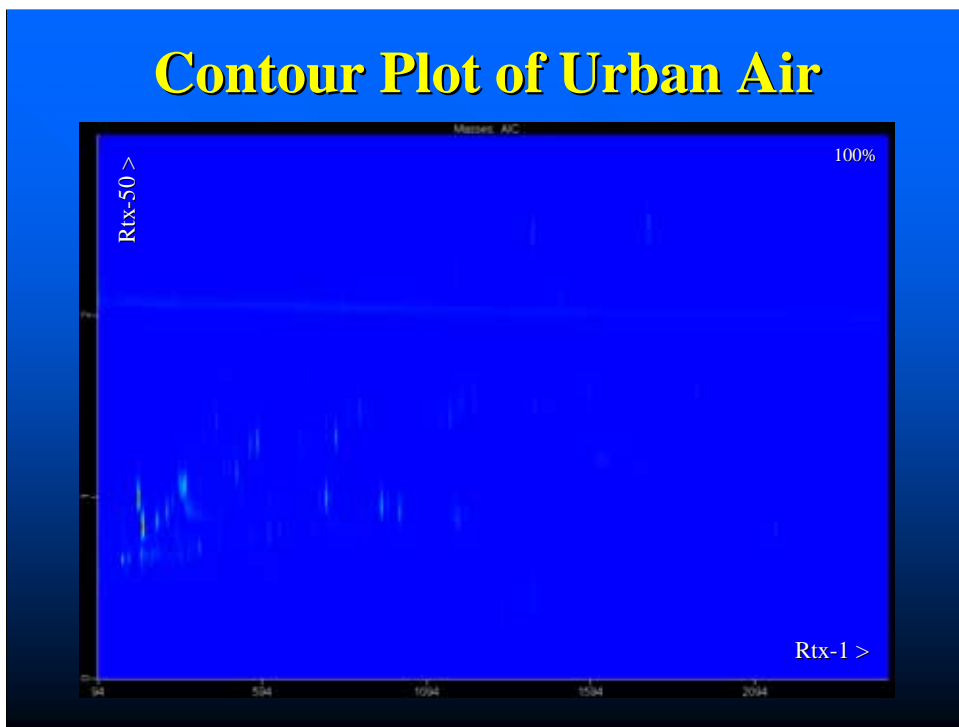
Let's zoom in on a select group and define the power of GCxGC and two independent separations.

Contour Plot of VOC Standard



Note that wherever you have alignment along the X axis (shown by the black lines being displayed) is where a coelution would occur if you were only doing a 1D analysis with the Rtx-1. Now of course it is possible to separate these compounds quite nicely on a column specifically made for VOC analysis (e.g. VMS, etc.), but when it comes to “real world” analyses (and complex samples say for urban air) it is not the separation of the standards we worry about; it is all the other compounds that tend to elute in one big “hump-o-gram” that make things difficult to sort out.

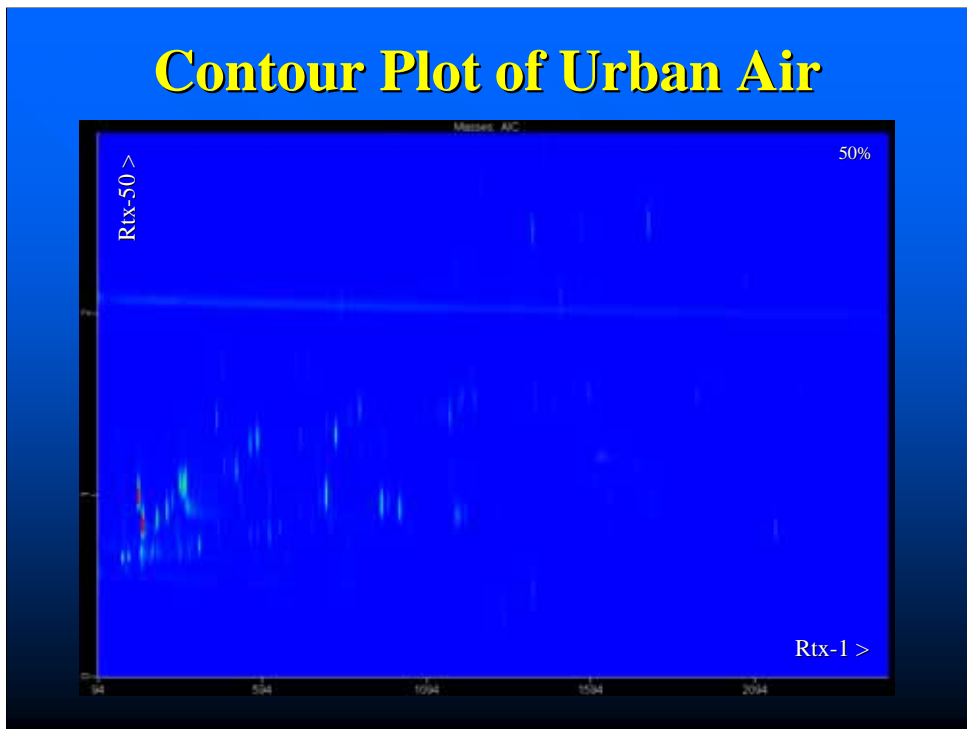
Contour Plot of Urban Air



The first display of a GCxGC-TOFMS contour plot of urban air. It doesn't really look that impressive, does it? That is because of the way that the data is currently being displayed where the most intense peak is dominating the "intensity" part of the plot (i.e. suppressing our view of the complexity).

