Pinenes in PAMS AutoGC Data: Where Are They?

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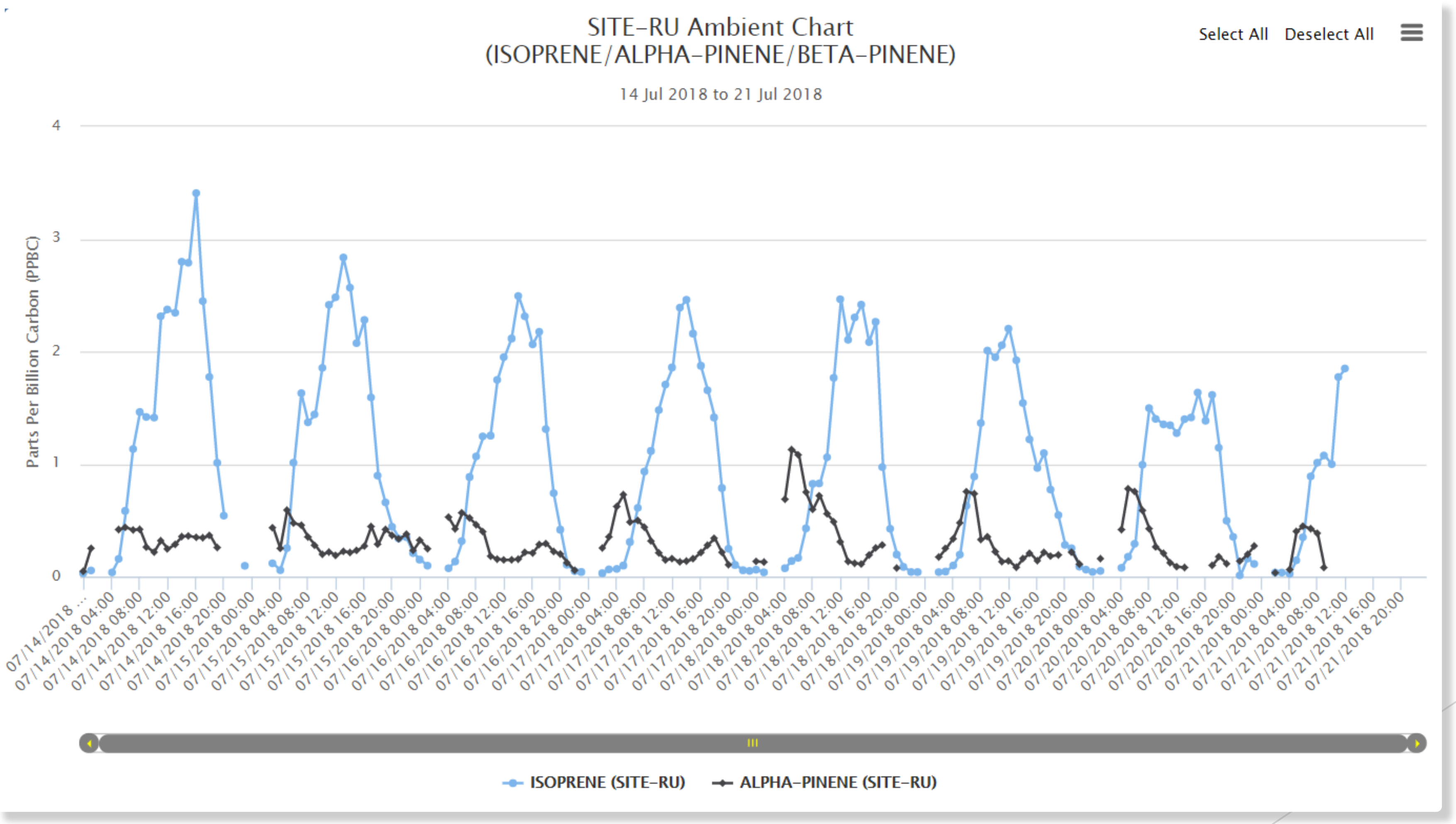
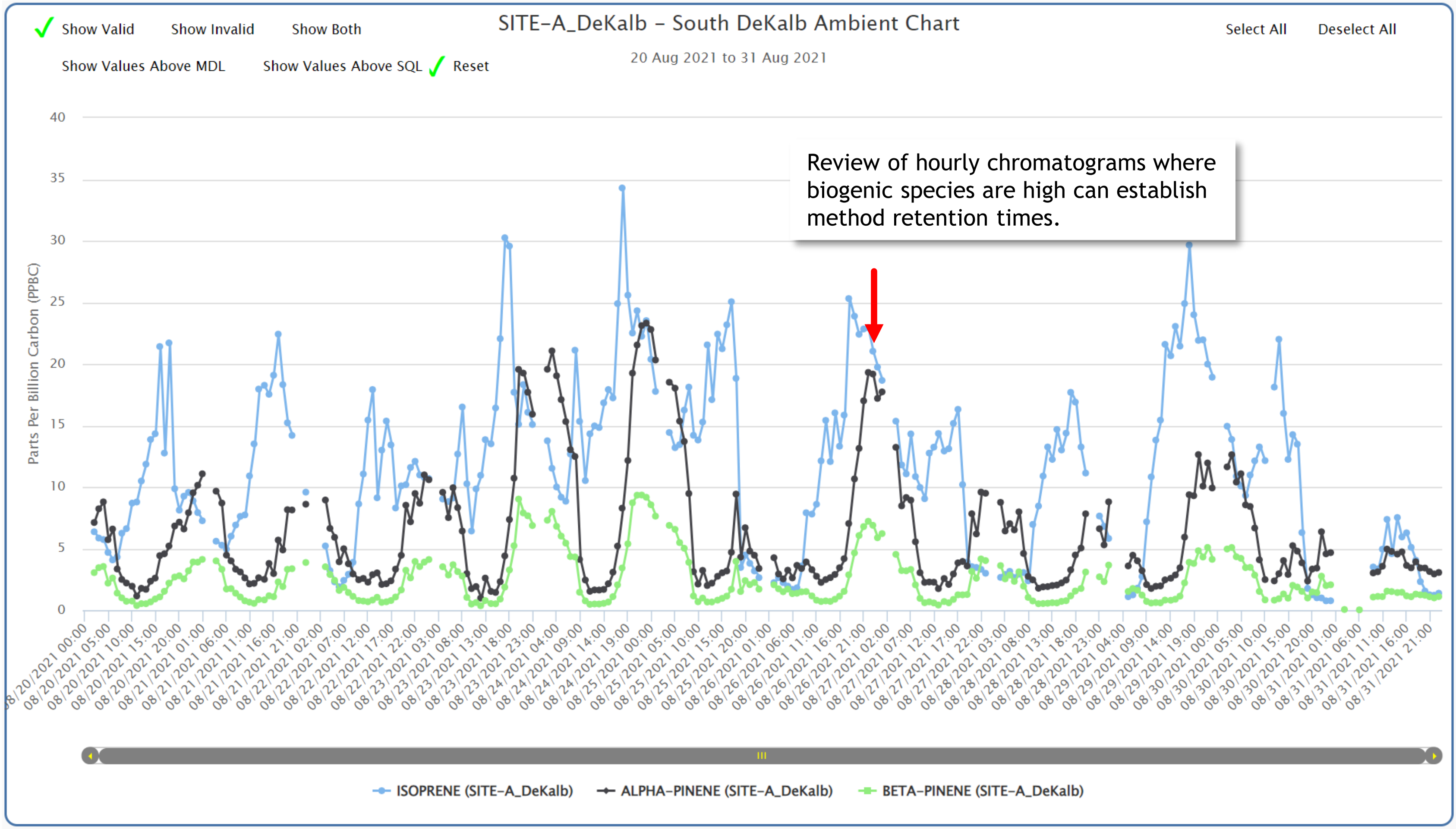
AutoGC Systems: Pinenes

