Field Evaluation of an Automated-Gas Chromatograph System for Monitoring Volatile Organic Compounds (VOCs) in Ambient Air

Louisville Metro Air Pollution Control District

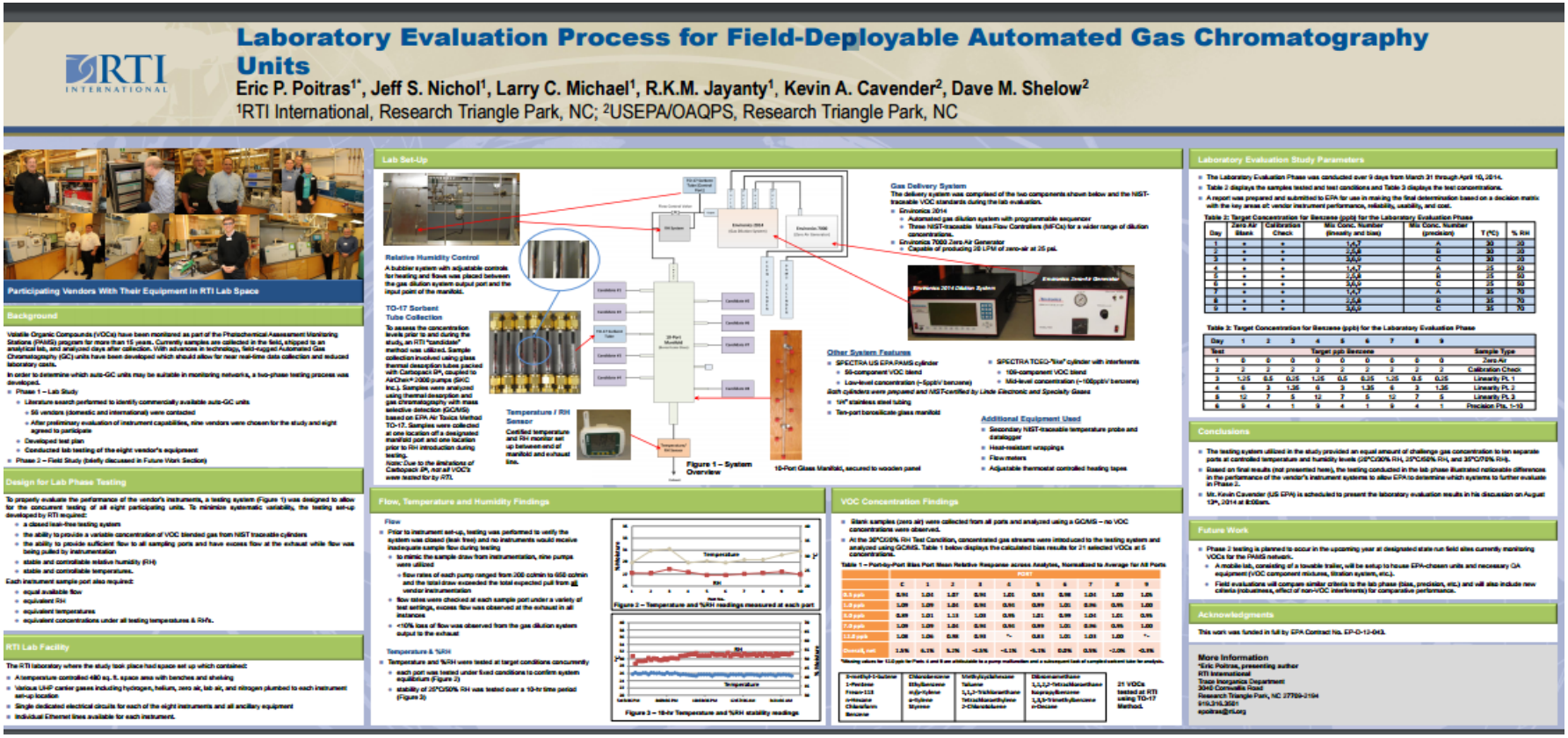
Louisville, KY

March 26, 2019

APCD Air Monitoring

- APCD is a Primary Quality Assurance Organization
- Robust Criteria Pollutant Network – including NCore, Near Road
- Adding Photochemical Assessment Monitoring (PAMS) in 2019

Auto GC "Shootout"



Laboratory Evaluation Process for Field-Deployable Automated Gas Chromatography Units

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Participating Vendors With Their Equipment in RTI Lab Space

Background

Volatile Organic Compounds (VOCs) have been monitored as part of the Photochemical Assessment Monitoring Stations (PAMS) program for more than 15 years. Currently samples are collected in the field, shipped to an analytical lab, and analyzed days after collection. With advances in technology, field-rugged Automated Gas Chromatography (GC) units have been developed which should allow for near real-time data collection and reduced laboratory costs.

In order to determine which auto-GC units may be suitable in monitoring networks, a two-phase testing process was developed.

- Phase 1 – Lab Study
  - Literature search performed to identify commercially available auto-GC units
  - 56 vendors (domestic and international) were contacted
  - After preliminary evaluation of instrument capabilities, nine vendors were chosen for the study and eight agreed to participate
  - Developed test plan
  - Conducted lab testing of the eight vendor's equipment
- Phase 2 – Field Study (briefly discussed in Future Work Section)

Design for Lab Phase Testing

To properly evaluate the performance of the vendor's instruments, a testing system (Figure 1) was designed to allow for the concurrent testing of all eight participating units. To minimize systematic variability, the testing set-up developed by RTI required:

- a closed loop-free testing system
- the ability to provide a variable concentration of VOC blended gas from NIST traceable cylinders
- the ability to provide sufficient flow to all sampling ports and have excess flow at the exhaust while flow was being pulled by instrumentation
- stable and controllable relative humidity (RH)
- stable and controllable temperatures.

Each instrument sample port also required:

- equal available flow
- equivalent RH
- equivalent temperatures
- equivalent concentrations under all testing temperatures & RH's.