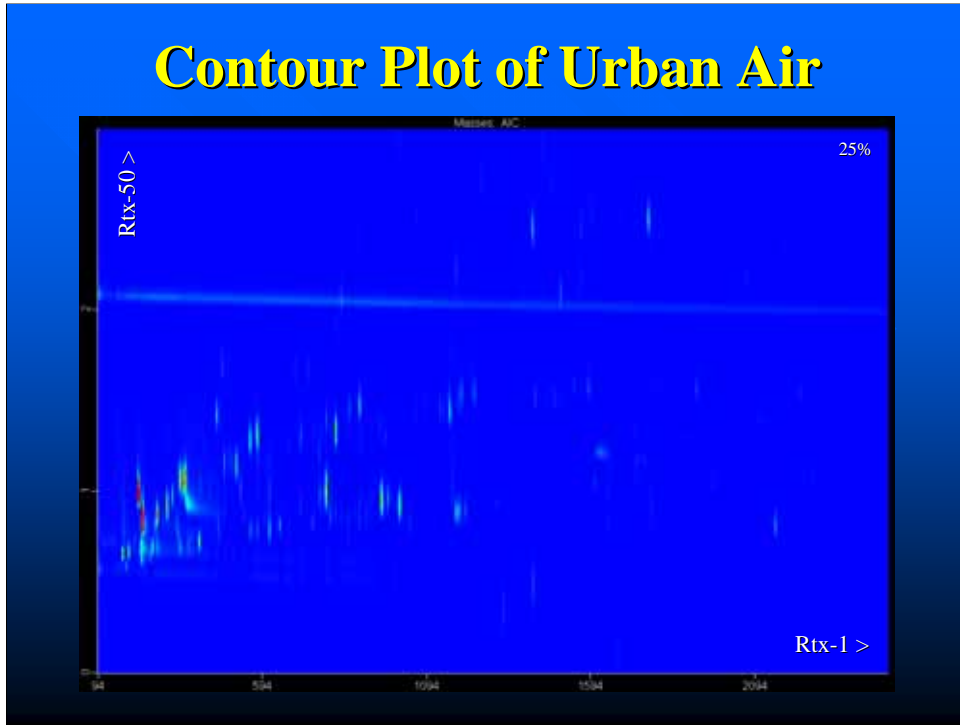
The next five contour plots are identical to this one as far as their X and Y axis scales, but the intensity display has been changed from 100% to 50, 25, 10, 5, and 2% to allow the viewer to really focus in on the complexity of this urban air sample taken near the Las Vegas airport.

Contour Plot of Urban Air



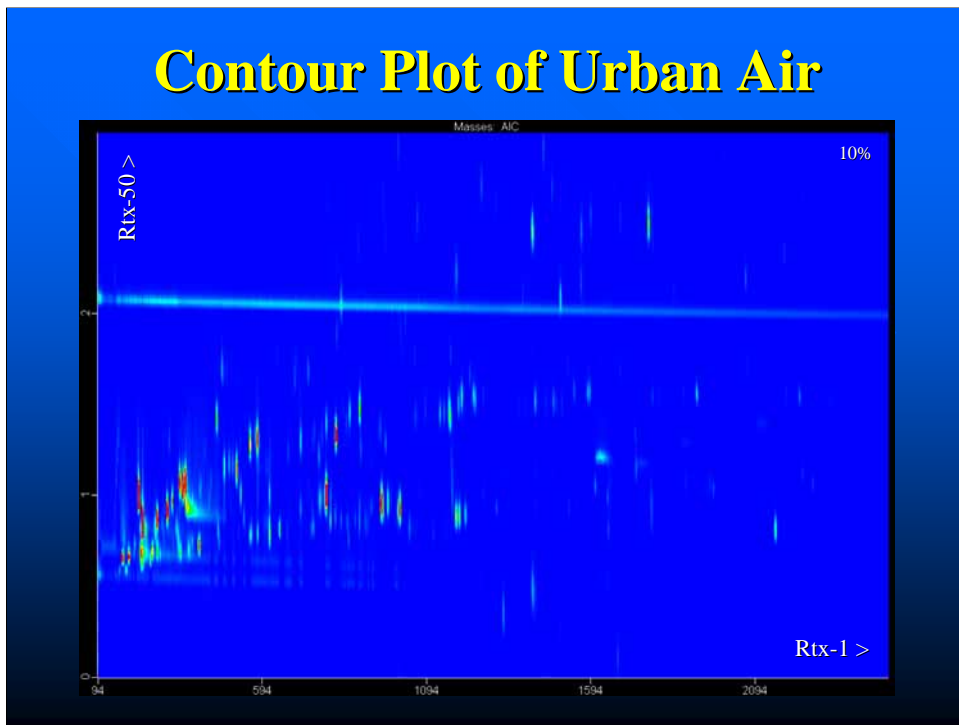
50%, and we can see more compounds appearing.