Ambient Measurements



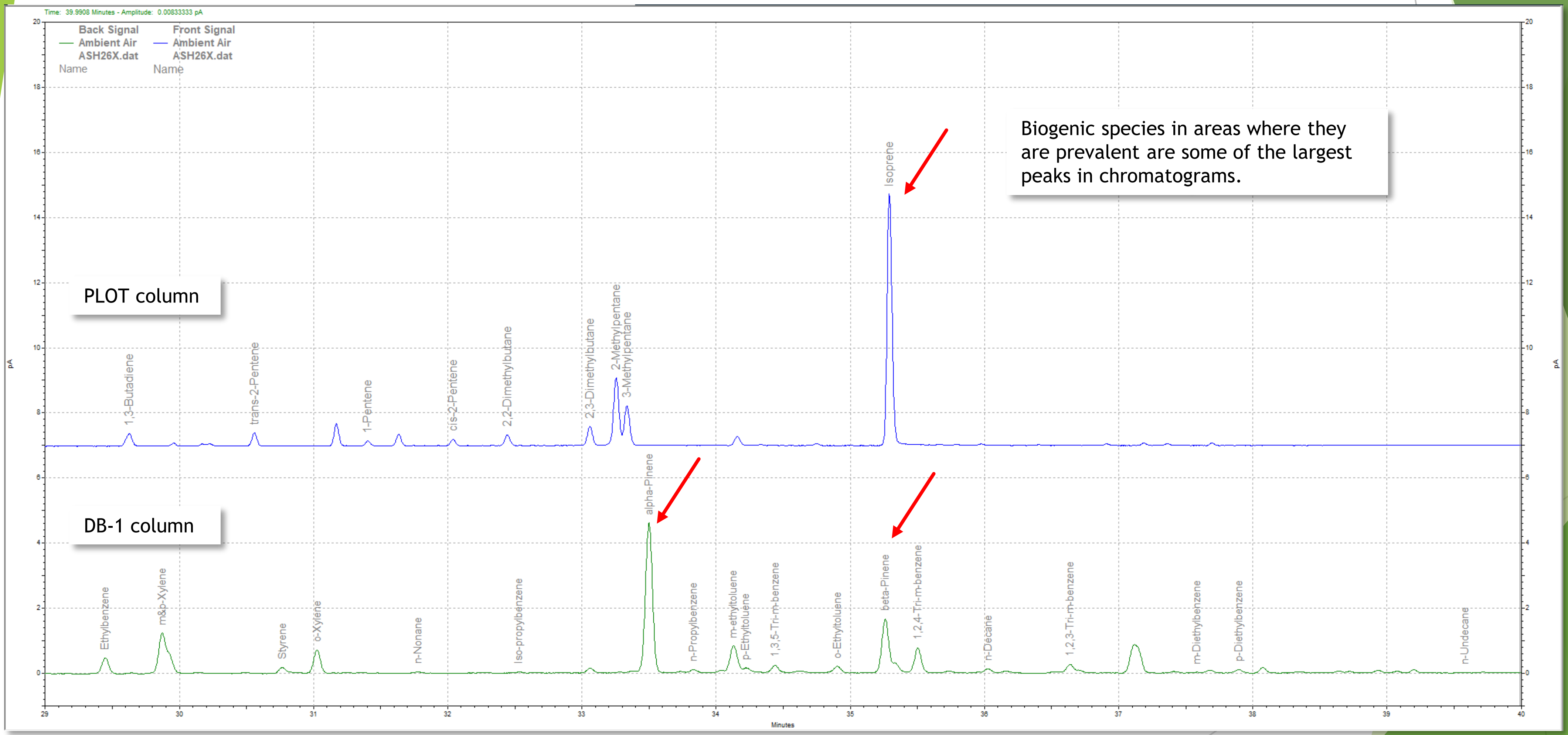
AutoGC Systems: Pinenes
Ambient Measurements



Review of hourly chromatograms where biogenic species are high can establish method retention times.