RTI Lab Facility

The RTI laboratory where the study took place had space set up which contained:

- A temperature controlled 480 sq. ft. space area with benches and shelving
- Various UHP carrier gases including hydrogen, helium, zero air, lab air, and nitrogen plumbed to each instrument set-up location
- Single dedicated electrical circuits for each of the eight instruments and all ancillary equipment
- Individual Ethernet lines available for each instrument.

Lab Set-Up

Figure 1 – System Overview

Relative Humidity Control

A bubbler system with adjustable controls for heating and flows was placed between the gas dilution system output port and the input port of the manifold.

TO-17 Sorbent Tube Collection

To assess the concentration levels prior to and during the study, an RTI "candidate" method was utilized. Sample collection involved using glass thermal desorption tubes packed with Carbopack B®, coupled to AirChek® 2000 pumps (SKC Inc.). Samples were analyzed using thermal desorption and gas chromatography with mass selective detection (GC/MS) based on EPA Air Toxics Method TO-17. Samples were collected at one location off a designated manifold port and one location prior to RH introduction during testing.

Note: Due to the limitations of Carbopack B®, not all VOC's were tested for by RTI.

Temperature / RH Sensor

Certified temperature and RH monitor set up between end of manifold and exhaust line.

Gas Delivery System

The delivery system was comprised of the two components shown below and the NIST-traceable VOC standards during the lab evaluation.

- Environics 2014
  - Automated gas dilution system with programmable sequencer
  - Three NIST-traceable Mass Flow Controllers (MFCs) for a wider range of dilution concentrations.
- Environics 7000 Zero Air Generator
  - Capable of producing 20 LPM of zero-air at 25 psi.

Other System Features

- SPECTRA US EPA PAMS cylinder
  - 56-component VOC blend
  - Low-level concentration (~5ppbV benzene)
- SPECTRA TCEQ-"lite" cylinder with interferents
  - 109-component VOC blend
  - Mid-level concentration (~100ppbV benzene)

Both cylinders were prepared and NIST-certified by Linde Electronic and Specialty Gases

- 1/4" stainless steel tubing
- Ten-port borosilicate glass manifold

Additional Equipment Used

- Secondary NIST-traceable temperature probe and datalogger
- Heat-resistant wrappings
- Flow meters
- Adjustable thermostat controlled heating tapes

10-Port Glass Manifold, secured to wooden panel

Flow, Temperature and Humidity Findings

Flow

- Prior to instrument set-up, testing was performed to verify the system was closed (leak free) and no instruments would receive inadequate sample flow during testing
  - to mimic the sample draw from instrumentation, nine pumps were utilized
    - flow rates of each pump ranged from 200 cc/min to 650 cc/min and the total draw exceeded the total expected pull from all vendor instrumentation
  - flow rates were checked at each sample port under a variety of test settings, excess flow was observed at the exhaust in all instances
  - <10% loss of flow was observed from the gas dilution system output to the exhaust

Temperature & %RH

- Temperature and %RH were tested at target conditions concurrently
  - each port was tested under fixed conditions to confirm system equilibrium (Figure 2)
  - stability of 25°C/50% RH was tested over a 10-hr time period (Figure 3)

Figure 2 – Temperature and %RH readings measured at each port

Figure 3 – 10-hr Temperature and %RH stability readings

VOC Concentration Findings

- Blank samples (zero air) were collected from all ports and analyzed using a GC/MS – no VOC concentrations were observed.
- At the 25°C/50% RH Test Condition, concentrated gas streams were introduced to the testing system and analyzed using GC/MS. Table 1 below displays the calculated bias results for 21 selected VOCs at 6 concentrations.

Table 1 – Port-by-Port Bias Port Mean Relative Response across Analytes, Normalized to Average for All Ports

	PORT									
	C	1	2	3	4	5	6	7	8	9
0.5 ppb	0.91	1.01	1.07	0.91	1.01	0.93	0.98	1.01	1.00	1.05
1.0 ppb	1.09	1.09	1.01	0.91	0.91	0.99	1.01	0.96	0.95	1.00
5.0 ppb	0.89	1.01	1.13	1.03	0.95	1.01	0.99	1.01	1.01	0.95
7.0 ppb	1.09	1.09	1.01	0.91	0.91	0.99	1.01	0.96	0.95	1.00
11.0 ppb	1.08	1.06	0.98	0.93	~	0.93	1.01	1.03	1.00	~
Overall, net	1.0%	6.1%	5.1%	-1.1%	-5.1%	-5.1%	0.0%	0.5%	-2.0%	-0.1%

Missing values for 11.0 ppb for Ports 4 and 8 are attributable to a pump malfunction and a subsequent lack of sampled sorbent tube for analysis.

2-methyl-1-butene	Chlorobenzene	Methylcyclohexane	Dibromomethane
1-Pentene	Ethylbenzene	Toluene	1,3,5,2-Tetrachlorobenzene
Freon-113	o/p-xylene	1,1,2-Trichloroethane	Isopropylbenzene
n-Hexane	a-Xylene	Tetrachloroethylene	1,3,5-Trimethylbenzene
Chloroform	Styrene	2-Chlorotoluene	n-Decane
Benzene			

21 VOCs tested at RTI using TO-17 Method.

Laboratory Evaluation Study Parameters

- The Laboratory Evaluation Phase was conducted over 9 days from March 31 through April 10, 2014.
- Table 2 displays the samples tested and test conditions and Table 3 displays the test concentrations.
- A report was prepared and submitted to EPA for use in making the final determination based on a decision matrix with the key areas of: vendor instrument performance, reliability, usability, and cost.