Contour Plot of Urban Air



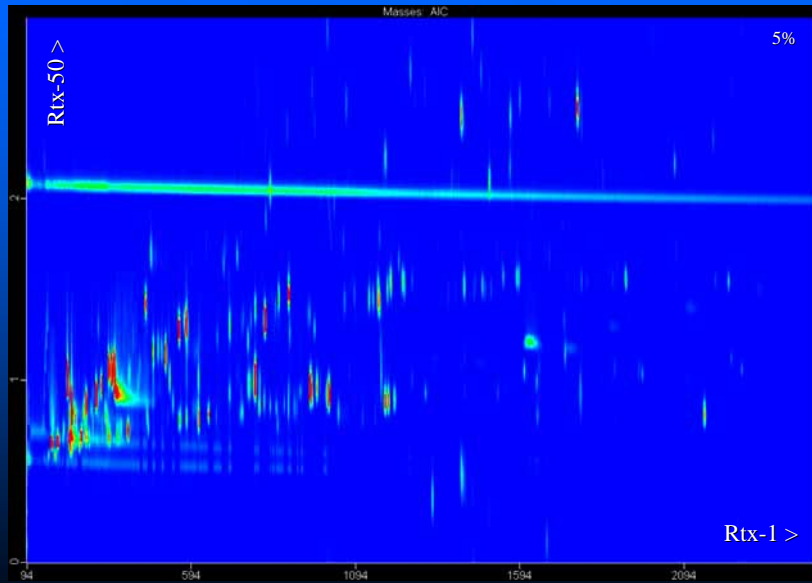
25%, even more.

Contour Plot of Urban Air



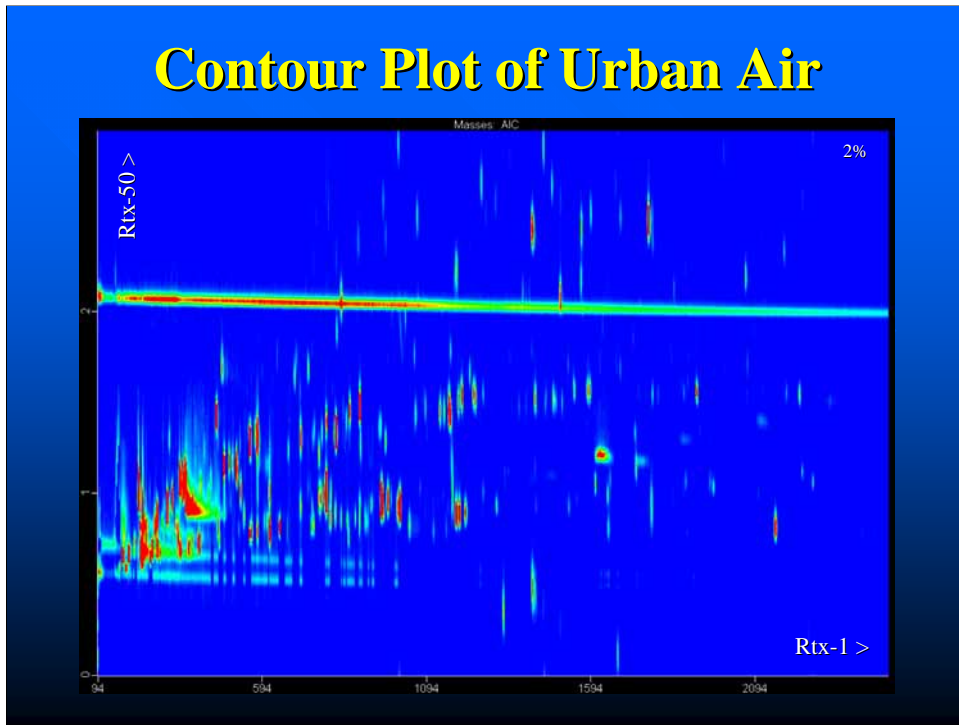
10%, and the real complexity of this sample is showing up.

Contour Plot of Urban Air



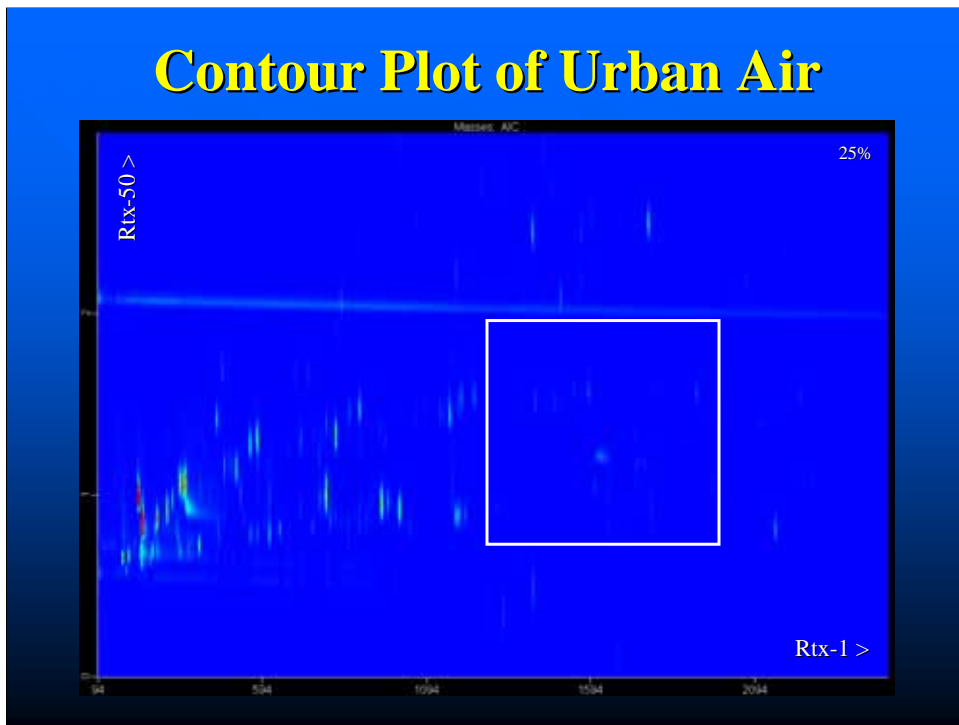
5%.

