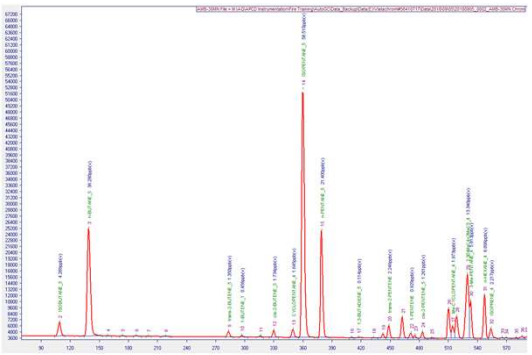
- a status update on APCD's air toxics auto-GC system

Chromatotec/CAS
Automated-Gas Chromatograph System



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- Auto-GC = automated-gas chromatograph but refers to the whole system
- The system is manufactured by Chromatotec, purchased through CAS
- Its job is to detect volatile organic compounds (VOCs) in ambient air nearly continuously
- VOCs are 1) air toxics that pose risks to human health and 2) precursors to ground level ozone
- This is a new approach for monitoring air toxics VOCs
- Typically, canisters used to collect 24-hour samples then, sent to a lab for analysis
- Auto-GC provides closer to real-time analysis than canisters
- Auto-GC system is located at APCD's Firearms Training site, downwind of Rubbertown facilities emitting VOCs of interest
- System fits into a rack generally used in air monitoring shelters rather than the instrument sitting on a benchtop
- System generates its own hydrogen gas & zero air eliminating the need for compressed gas cylinders for those 2 supply gases
- Auto-GC has 4 internal calibration gases
- Auto-GC houses actually 2 GCs - one to analyze the "light" VOCs, one to analyze the "heavy" VOCs

65 VOCs Selected for Firearms Training Auto-GC

APCD Target Compounds

Acrylonitrile
Benzene
Bromoform
1,3-Butadiene
Carbon tetrachloride
Chloroform
1,4-Dichlorobenzene
Dichloromethane
Tetrachloroethene
Trichloroethene
Vinyl chloride
Ethyl acrylate
Ethylbenzene
Methyl methacrylate
MIBK
Styrene
Toluene

Additional PAMS Compounds

Propylene
Isobutane
n-Butane
trans-2-Butene
1-Butene
cis-2-Butene
Cyclopentane
Isopentane
n-Pentane
trans-2-Pentene
1-Pentene
cis-2-pentene
Methylcyclopentane
2,3-Dimethylbutane
2-Methylpentane
3-Methylpentane
n-Hexane
Isoprene
2,2-Dimethylbutane
2,4-Dimethylpentane
Cyclohexane
2-Methylhexane
2,3-Dimethylpentane
3-Methylhexane
2,2,4-Trimethylpentane
n-Heptane
Methylcyclohexane
2,3,4-Trimethylpentane
2-Methylheptane
3-Methylheptane
n-Octane
m+p-Xylenes
o-Xylene
n-Nonane
Isopropylbenzene
a-Pinene
n-Propylbenzene
m+p-Ethyltoluene
1,3,5-Trimethylbenzene
o-Ethyltoluene
b-Pinene
1,2,4-Trimethylbenzene
n-Decane
1,2,3-Trimethylbenzene
m-Diethylbenzene
o-Diethylbenzene
n-Undecane
n- Dodecane

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- These are the compounds selected for monitoring with the auto-GC at APCD's Firearms Training site
- Initially 17 compounds selected called the APCD Target Compounds
- Those 17 include 11 VOCs from Category 1 Toxic Air Contaminants (TACs) under the STAR program (11 shown in green) & 6 VOCs known from emission inventories to be released by Rubbertown facilities & are photoreactive in forming ground level ozone (6 shown in red)
- The rest of the 65 VOCs come from EPA's PAMS list of VOCs
- PAMS = Photochemical Assessment Monitoring Stations, an EPA program going online in 2019 across US cities to better understand ozone formation
- In 2019, APCD will have 2 auto-GC systems (Firearms Training site & Cannons Lane site = PAMS site)
- 2 auto-GC systems will provide a comparison of VOC levels in 2 locations in Louisville

Benchtop Gas Chromatograph-
Flame Ionization Detector (GC-FID)