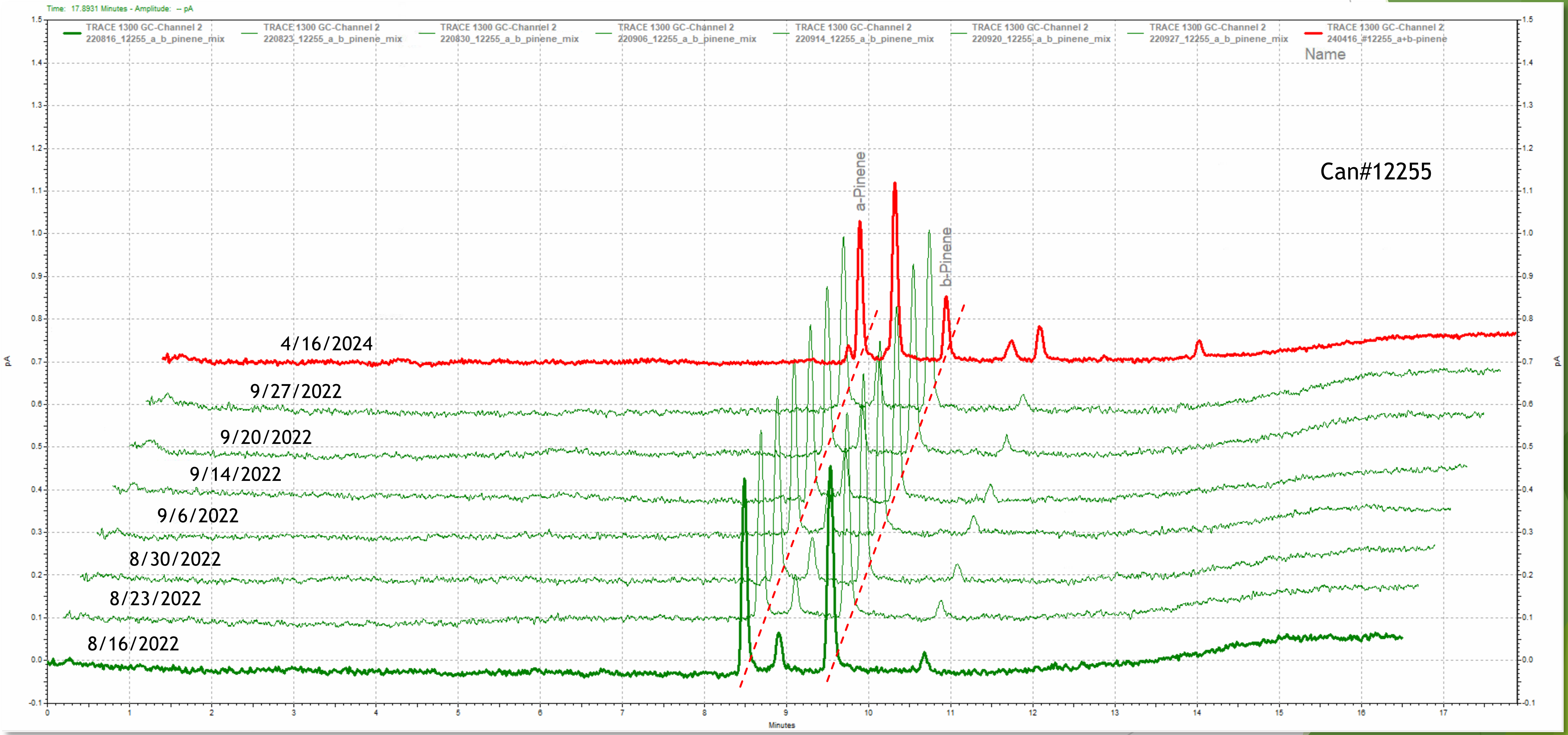
AutoGC Systems: Pinenes

Ambient Measurements



Biogenic species in areas where they are prevalent are some of the largest peaks in chromatograms.

AutoGC Systems: Pinenes



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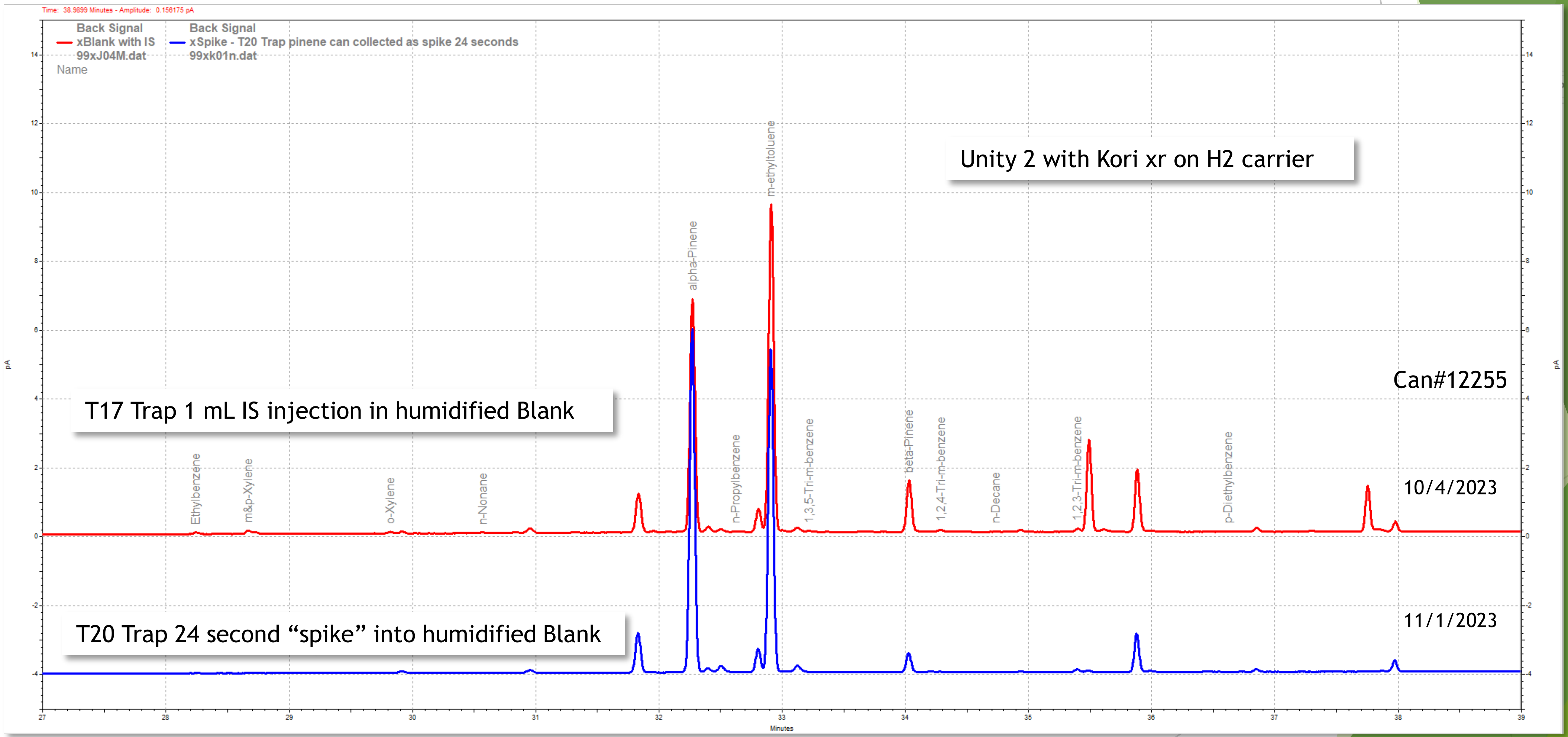