Contour Plot of Urban Air



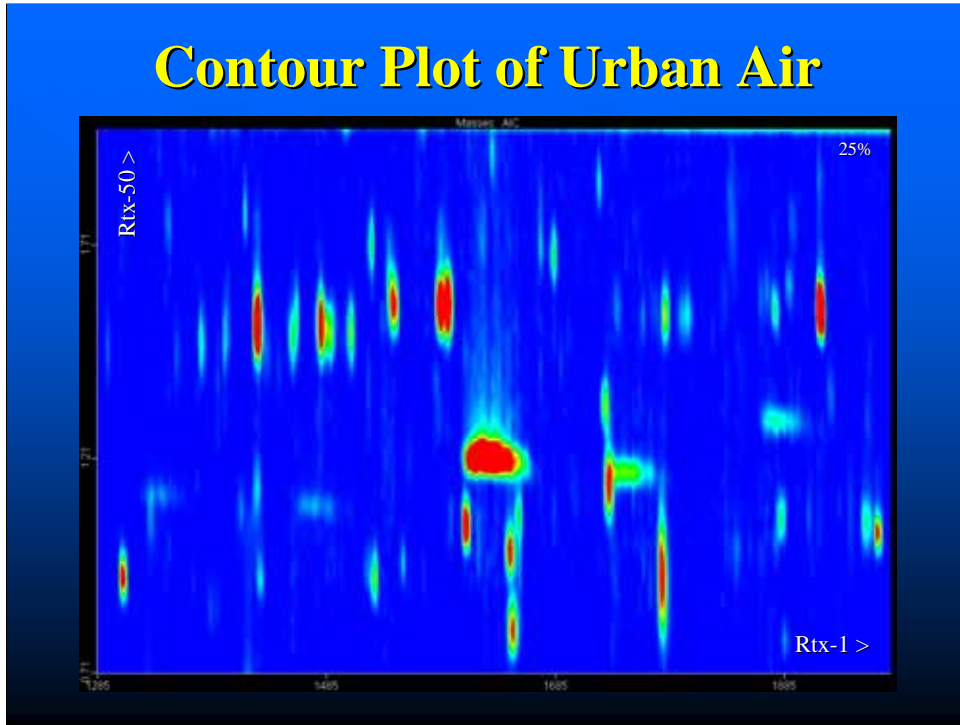
And finally 2%, and you can really see how many compounds are in this sample. Again, note that wherever compounds line up on the X axis, that would have been a coelution (or several coelutions) when only doing a 1D analysis. The 2D space is being used quite nicely here, where compounds, especially later in the analysis, are moved “back” along the Rtx-50 axis (the Y axis).

Contour Plot of Urban Air



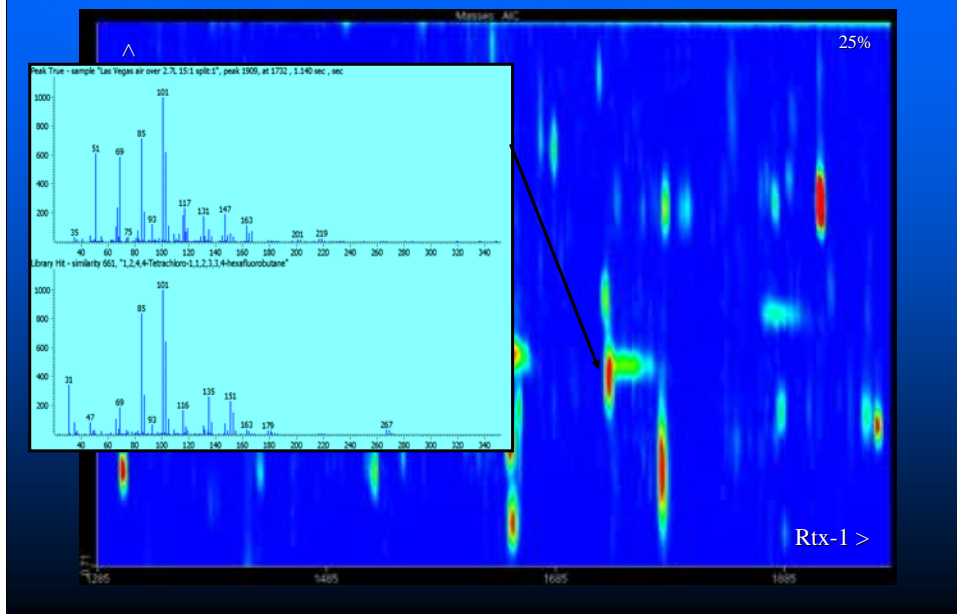
Another way to really see the complexity of the sample, and focus in on compounds of interest, is just use the mouse to draw a box (or zoom), in particular chromatographic areas.