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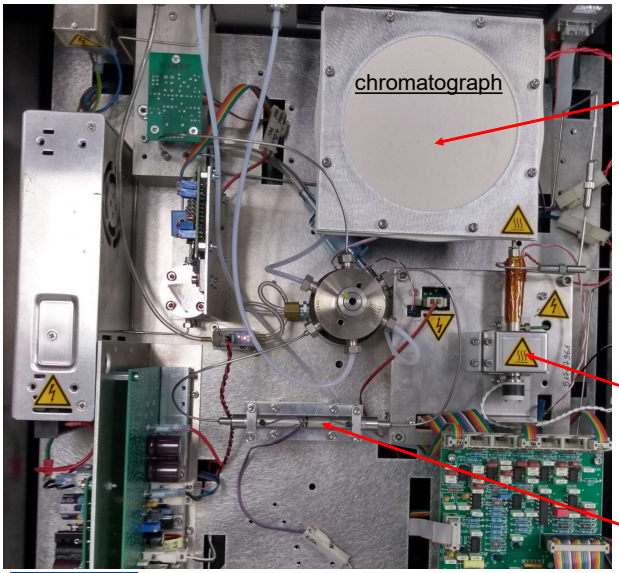
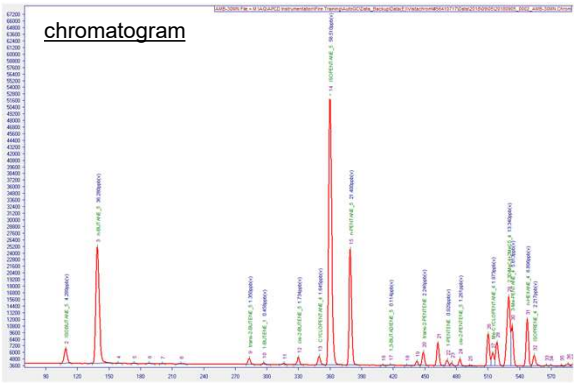
- A benchtop gas chromatograph with a flame ionization detector (FID)
- Open the front door, inside is the GC oven where a long capillary column hangs
- A sample containing a mixture of VOCs is “injected” onto the column and a clock starts ticking to time each compound’s journey through the long column
- Inside the column, the VOCs get “stuck” to a film attached to the walls of the column
- The oven temperature oven is ramped up at a programmed rate
- VOCs are released from the film when the column reaches a temperature in which each VOC is no longer “stuck” to the film
- VOCs are carried by a gas through the rest of the column to the exit where the FID is waiting to detect VOCs
- When the FID detects a VOC, a peak appears in a chromatogram and the time is recorded = Retention Time
- The GC column’s job is to separate VOCs from one another such that exit at their own unique retention time
- Retention times need to stay consistent run after run in order to identify VOCs in samples

Inside Auto-GC-FID





Vocabulary:
A chromatograph uses chromatography to generate a chromatogram.

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- The cover removed from one of the GCs in APCD's auto-GC system
- Walk through from sample collection to detection…
- Sample first collected onto preconcentrator trap for set amount of time, improves sensitivity
- Trap is rapidly heated, back flushed with hydrogen gas and sample is swept onto the column = "injection"
- Chromatograph = column surrounded by a heater and insulation (not an oven box as shown with benchtop GC)
- As VOCs exit the column separately, FID is waiting to detect them
- A chromatogram is generated, first compound to exit column is on the left side of the chromatogram

Field Evaluation

- Verified & Determined Peaks' Retention Time Windows (RTWs)
- Identified Coeluting Compounds
  - Elution order for each GC column (VOC lineup)
  - EPA prepared canisters
    - PAMS compounds (57)
    - TO-14 (39)
    - TO-15 Subset (25)
    - TO-15 Plus (16)