Unity 2 with Kori xr on H2 carrier

Can#12255

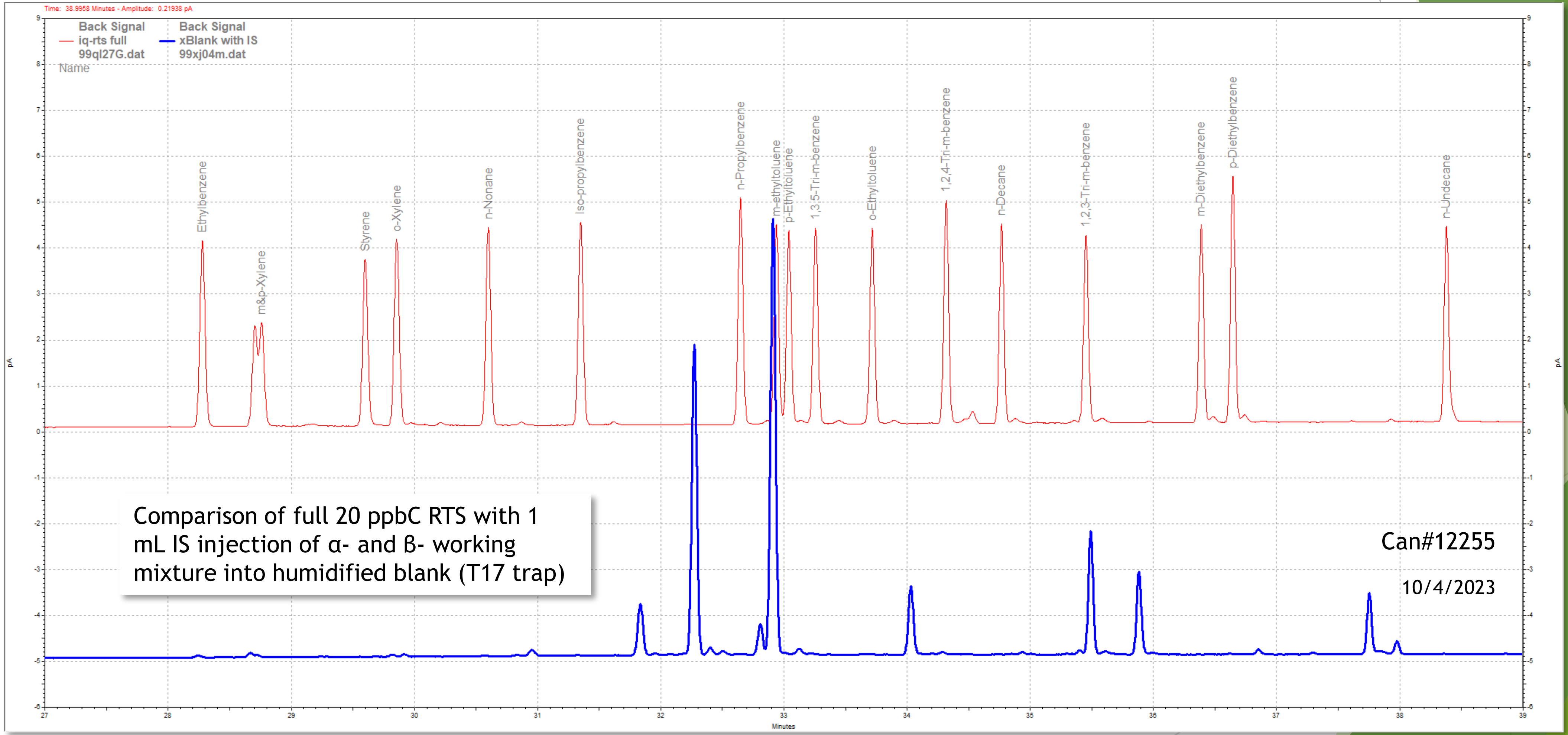
T17 Trap 1 mL IS injection in humidified Blank