Table 2: Target Concentration for Benzene (ppb) for the Laboratory Evaluation Phase

Day	Zero Air Blank	Calibration Check	Mix Conc. Number (linearity and bias)	Mix Conc. Number (precision)	T (°C)	% RH
1	+	+	1,4,7	A	30	20
2	+	+	2,5,8	B	30	20
3	+	+	3,6,9	C	30	20
4	+	+	1,4,7	A	25	50
5	+	+	2,5,8	B	25	50
6	+	+	3,6,9	C	25	50
7	+	+	1,4,7	A	35	70
8	+	+	2,5,8	B	35	70
9	+	+	3,6,9	C	35	70

Table 3: Target Concentration for Benzene (ppb) for the Laboratory Evaluation Phase

Day	1	2	3	4	5	6	7	8	9	
Test	Target ppb Benzene									Sample Type
1	0	0	0	0	0	0	0	0	0	Zero Air
2	2	2	2	2	2	2	2	2	2	Calibration Check
3	1.25	0.5	0.15	1.25	0.5	0.25	1.25	0.5	0.15	Linearity Pt. 1
4	6	3	1.35	6	3	1.35	6	3	1.35	Linearity Pt. 2
5	12	7	5	12	7	5	12	7	5	Linearity Pt. 3
6	5	4	1	9	4	1	9	4	1	Precision Pts. 1-10

Conclusions

- The testing system utilized in the study provided an equal amount of challenge gas concentration to ten separate ports at controlled temperature and humidity levels (25°C/20% RH, 25°C/50% RH, and 35°C/70% RH).
- Based on final results (not presented here), the testing conducted in the lab phase illustrated noticeable differences in the performance of the vendor's instrument systems to allow EPA to determine which systems to further evaluate in Phase 2.
- Mr. Kevin Cavender (US EPA) is scheduled to present the laboratory evaluation results in his discussion on August 13th, 2014 at 8:00am.

Future Work

- Phase 2 testing is planned to occur in the upcoming year at designated state run field sites currently monitoring VOCs for the PAMS network.
  - A mobile lab, consisting of a towable trailer, will be setup to house EPA-chosen units and necessary QA equipment (VOC component mixtures, titration system, etc.).
  - Field evaluations will compare similar criteria to the lab phase (bias, precision, etc.) and will also include new criteria (robustness, effect of non-VOC interferents) for comparative performance.

Acknowledgments

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More Information

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Toxics Background

1940s

WWII rubber manufacturing

"Rubbertown"

2000-2001

West Louisville Air Toxics Study (WLATS)

2005

Strategic Toxics Air Reduction (STAR) Program

2005-2013

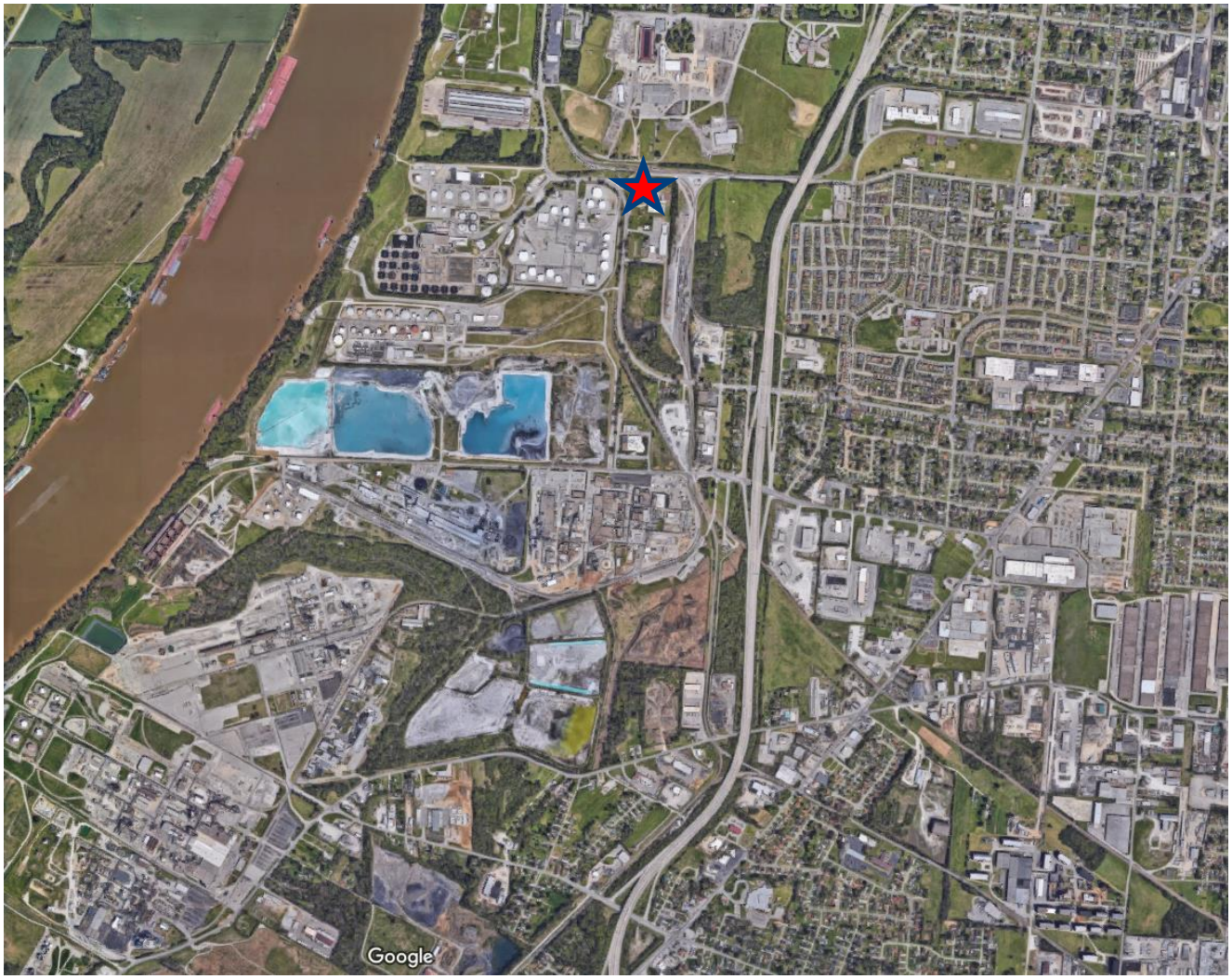
University of Louisville EPA TO-15 air toxics monitoring