Contour Plot of Urban Air



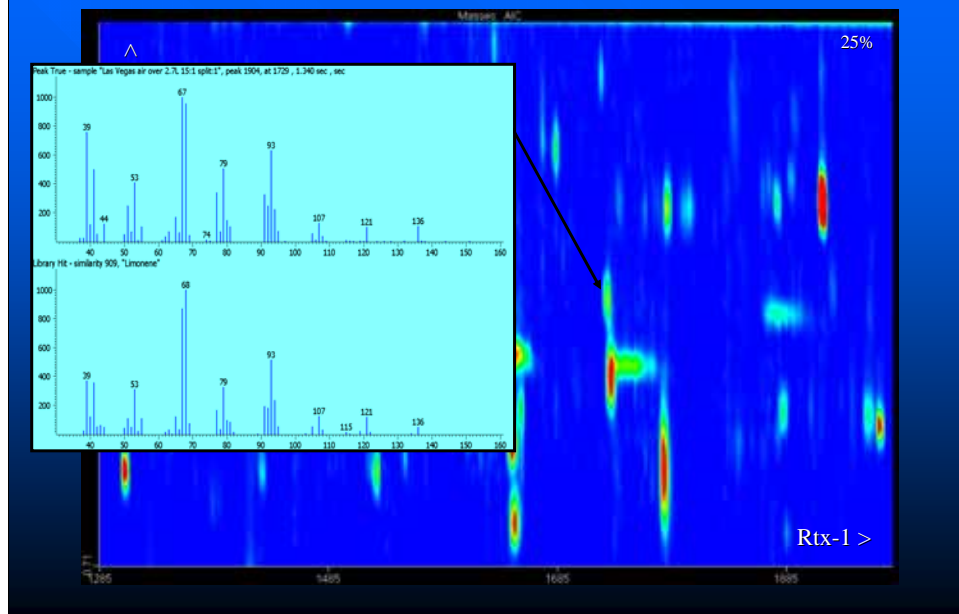
This (re-) normalizes the display and compounds “jump” out at the viewer.

Contour Plot of Urban Air



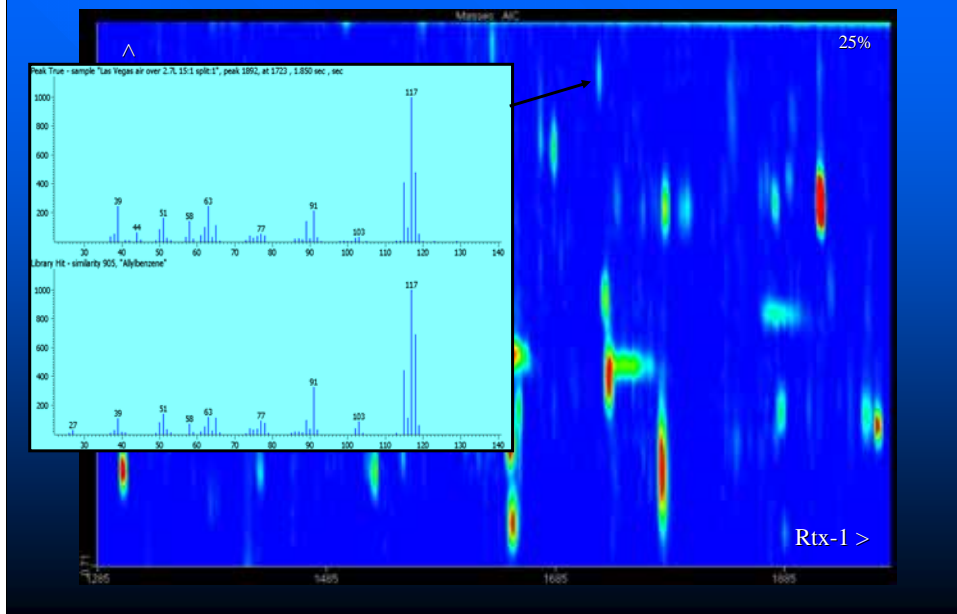
Remember, we have a mass spectrometer, so we can take spectra and library search for identification. Here is an interesting fluorinated compound that because of its low library similarity is not in the NIST library, likely.