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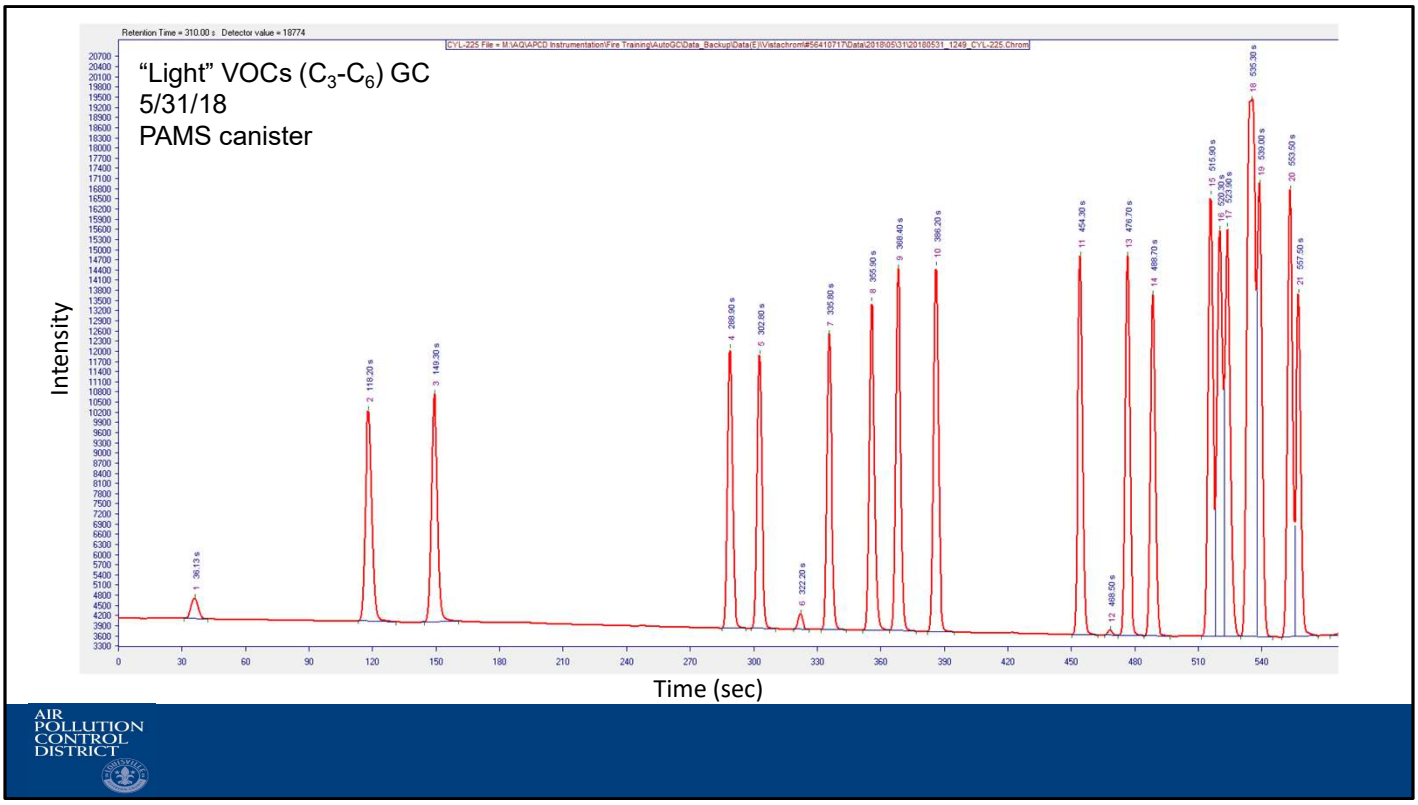
- Discuss some of the things we have learned this year
- First task was to verify retention times (RTs) of VOCs (remember with FID detection, RT is what is used to identify the VOC in an analyzed sample)
- Also, wanted to identify any compounds with the same RTs = coelution
- If there are coeluting compounds, can't say for certain which compound is actually being detected in ambient
- To assess retention times, need 2 things: 1) the order that VOCs exit each GC's column = Elution order, 2) canisters that contain compounds of interest (number in parentheses is number of compounds in each canister)



- Results of PAMS canister run on C3-C6 GC (light VOC GC, C3=compounds containing 3 carbon atoms, C6=compounds containing 6 carbon atoms)
- Up until 500 seconds, there is good peak separation and resolution, each peak represents one VOC (no coelution) therefore each VOC has its own unique RT – this is what we want

"Light" VOCs (C_3-C_6) GC Substance Table

#	Name	RT Min	RT Max
1	PROPENE_5	15	25
2	ISOBUTANE_5	100	110
3	n-BUTANE_5	130	140
4	trans-2-BUTENE_5	276	286
5	1-BUTENE_1	290	300
6	VINYL CHLORIDE_3	307	310
7	cis-2-BUTENE_5	322	332
8	CYCLOPENTANE_4	342	352
9	ISOPENTANE_5	354	364
10	n-PENTANE_5	372	382
11	1,3-BUTADIENE_5	410	418
12	trans-2-PENTENE	442	450
13	1-PENTENE	465	471
14	cis-2-PENTENE_5	476	486
15	Me-CYCLOPENTANE_4	509	514
16	2,3DiMeC4+2MeC5_4	522	529
17	3-Me-PENTANE_4	528	534
18	n-HEXANE_4	540	548
19	ISOPRENE_4	548	556
20	DICHLOROMETHANE	559	564