2017

APCD installed auto-GC

Rubbertown Area

N



~3.5 km

★ = APCD Auto-GC

VOCs Selected for Monitoring

Louisville APCD Target Compounds

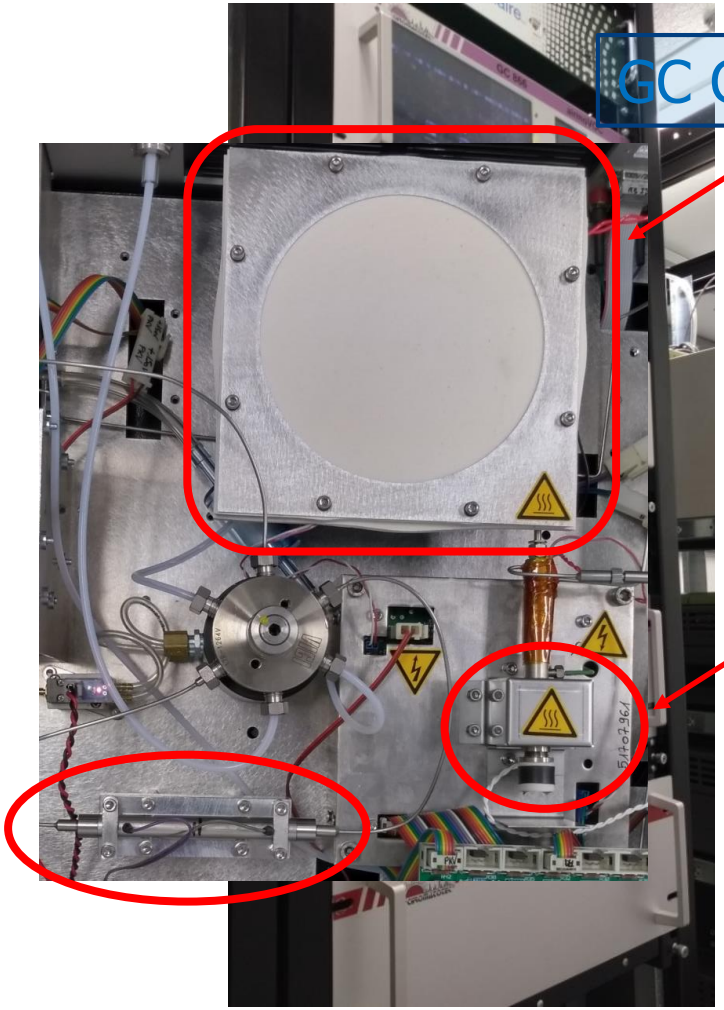
1,3-butadiene
acrylonitrile
benzene
bromoform
chloroform
carbon tetrachloride
1,4-dichlorobenzene
methylene chloride
tetrachloroethylene
trichloroethylene
vinyl chloride
ethyl acrylate*

ethyl acrylate
ethylbenzene
MIBK
methyl methacrylate
toluene
styrene

48 additional PAMS priority & optional C_3-C_{12} compounds

Chromatotec/CAS Auto-GC System

- Zero air generator
- Hydrogen generator
- Internal calibration
- C_3-C_6 GC
- C_6-C_{12} GC+Supervisor