Contour Plot of Urban Air



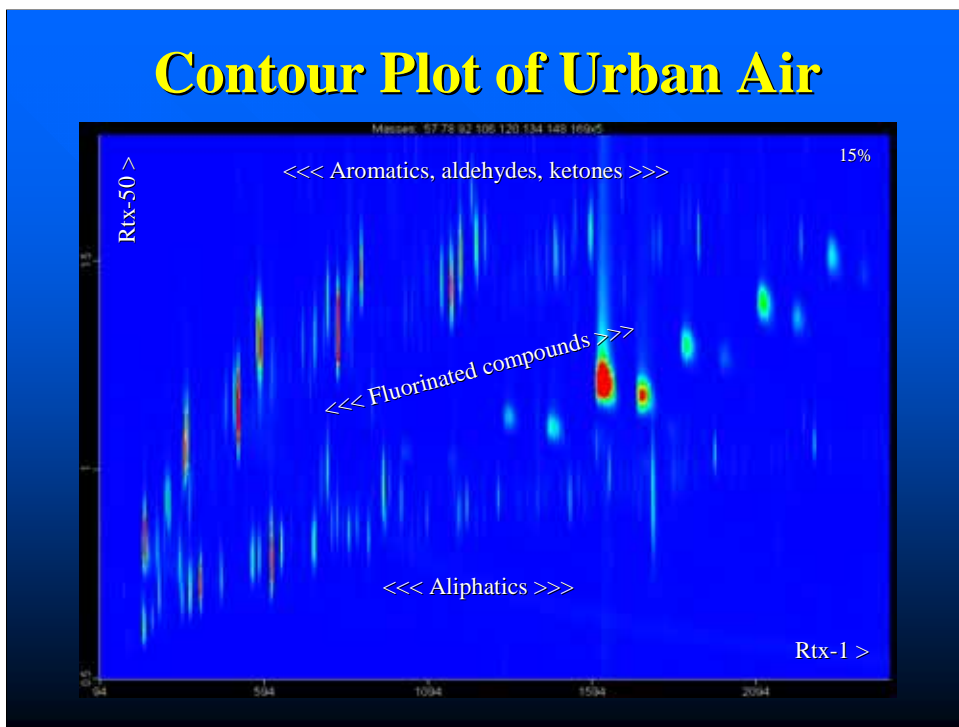
Here is another compound identified, Limonene, and this time the Similarity is much better at 900+ (out of 1000). Note that Limonene would have coeluted (in 1D) with the more concentrated fluorinated compound (below it and from the previous slide), which would have complicated its identification in a 1D analysis.

Contour Plot of Urban Air



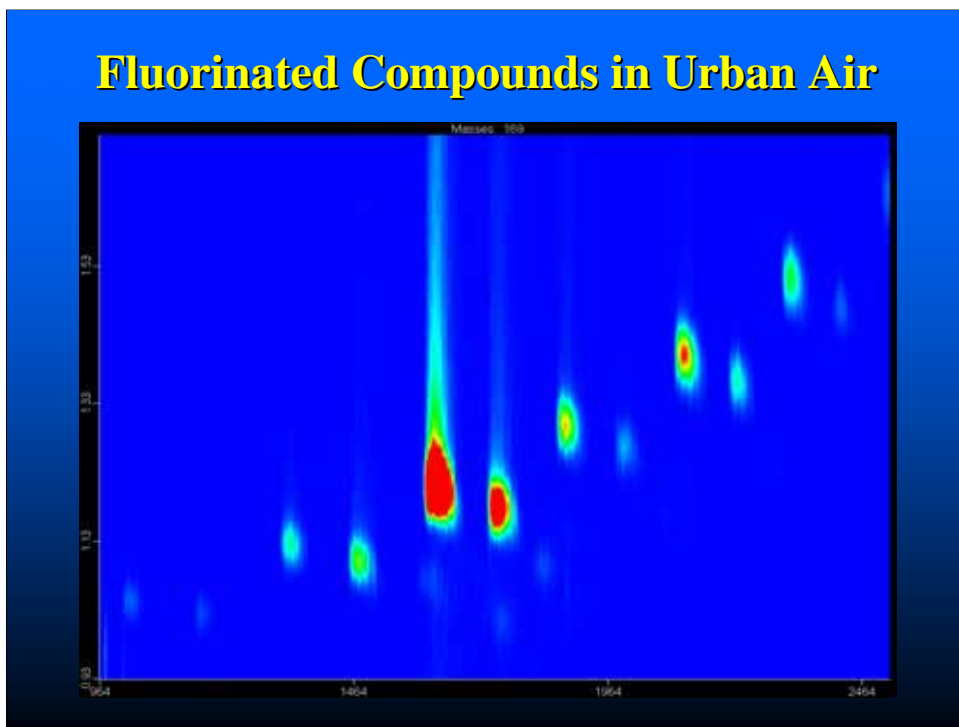
And yet another, less concentrated, compound, that would have coeluted in a 1D analysis on Rtx-1 with Limonene and the fluorinated compound, Allylbenzene (Similarity is 900+). This series of slides (this one and the previous 2) demonstrates very well the power of GCxGC, especially as coupled with TOFMS.