10/4/2023

T20 Trap 24 second “spike” into humidified Blank

11/1/2023

AutoGC Systems: Pinenes

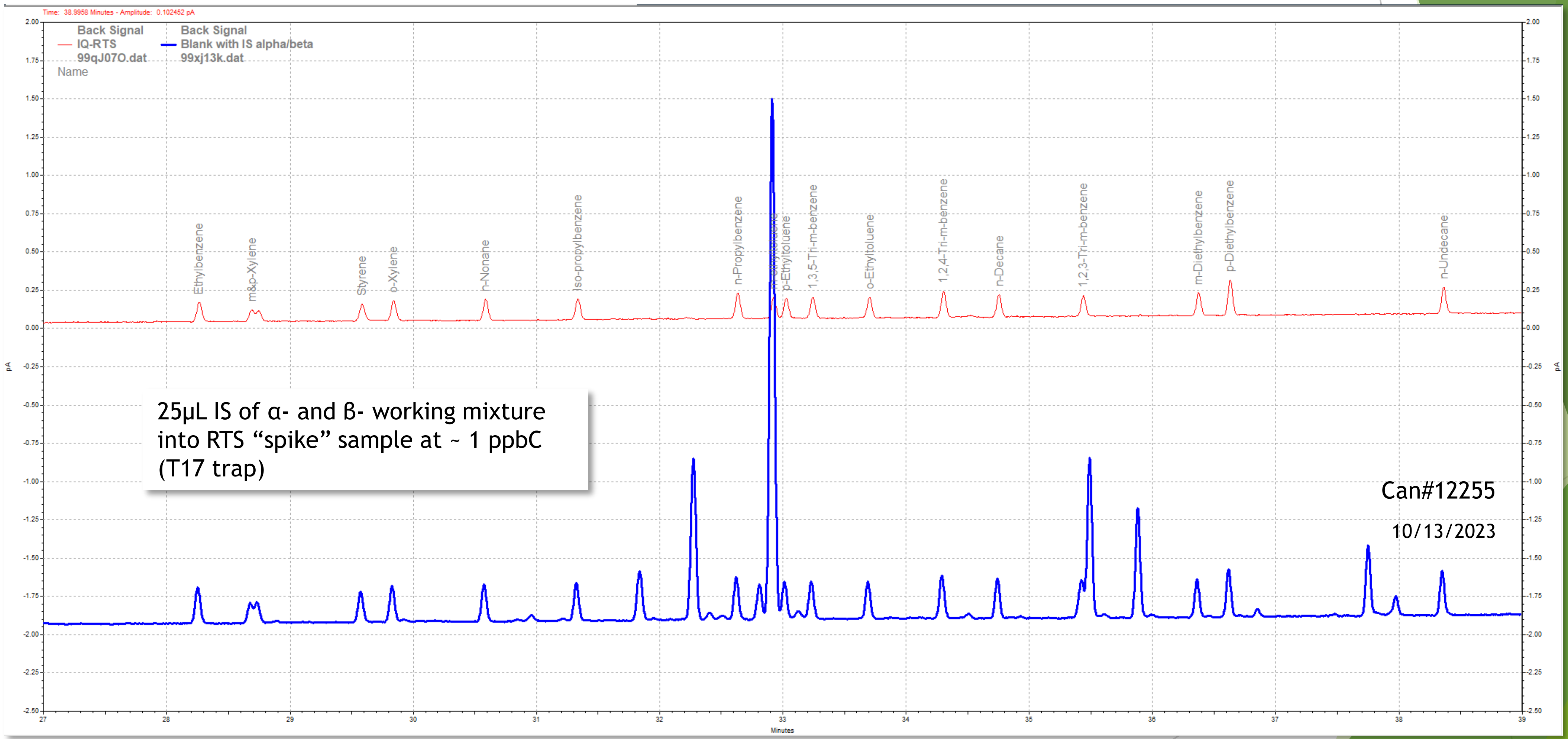


Comparison of full 20 ppbC RTS with 1 mL IS injection of α- and β- working mixture into humidified blank (T17 trap)

Can#12255

10/4/2023

AutoGC Systems: Pinenes

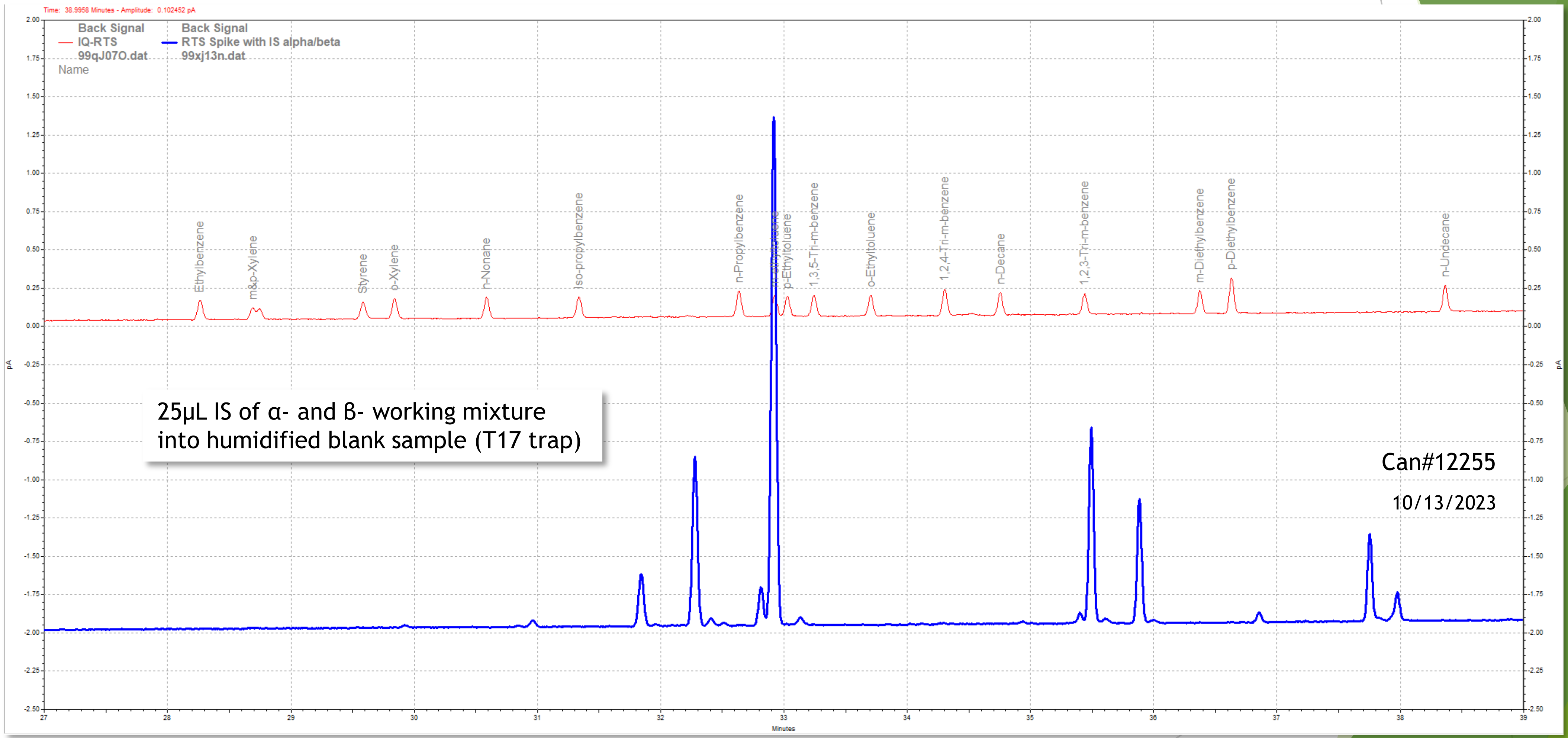


25µL IS of α- and ß- working mixture into RTS “spike” sample at ~ 1 ppbC (T17 trap)