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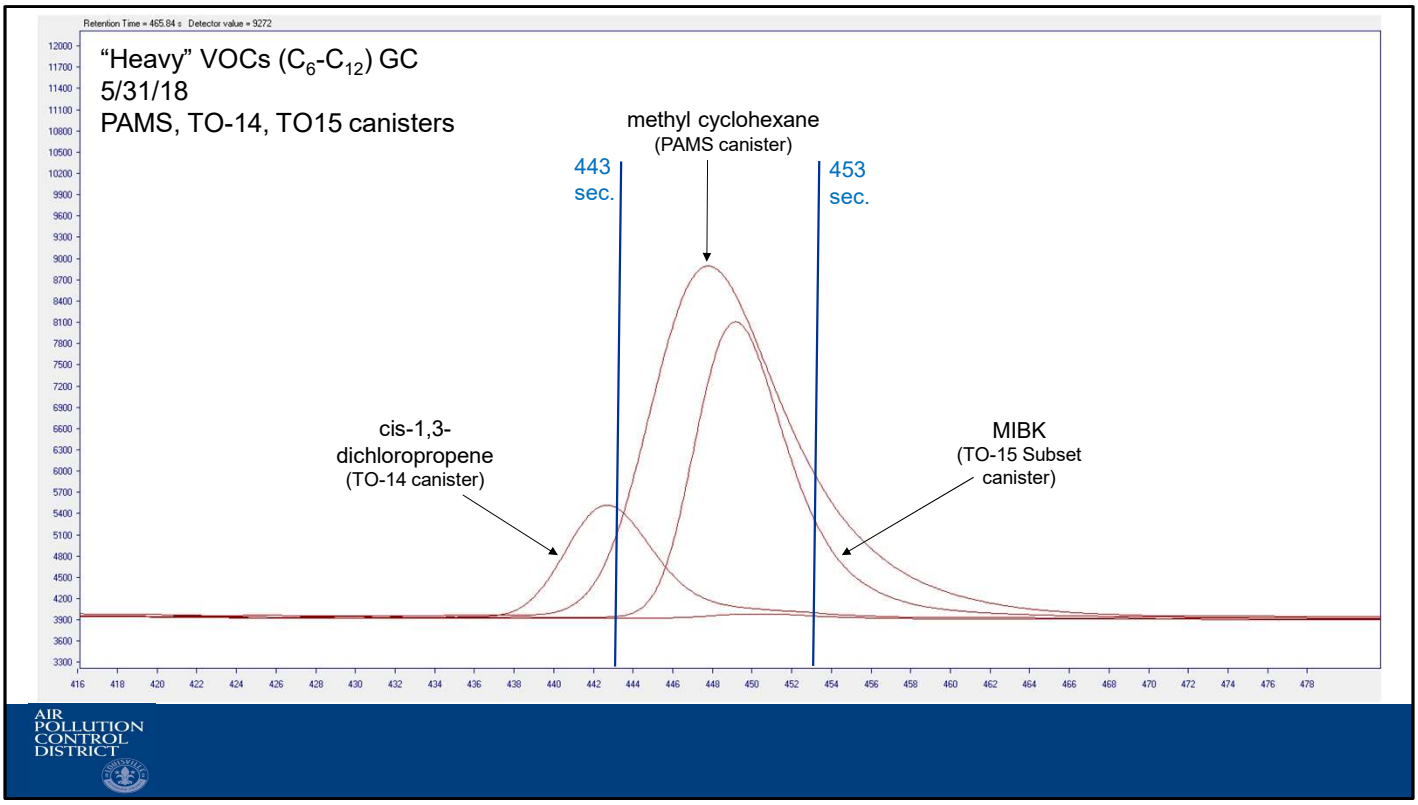
- When a VOC has its own unique RT, a Substance Table can be created
- A Substance Table is a lookup table in the auto-GC software
- A Substance Table contains the names of VOCs interested in analyzing and the RT range (minimum to maximum) one should expect to see that VOC in a chromatogram
- Minimum and maximum RTs create the retention time window (RTW) for each VOC
- RTWs should be no more than 10 seconds wide
- Once the Substance Table is created for each GC and an ambient, blank, or calibration sample is analyzed, if a peak in the chromatogram falls within one of the RTWs listed in the Substance Table, that peak is given the appropriate name
- Then, a concentration for that VOC can be calculated



- No major coelution concerns with C3-C6 GC
- With C6-C12 GC several coeluting compounds discovered from the canister runs (C6=compounds containing 6 carbon atoms, C12=compounds containing 12 carbon atoms)
- This shows 3 canister runs overlaid
- Methyl cyclohexane is contained in the PAMS canister, methyl cyclohexane RT=448 seconds, RTW=443-453 seconds
- Methyl isobutyl ketone (MIBK) is contained in the TO-15 Subset toxics canister, MIBK RT=450 seconds which is in methyl cyclohexane's RTW
- If a peak was detected between 443-453 seconds in an ambient sample, there would be no way to know for sure whether the peak was methyl cyclohexane or MIBK or a combination of the 2 VOCs
- This is what complete coelution looks like
- If we are to say with confidence how much of methyl cyclohexane and MIBK are present in an ambient sample, must find a way to pull these 2 peaks apart in the chromatogram