Contour Plot of Urban Air



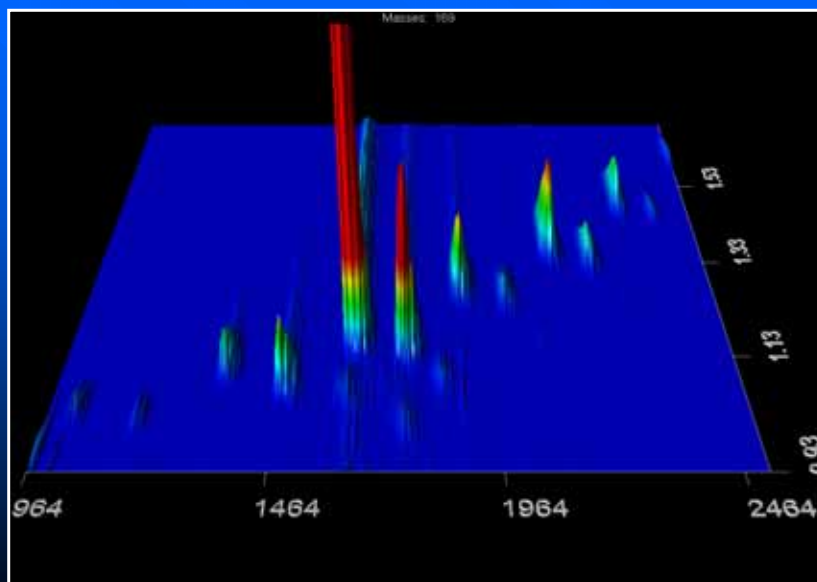
This slide gives a visual on the “order” of a contour plot that is achieved with a 100% polydimethylsiloxane column in the first dimension and a 50% diphenyl/50% polydimethylsiloxane column in the second dimension. Note the aromatics elute later in the second dimension, as expected (along with aldehydes and ketones), and that the fluorinated compounds fall between the aliphatics and aromatics.

Fluorinated Compounds in Urban Air



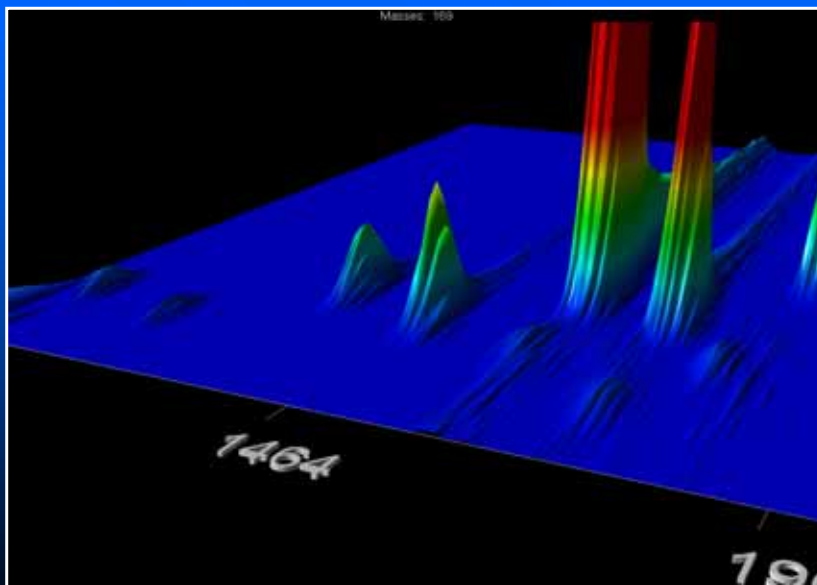
I zoomed in on the fluorinated compounds so that you could see the “ridges” associated with each “spot” in the contour plot. At first I thought there was something strange going on with the modulation, but I then figured out that there are numerous isomers for each “compound”, probably branching in the C chain, eluting very close to each other.

Fluorinated Compounds in Urban Air



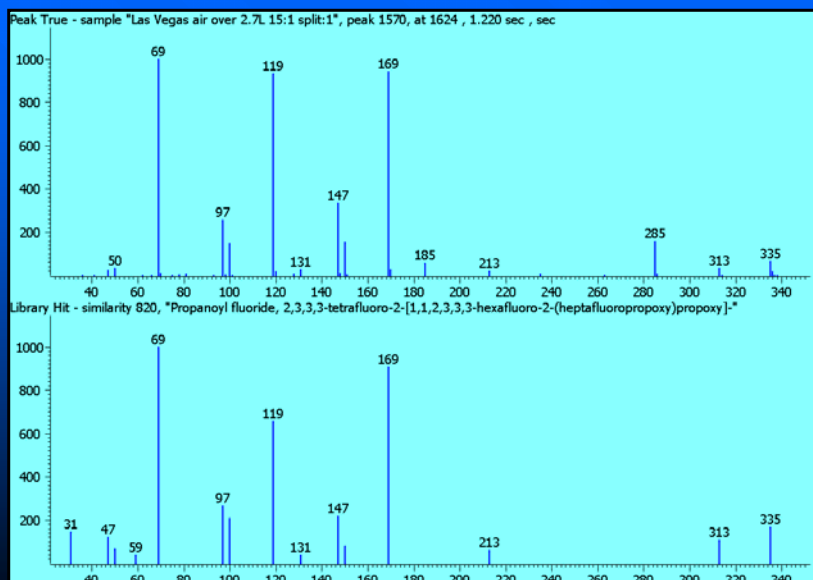
You can see that a bit better in this plot, another way to display GCxGC data, which is known as a Surface Plot. Note now that we actually have a Z axis for intensity in addition to the X axis (first dimension retention time) and the Y axis (second dimension retention time).

Fluorinated Compounds in Urban Air



And, we can turn the Surface Plot so you can see the isomers even better. There is just the slightest chromatographic separation in the first dimension for these isomers.

Fluorinated Compounds in Urban Air



Even though this fluorinated compound from the urban air sample (top spectrum) shows a good Similarity (>800) to the NIST library spectrum on the bottom, it is obvious that the library identification is incorrect due to the difference in spectra (e.g. note m/z ions 285 and 185 in the Peak True or sample spectrum). In fact, these fluorinated compounds are so volatile that I likely did not acquire at a high enough u on the upper end (I went to 350) and missed some additional ions that could be important from a diagnostic standpoint.