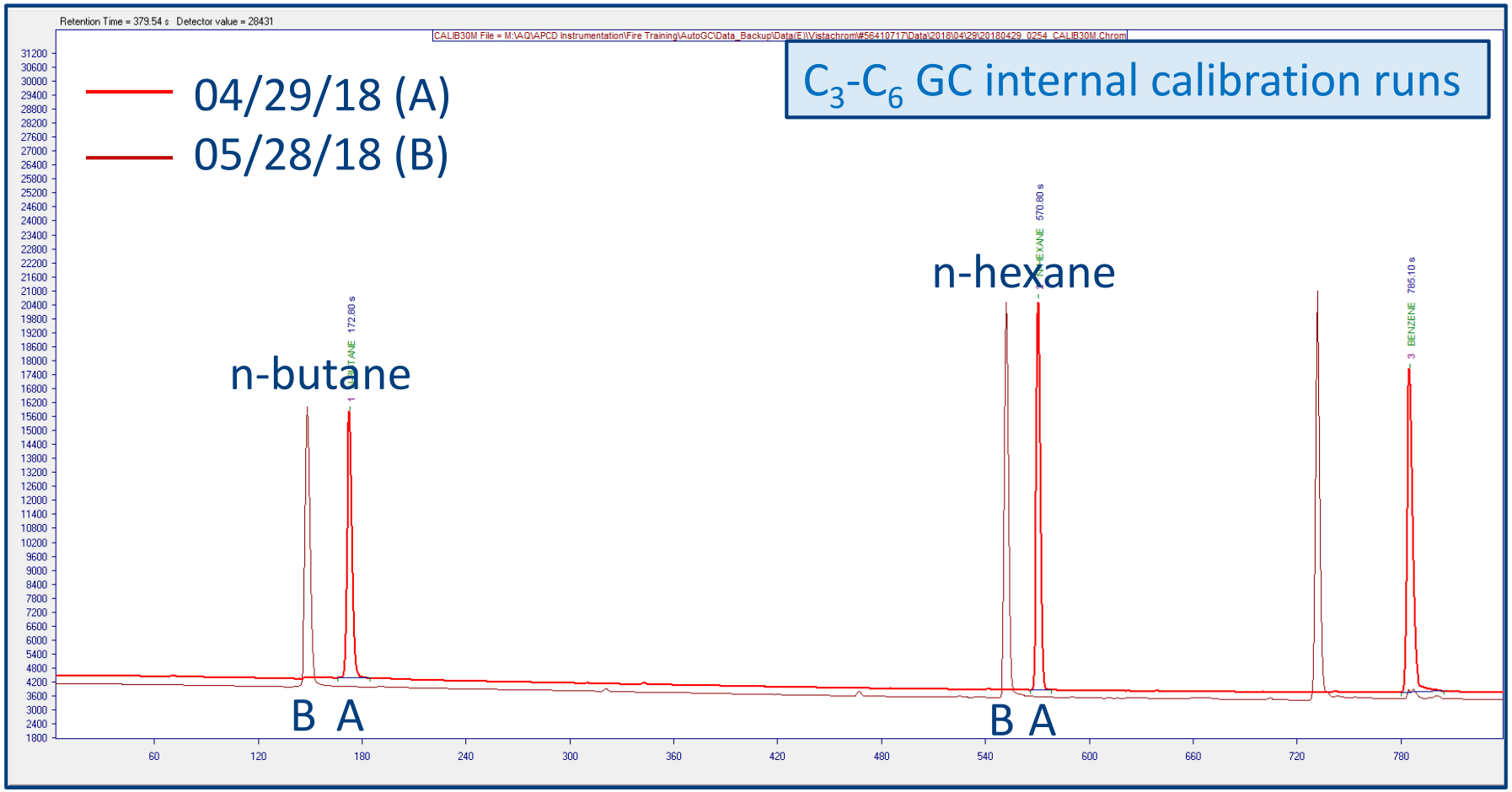


Field Evaluation Goals

- Determine
  - VOC elution order
  - VOC retention time windows
  - Coeluting VOCs

- Assess
  - System cleanliness
    - Nightly zero air runs
  - Retention time stability
    - Nightly permeation tube calibration runs
  - System stability & performance
    - Biweekly system checks