Field Evaluation

- Verified & Determined Peaks' Retention Time Windows (RTWs)
- Identified Coeluting Compounds
- Retention Time Shifting

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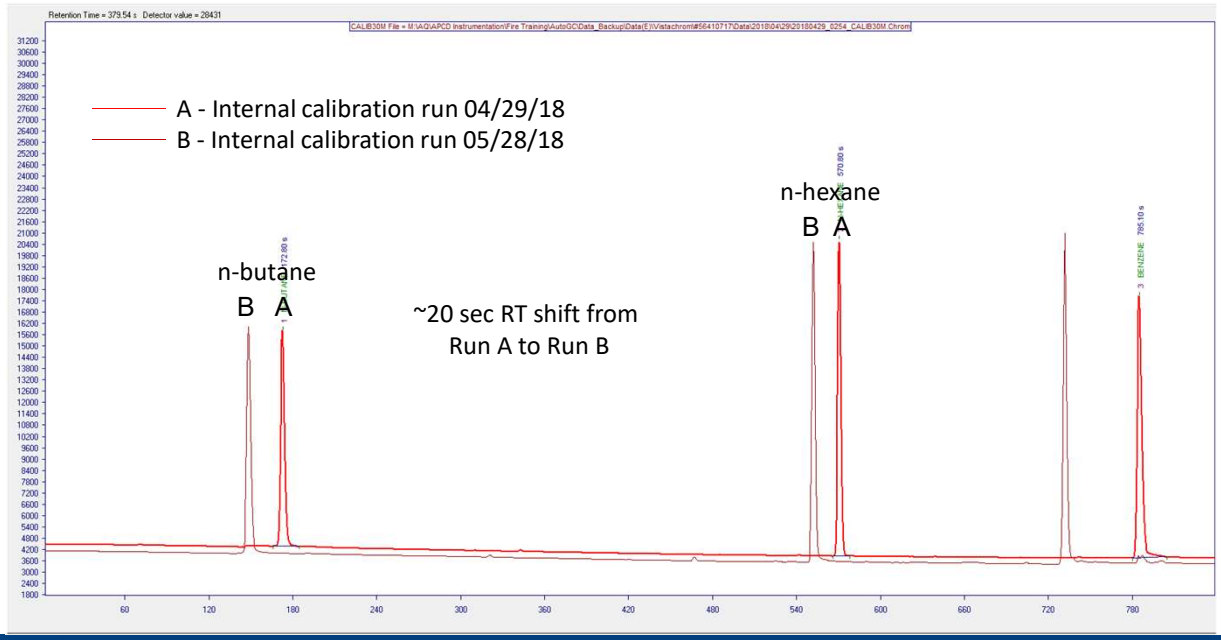
- Goal today is to explain what we've learned and demonstrate some of the issues that have prevented field-readiness of the auto-GC system
- Determined RTs for the 65 selected compounds and identified which of those compounds have coelution concerns
- Next, retention time shifting observed with C3-C6 GC