Fluorinated compounds in the environment is a hot topic now due to their relatively recent discovery as being ubiquitous due to their use for stain protection, etc. (think 3M's Scotchgard).

RT 1 (sec)	RT 2 (sec)	Compound Name
289	0.85	Carbon disulfide
322	0.97	Methacrolein
403	0.73	Hexane
460	0.81	Methylcyclopentane
538	0.88	Cyclohexane
616	0.79	2,2-Dimethylhexane
649	0.82	Heptane
1012	0.92	Hexafluoro-1,1,3,4-tetrachloroethane
253	1.02	Acrylonitrile
409	1.06	Chloroform
457	1.42	2-Butenal
460	1.29	1,2-Dichloroethane
517	1.14	Benzene
529	1.01	Carbon tetrachloride
970	1.29	Tetrachloroethene
1165	1.44	m- and p-Xylene

This is a table of compounds found in the urban air sample, with very high library Similarities. I have grouped them according to their second dimension retention times (RT 2 sec) so you can visualize the “structure” afforded using GCxGC, which should be another way to help with compound identification (or check the library identifications). Note that for second dimension retention times up to 1 sec, there are quite a few aliphatic compounds (e.g. hexane, cyclohexanes, heptane, etc.). Then as you move to second dimension retention times of 1-1.5 sec, you start seeing some aromatics (like the xylenes).

Note this is not only a small, abbreviated list (not complete at all) of what was found in the sample.

RT 1 (sec)	RT 2 (sec)	Compound Name
820	1.90	3-Methyl-2-butenal
1168	1.78	Phenylethyne
1192	1.50	3-Heptanone
1201	1.55	2-Heptanone
1225	1.66	Styrene
1243	1.57	o-Xylene
1480	1.52	1-Ethyl-2-methylbenzene
1591	1.57	1,2,3-Trimethylbenzene
835	2.06	Cyclopentanone
970	2.41	Furfural
1186	2.22	Cyclohexanone
1417	2.45	Benzaldehyde
1783	2.39	3-Methylbenzaldehyde
1882	2.22	Benzoic acid, methyl ester
2065	2.19	Benzenecarboxylic acid
2182	2.33	Naphthalene

Continuing as in the previous table. See the aromatics in the 1.5 to 2 sec (RT 2) range. And some ketones and aldehydes are appearing.

Then you get more polar compounds eluting later (the 2 to 2.5 sec range).

Again, this is only a partial list.

RT 1 (sec)	RT 2 (sec)	Compound Name
961	2.62	2-Cyclopentene-1-one
1303	2.61	2-Cyclohexene-1-one
1474	2.50	Benzonitrile
1684	2.70	Benzeneacetaldehyde
1771	2.50	Acetophenone
1780	2.53	1-Phenyl-1,2-propanedione
2239	2.61	2-Phenoxyethanol
2269	2.97	Benzothiazole
1327	3.36	Dihydro-5-methyl-2(3H)-furanone
1417	3.49	3-Methyl-2(5H)-furanone
1450	3.36	1-Pyrole-2,5-dione
1501	3.26	3-Aminopyrazole
1748	3.17	6-Hydroxy-2(1H)-pyridinone
1954	3.14	1-Isocyano-2-methylbenzene
2257	3.24	2-Coumaranone
2446	3.17	5H-1-Pyridine

And finally, even more polar compounds eluting in the ranges of 2.5 to 3 sec, and 3 to 3.5 sec. Someone who is really paying attention may have noticed that the modulation time (or second dimension separation time) for this work was set at 3 sec, which prompts the question, “how can you have things eluting at 3.49 sec?” The answer is that we call this “wrap around”, where the compounds that are more retained by the 50% diphenyl column here did not elute prior to the next modulation cycle beginning. When plotted, they show up as having retention times of 0.24 sec (for the 2-Coumaranone, e.g.), but that is really in the void volume of the second dimension column, and not possible for them to elute that early.

Conclusions

- GCxGC-TOFMS is an excellent tool for analysis of complex air samples
 - Sensitivity: modulation enhances detection
 - Selectivity: 2nd dimension separations
- Full mass spectra provide powerful confirmations of target (and non-target!) compounds
- Ordered chromatograms provide additional confirmation and help with identifications when no NIST library spectrum is available

Hopefully, this slide is self-explanatory.

Future Work

- Hook up a preconcentrator to GCxGC-TOFMS for a TO-15 analysis for urban air
- Quantify target compounds and define method detection limits
 - Instrument detection limits for VOCs are sub pg for GCxGC-TOFMS
- Use enhanced peak capacity of GCxGC and full mass spectrum of TOFMS to discover emerging volatile contaminants in urban air

Even though the focus of the presentation was the GCxGC-TOFMS work, to complete the study a preconcentrator and more appropriate sample collection and introduction techniques need to be employed.

In addition, quantification and method detection limits should be fully examined (it is expected that quantification will be very good, and detection limits should be excellent, far below what is typically achievable due the sensitivity enhancement afforded when using GCxGC with thermal modulation).

Surface Plot of Urban Air