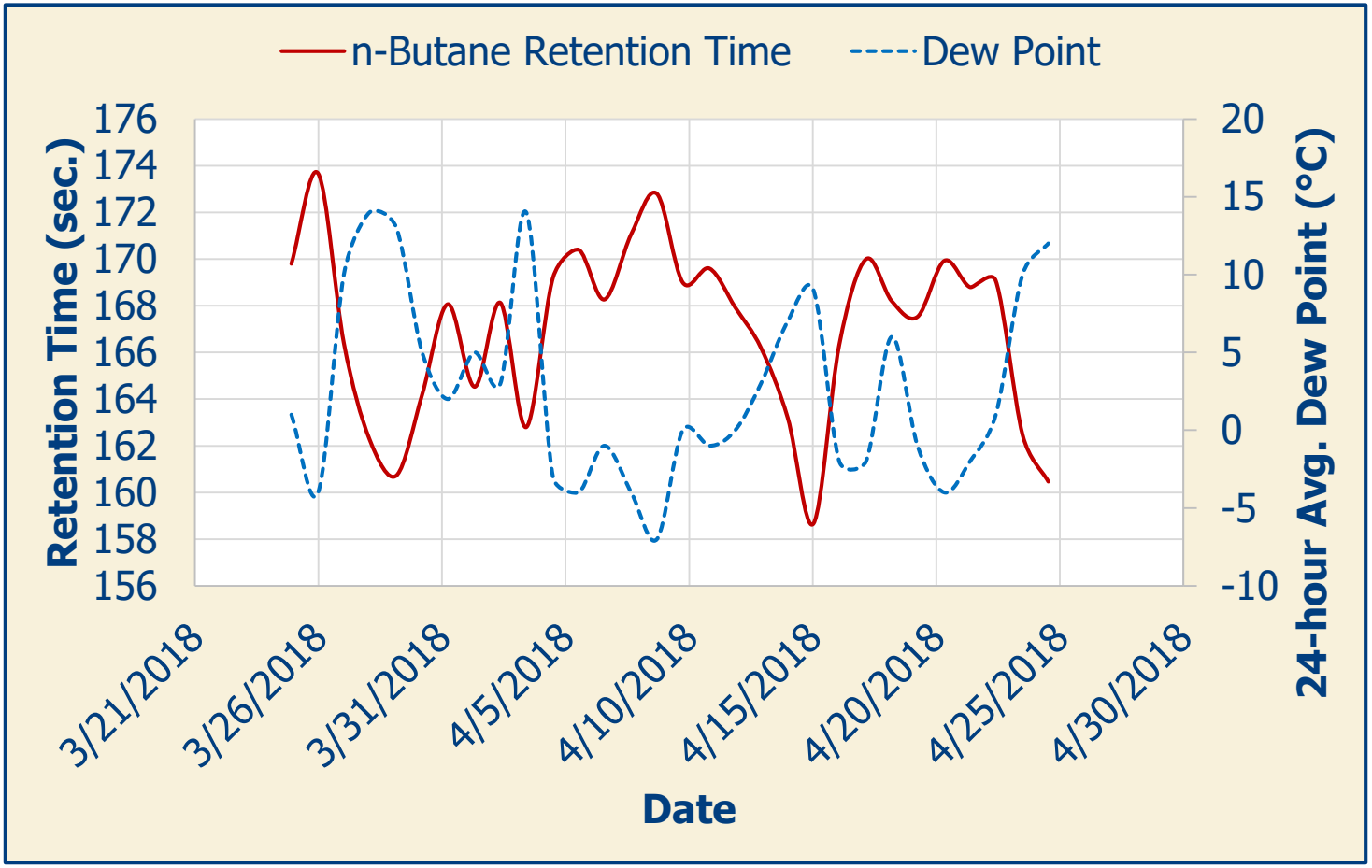
Retention Time Shifting



From run A to run B, ~20 sec RT shift

Dew Point & PLOT Column Retention Time

Mar. 24 - April 24, 2018



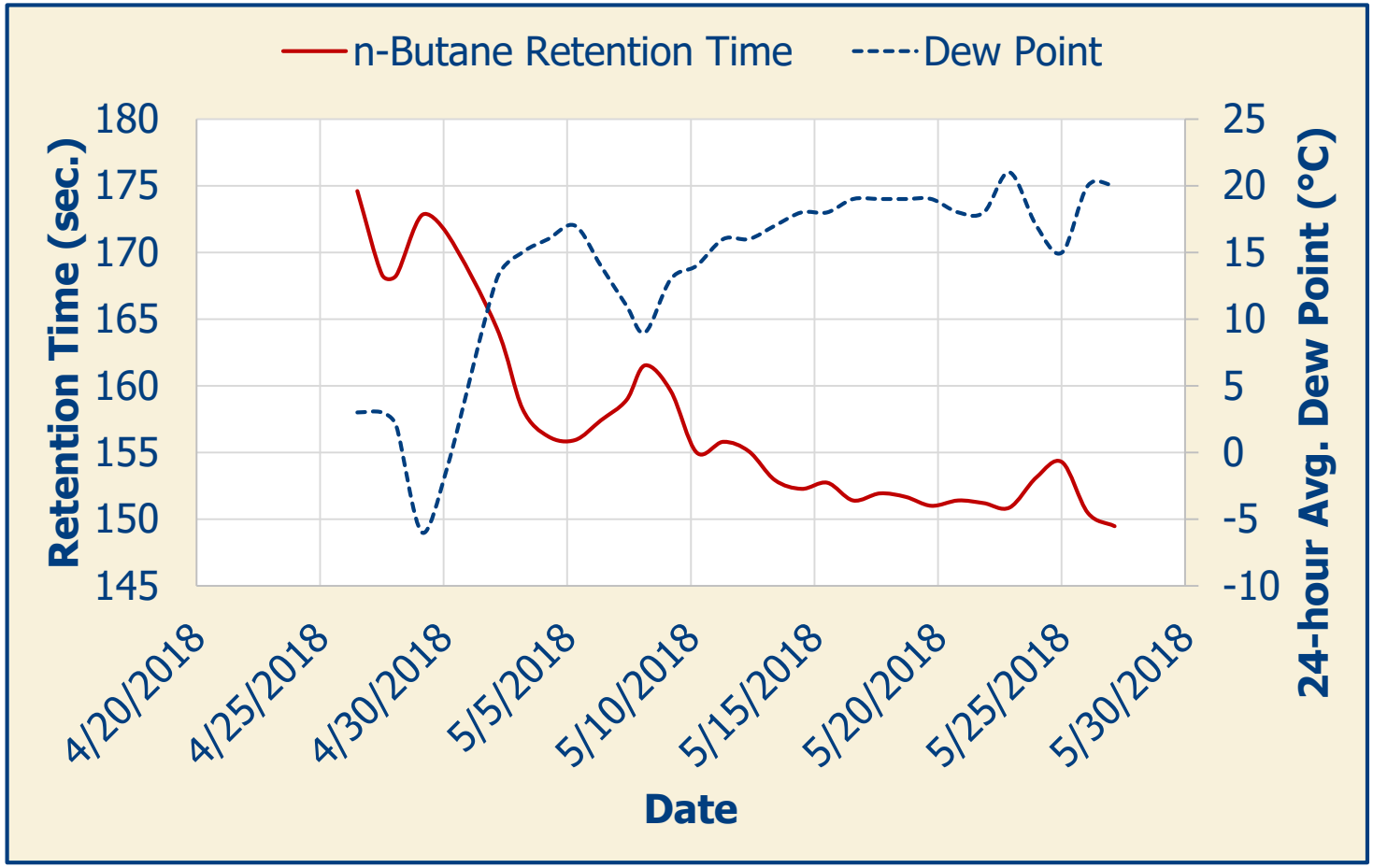
Dew point range = 21°C

RT range = 15 sec.