“Light” VOCs (C_3-C_6) GC Retention Time Shifting



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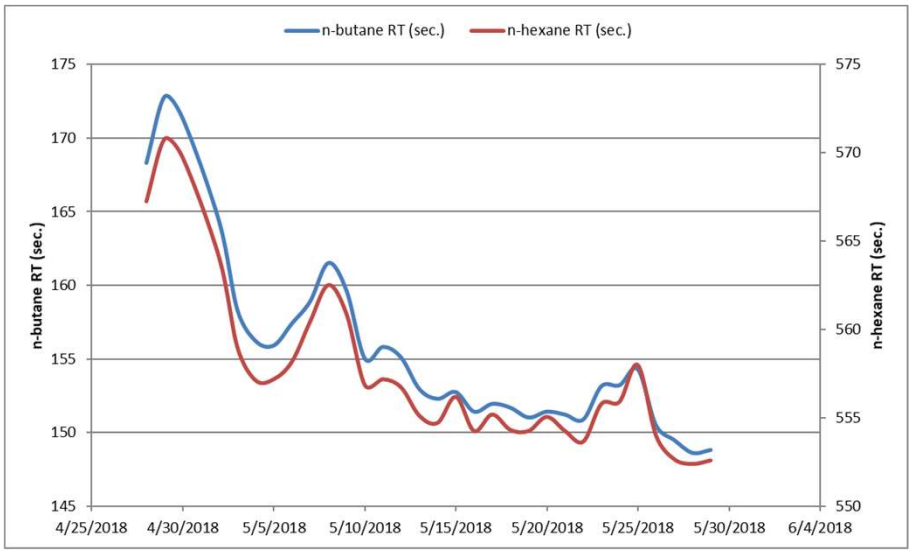
- To demonstrate RT shifting, 2 internal calibration runs on the C3-C6 GC
- Focus on n-butane & n-hexane internal calibration gases
- Peaks labeled with A’s are from the calibration run on 4/29/18, peaks labeled with B’s are from the calibration run on 5/28/18
- Over the course of a month, the RTs of each of these VOCs had shifted about 20 seconds such that they were exiting the column sooner than they had been a month earlier
- The Substance Table used on 4/29/18 to identify n-butane & n-hexane may not identify those compounds on 5/28/18 since RTWs are no more than 10 seconds wide
- Substance Tables can be updated and chromatograms reprocessed but ideally RTs should be more stable

Retention Times of n-butane & n-hexane 4/28/18 – 5/29/18



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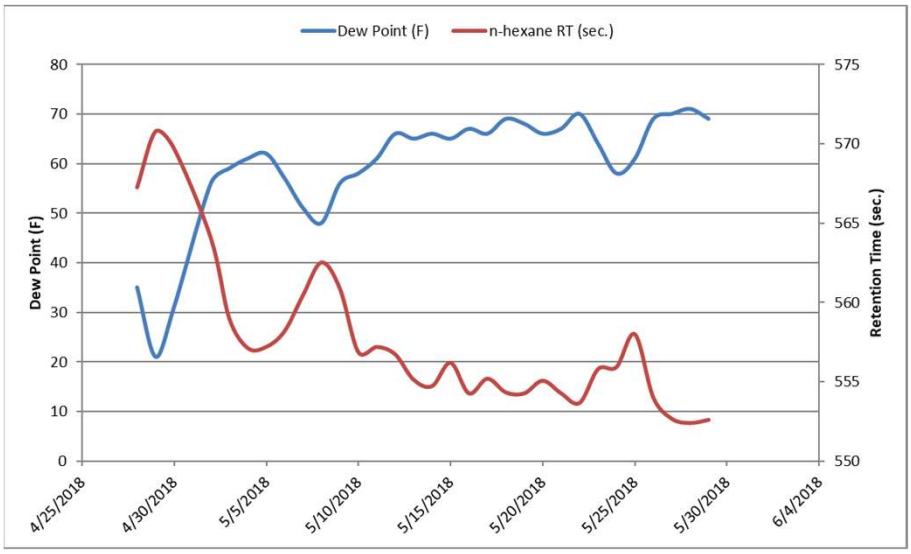
- Calibration runs are performed every night
- This shows RT trends for n-butane & n-hexane from 4/28/18 through 5/29/18 (RTs getting earlier and earlier as we approached summer)
- Noticed RT shifting was worse on rainy days
- Suggestion made to see if any correlation between retention time and dew point

Retention Time & Dew Point 4/28/18 – 5/29/18



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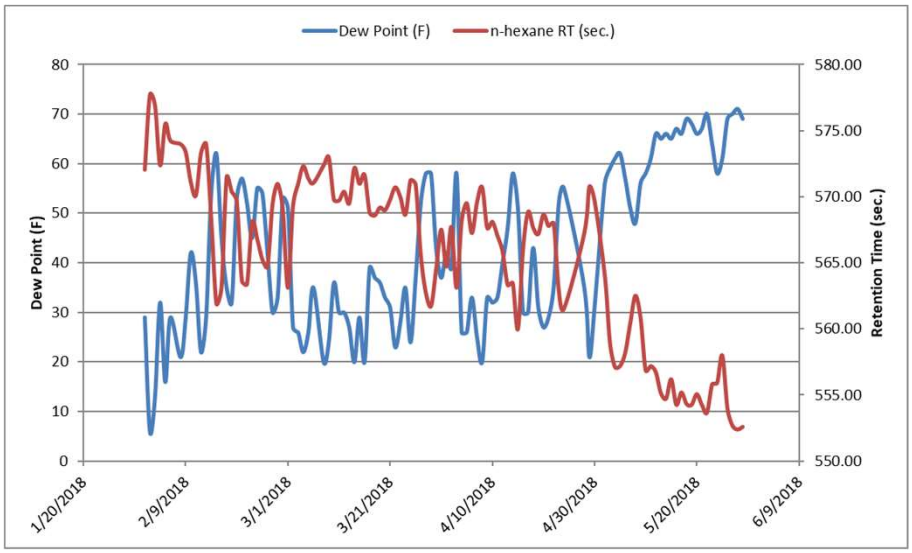
- RTs of n-hexane over same time period (4/28/18-5/29/18) and daily dew point values
- A close inverse relationship
- As dew point increased (humidity in air increased), RT became earlier
- How long had these 2 factors been linked?