Can#12255

10/13/2023

AutoGC Systems: Pinenes

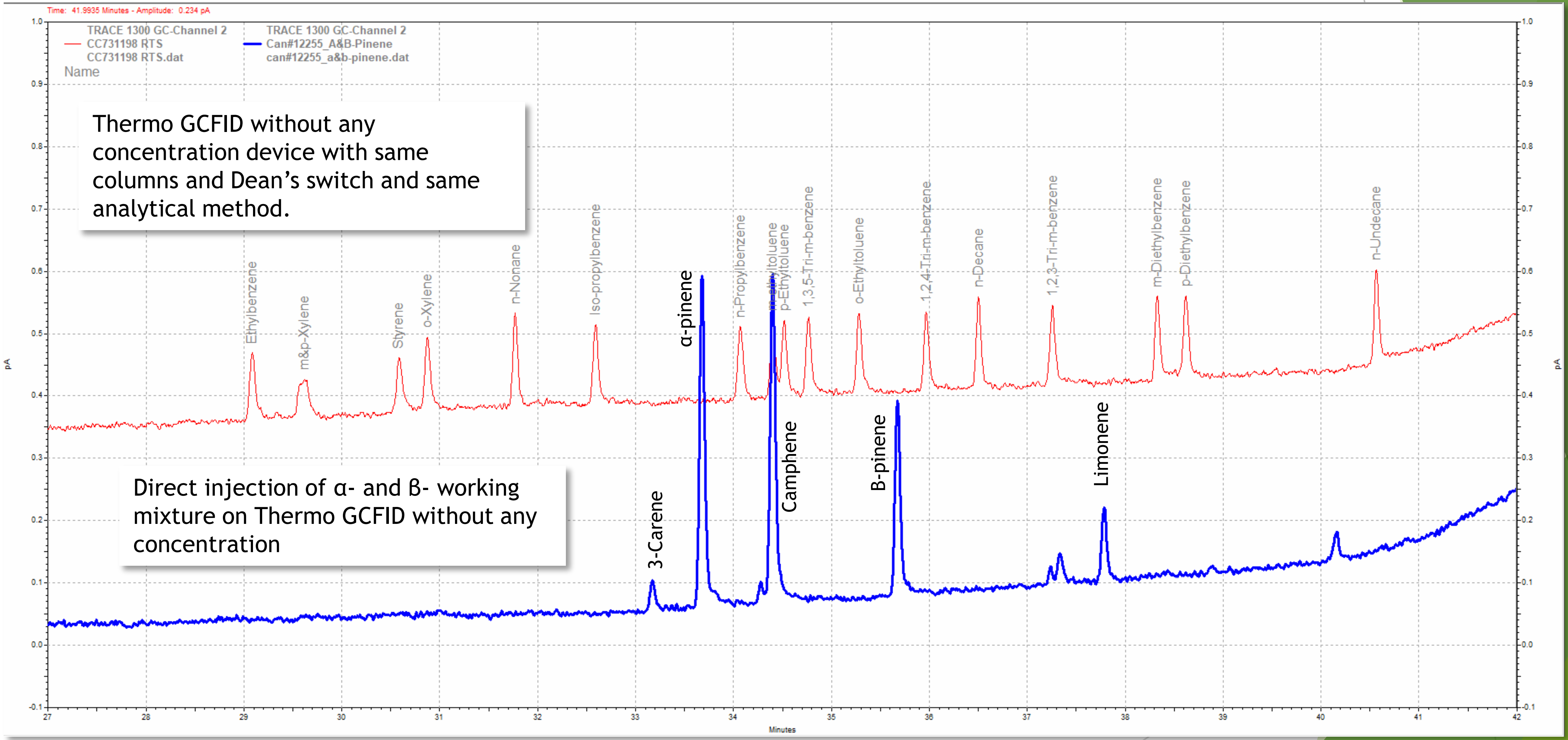


25µL IS of α- and β- working mixture into humidified blank sample (T17 trap)

Can#12255

10/13/2023

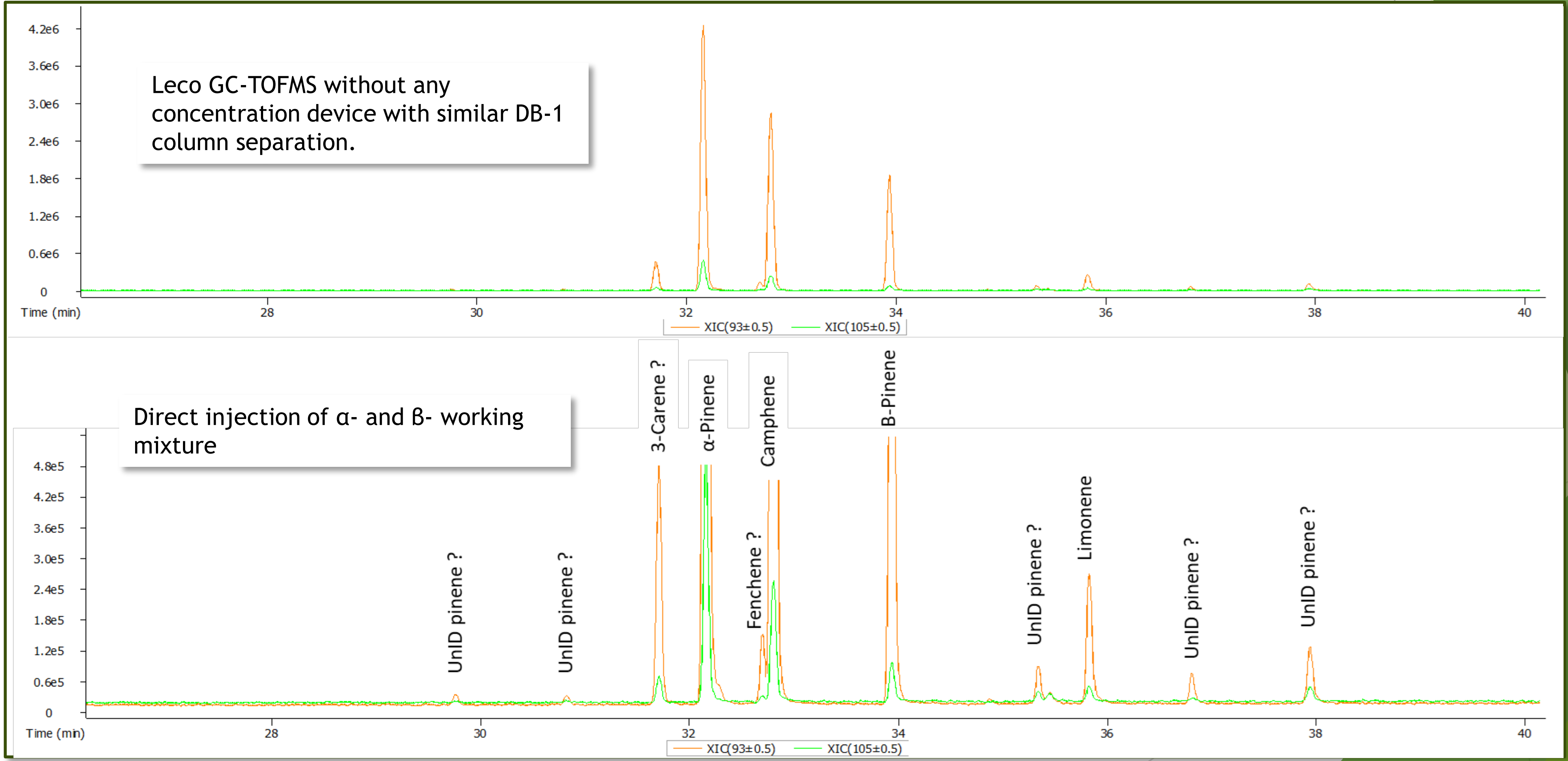
AutoGC Systems: Pinenes



Thermo GCFID without any concentration device with same columns and Dean's switch and same analytical method.