Dew Point & PLOT Column Retention Time

April 26 - May 27, 2018

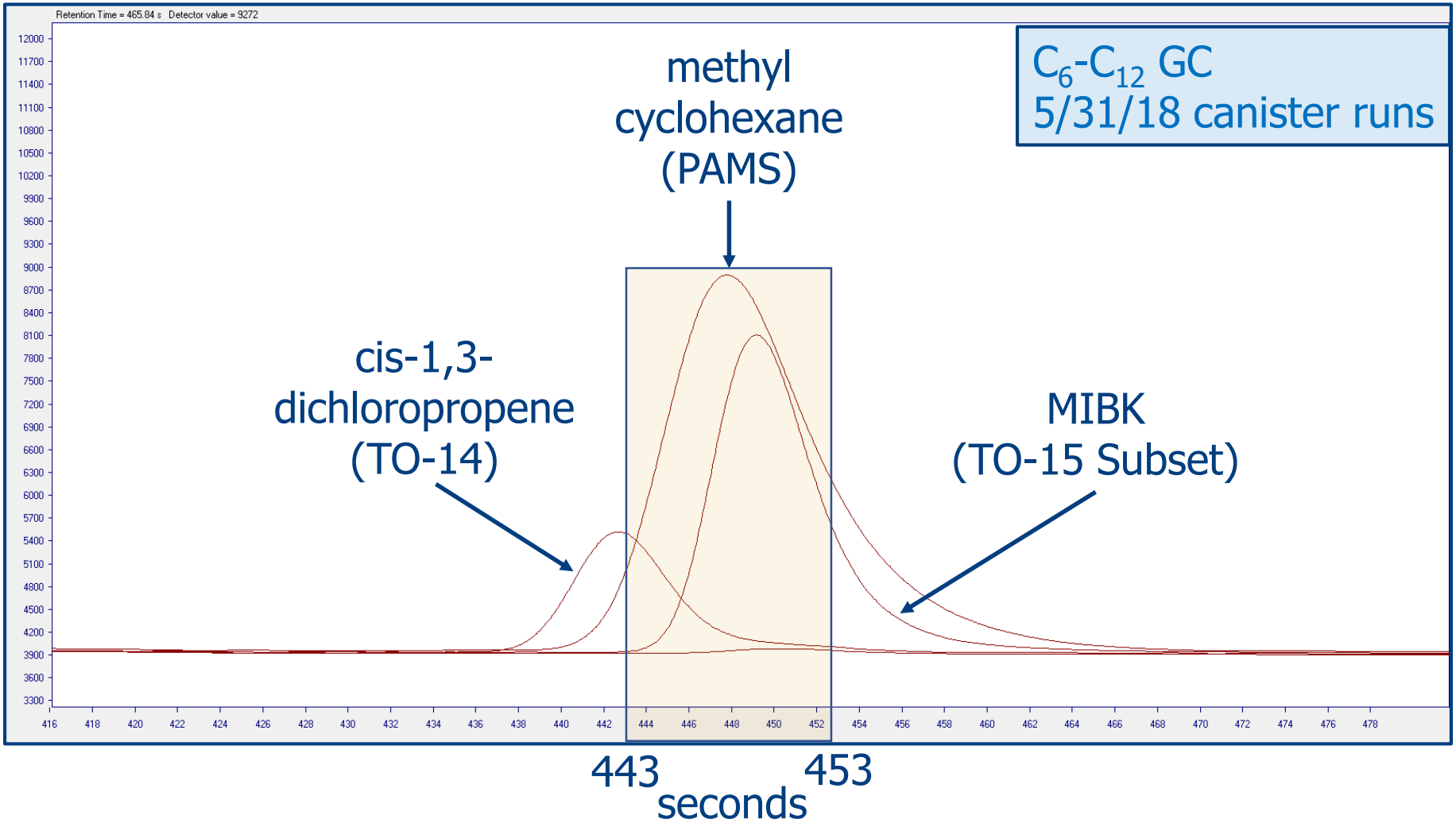
After additional Nafion®



Dew point range = 27°C

RT range = 26 sec.

Coelution


Retention Time = 465.84 s Detector value = 9272
C_6-C_{12} GC
5/31/18 canister runs
methyl
cyclohexane
(PAMS)
cis-1,3-
dichloropropene
(TO-14)
MIBK
(TO-15 Subset)
443
453
seconds

Confidence in Peak Identification

Retention Time Shifting Score	
S - Satisfactory	Low probability RT shifting > RTW Post-processing not likely required
U - Unsatisfactory	High probability RT shifting > RTW Post-processing likely required

Coelution Score	
1	No known coelution
2	Partial coelution, each peak is quantified
3	Partial coelution, quantification is concentration dependent
4	Complete coelution with VOC of interest
5	Complete coelution with unidentified VOC

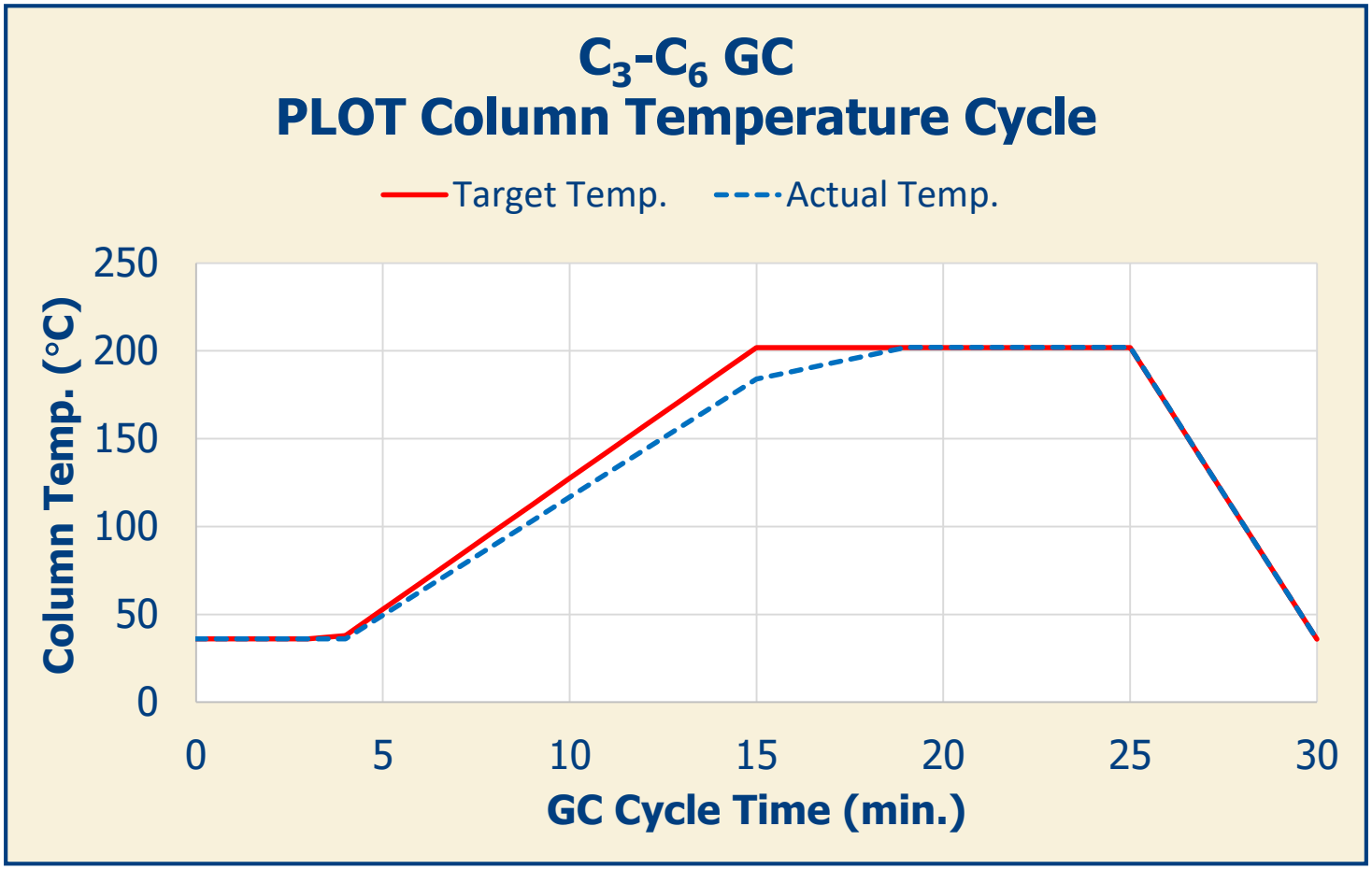
Data Quality Score (DQS)