Retention Time & Dew Point 2/1/18 – 5/28/18



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- RTs of n-hexane going back to February and daily dew point values
- RT and dew point on C3-C6 GC have been linked for a long time
- C3-C6 GC column is susceptible to water vapor molecules occupying places on GC column's film (on column walls)
- VOCs are crowded out and forced to exit column sooner than they would if water vapor wasn't present
- Nafion dryers in place to remove water vapor from samples before they enter C3-C6 GC preconcentrator trap, but this shows that they are not as effective as they should be

Field Evaluation

- Verified & Determined Peaks' Retention Time Windows (RTWs)
- Identified Coeluting Compounds
- Retention Time Shifting
- GC columns are not meeting target temperatures

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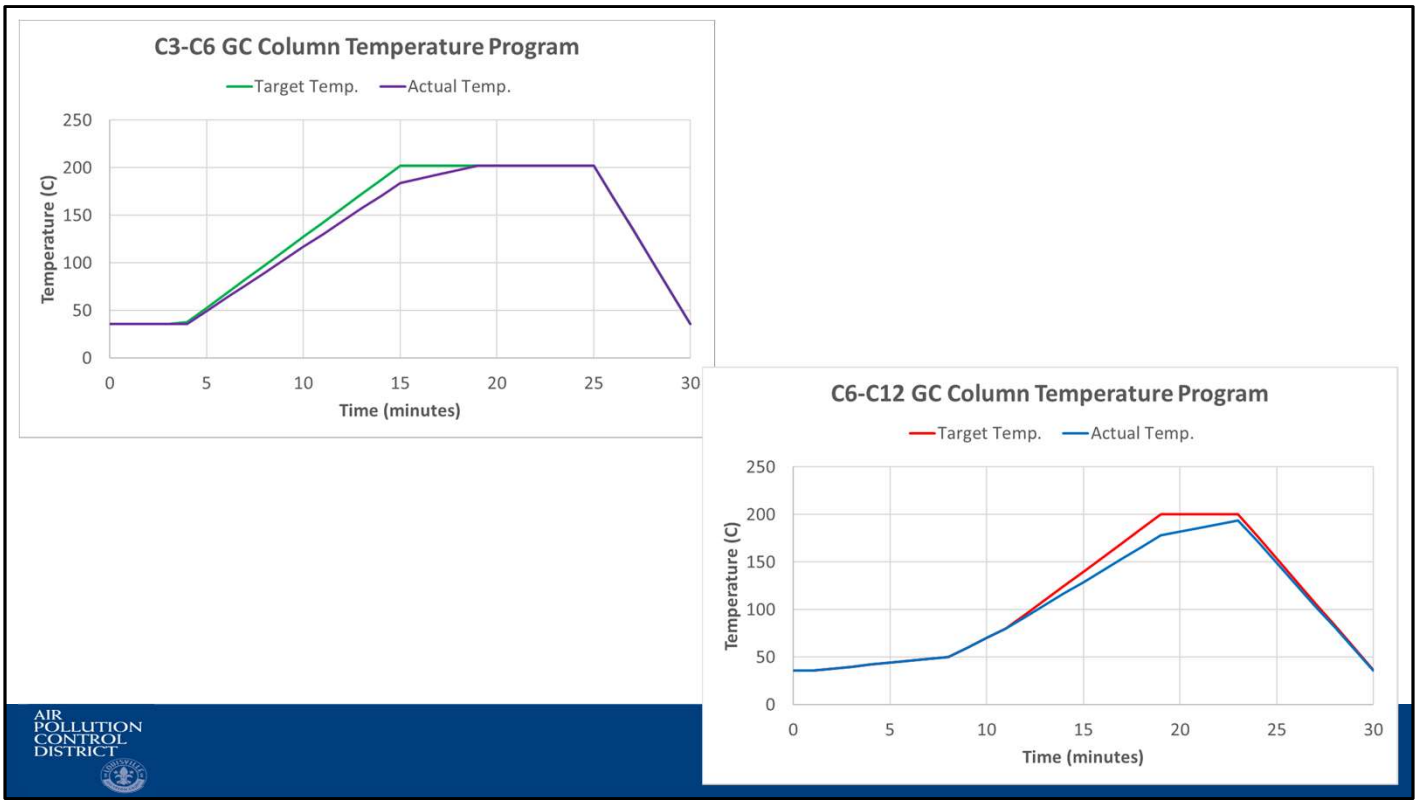
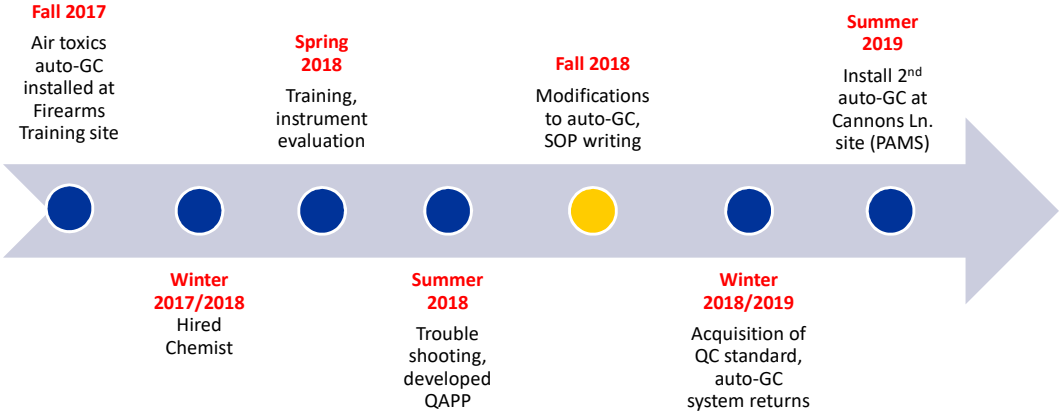
- Remember that heat is applied to the GC columns to get the "stuck" VOCs to release from the film on the column walls
- Column temperature therefore determines retention time of each VOC
- Therefore, it's important that the GC column temperature profile during analysis be the same run after run