Direct injection of α- and β- working mixture on Thermo GCFID without any concentration

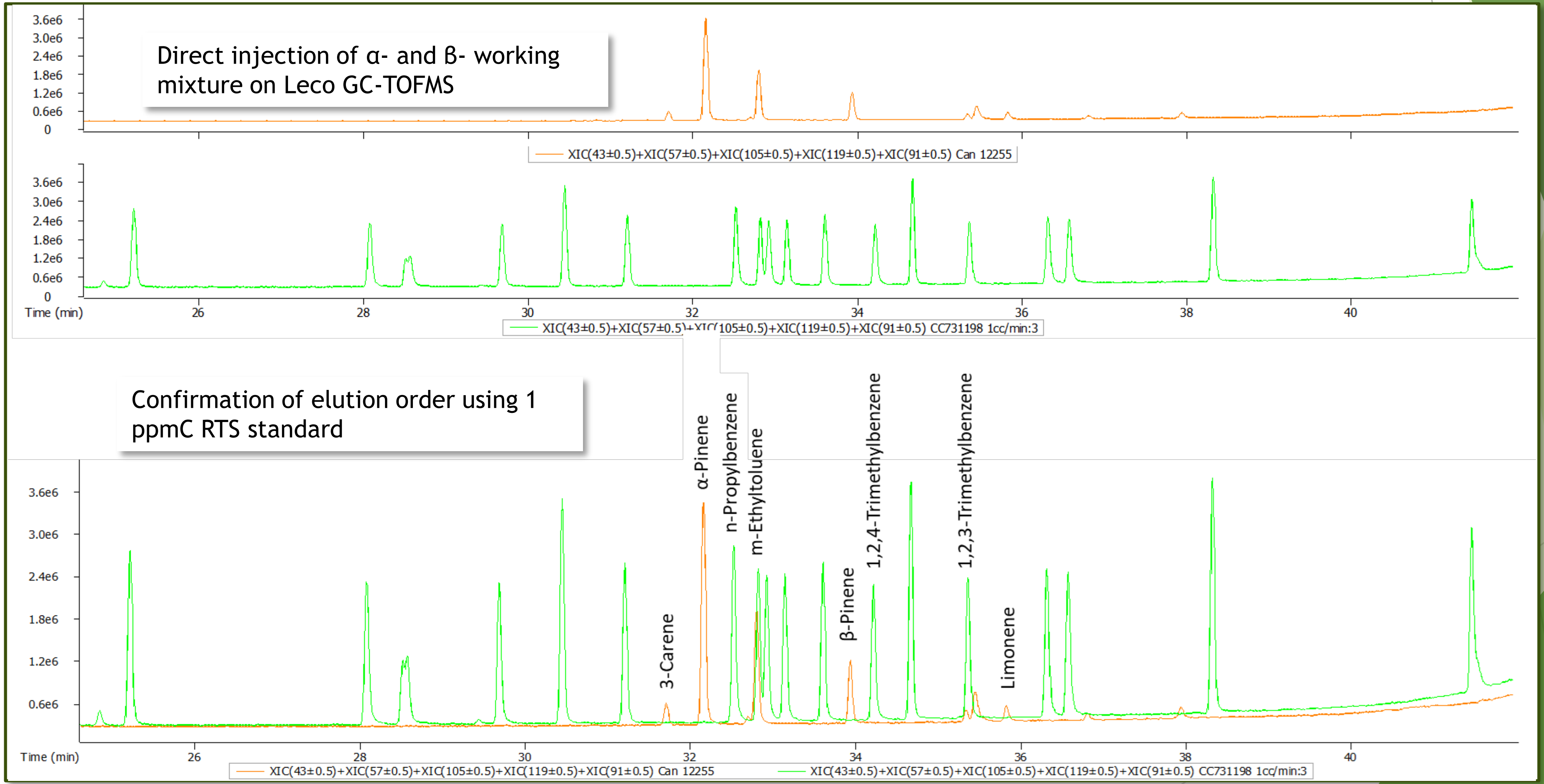
AutoGC Systems: Pinenes



Leco GC-TOFMS without any concentration device with similar DB-1 column separation.