DQS	
GREEN	Low RT shifting potential No significant coelution concerns
YELLOW	High RT shifting potential OR No significant coelution concerns
RED	High RT shifting potential AND No significant coelution concerns

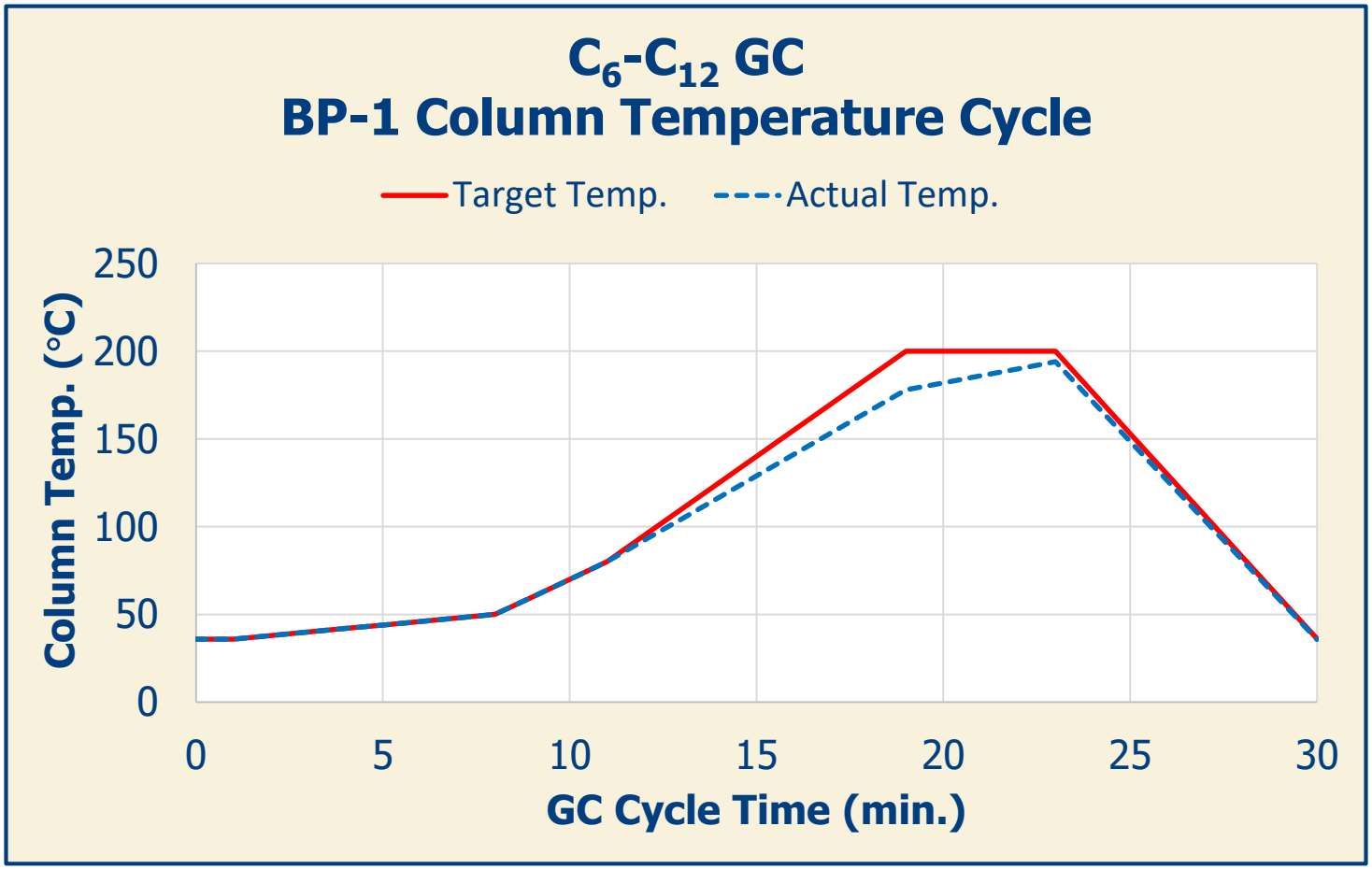
Data Quality Score (DQS)

GC	Compound	RT Shifting Score	Coelution Score	Raw DQS	Post DQS
C_3-C_6	vinyl chloride	U	3		
	1,3-butadiene		5		
C_6-C_{12}	benzene	S	3		
	carbon tetrachloride		3		
	trichloroethylene		1		
	toluene		5		
	tetrachloroethylene		2		
	ethylbenzene		3		
	styrene		4		

Column Temperatures



Column Temperatures



Next Steps

Modification	Purpose
69 VOC calibration cylinder	Nightly RTS/CCV
60-meter C_6-C_{12} GC column	Improve peak separation
60-minute GC cycles	Improve peak separation Consistent with PAMS program
Peltier-cooled 3-phase C_2-C_6 trap	Capture more volatile VOCs Consistent with PAMS program
Redesign GC column ovens	Improve temperature control

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Thank You!

Questions

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