- Temperature program for either GC column is a 30 minute cycle performed each time a collected sample is analyzed
- C3-C6 GC column temperature program is shown in green - GC column begins at ambient temperature, heater turns on and ramps up the column temperature at a programmed rate to 200 degrees Celsius, column temperature is held at 200C for about 10 minutes, then cools off to ambient ready to analyze the next collected mixture of VOCs
- Purple profile shows the actual C3-C6 GC column temperature where the column eventually reaches 200C but later than programmed to do so
- C6-C12 GC column temperature program is shown in red
- Blue profile shows the actual C6-C12 GC column temperature where the column almost reaches 200C but doesn't make it before cooling off to ambient for the next cycle to begin
- Good news - the purple and blue temperature profiles are followed by each GC run after run (consistent/precise)
- Bad news - since the columns are not reaching the programmed target temperatures (not accurate) there is possibly a problem with the column heaters or perhaps their insulation

Air Toxics & PAMS VOC Monitoring Timeline



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Next Steps

- Auto-GC system at CAS
  - Fix column heating (both GCs)
  - Adjust column temperature ramp, lengthen column (C_6-C_{12} GC)
  - Reduce moisture (C_3-C_6 GC)
  - Upgrades to all PAMS systems
- Calibration cylinder w/68 VOCs
- AirVision updates to handle VOC data
- 2nd auto-GC for PAMS Network……Summer 2019
- Report auto-GC results to website……Louisville Air Watch 2.0
  - Update every hour
  - More user friendly
  - Historical data

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- APCD air toxics auto-GC system is at CAS's facility for modifications and upgrades (some due to issues discovered during APCD field evaluation, others are based on requests by EPA for the PAMS auto-GC systems)
- All agencies with CAS PAMS auto-GCs were returned to CAS for modifications and upgrades
- When APCD auto-GC system returns, APCD will have a calibration cylinder w/68 VOCs to run each night as a retention time check
- APCD data handling software, AirVision, is being upgraded by Agilaire to be able to handle all of the VOC data
- Goal is still to report auto-GC VOC results to our website, which is also being upgraded to Louisville Air Watch 2.0
- New feature = historical data will be available

Questions?

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References

Air Pollution Control District

Louisvilleky.gov/APCD

Federal Regulations

Code of Federal Regulations (CFR)

EPA Auto-GC Shootout

https://www3.epa.gov/ttnamti1/files/2014conference/posterpoitras.pdf

EPA PAMS VOC List

https://www3.epa.gov/ttnamti1/files/ambient/pams/targetlist.pdf

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