Direct injection of α- and ß- working mixture

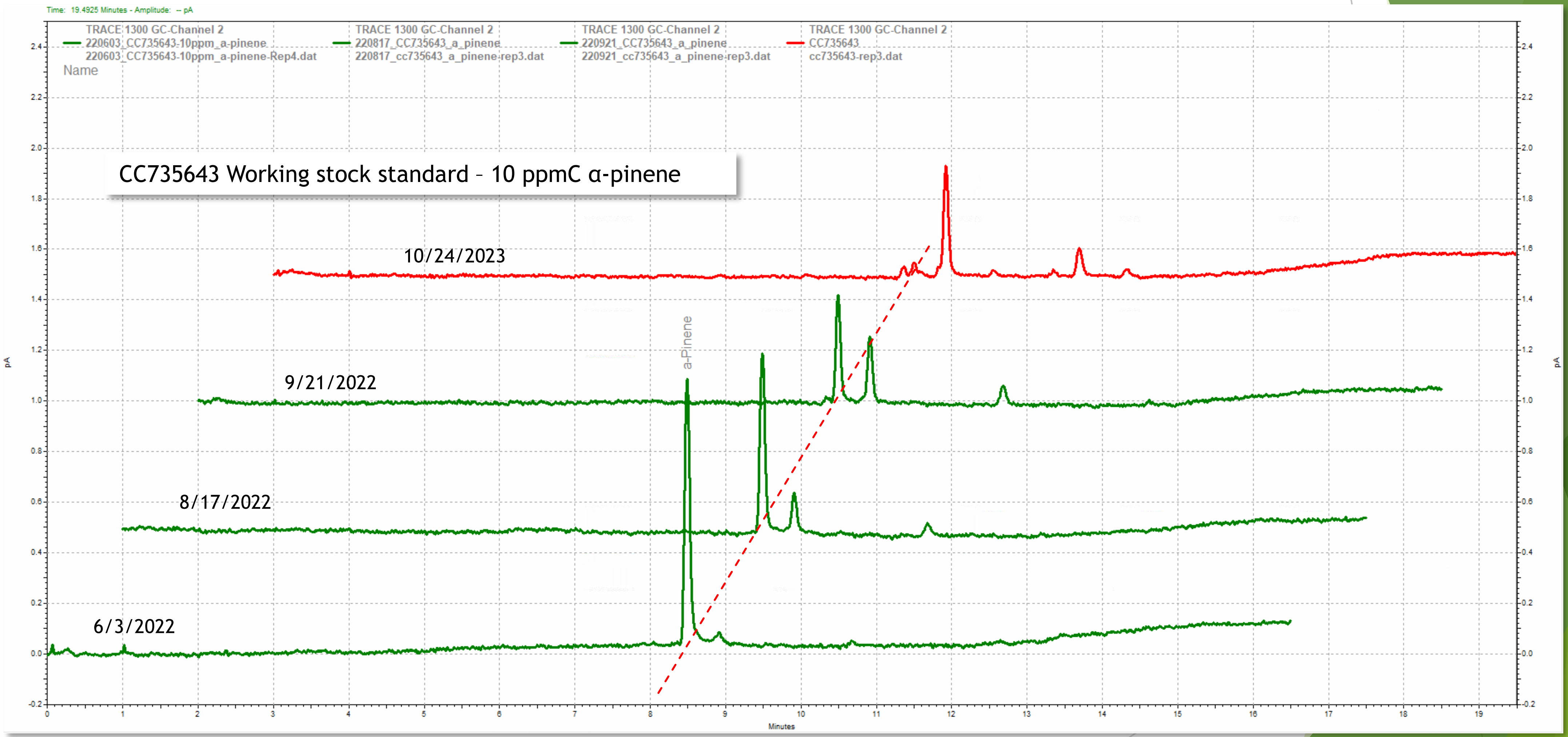
AutoGC Systems: Pinenes



Direct injection of α- and ß- working mixture on Leco GC-TOFMS

Confirmation of elution order using 1 ppmC RTS standard

AutoGC Systems: Pinenes



CC735643 Working stock standard – 10 ppmC α-pinene

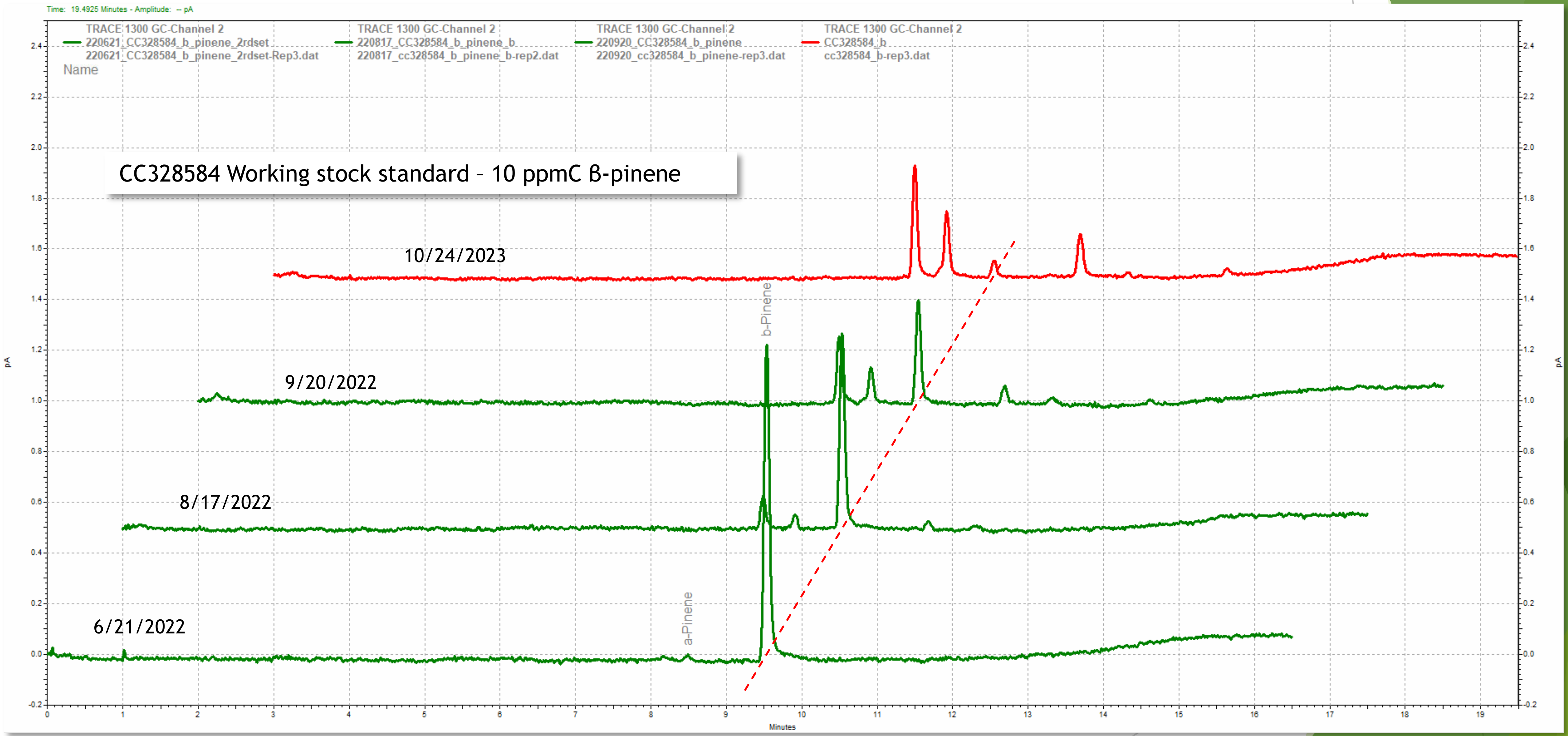
10/24/2023

9/21/2022

8/17/2022

6/3/2022

AutoGC Systems: Pinenes



CC328584 Working stock standard – 10 ppmC ß-pinene

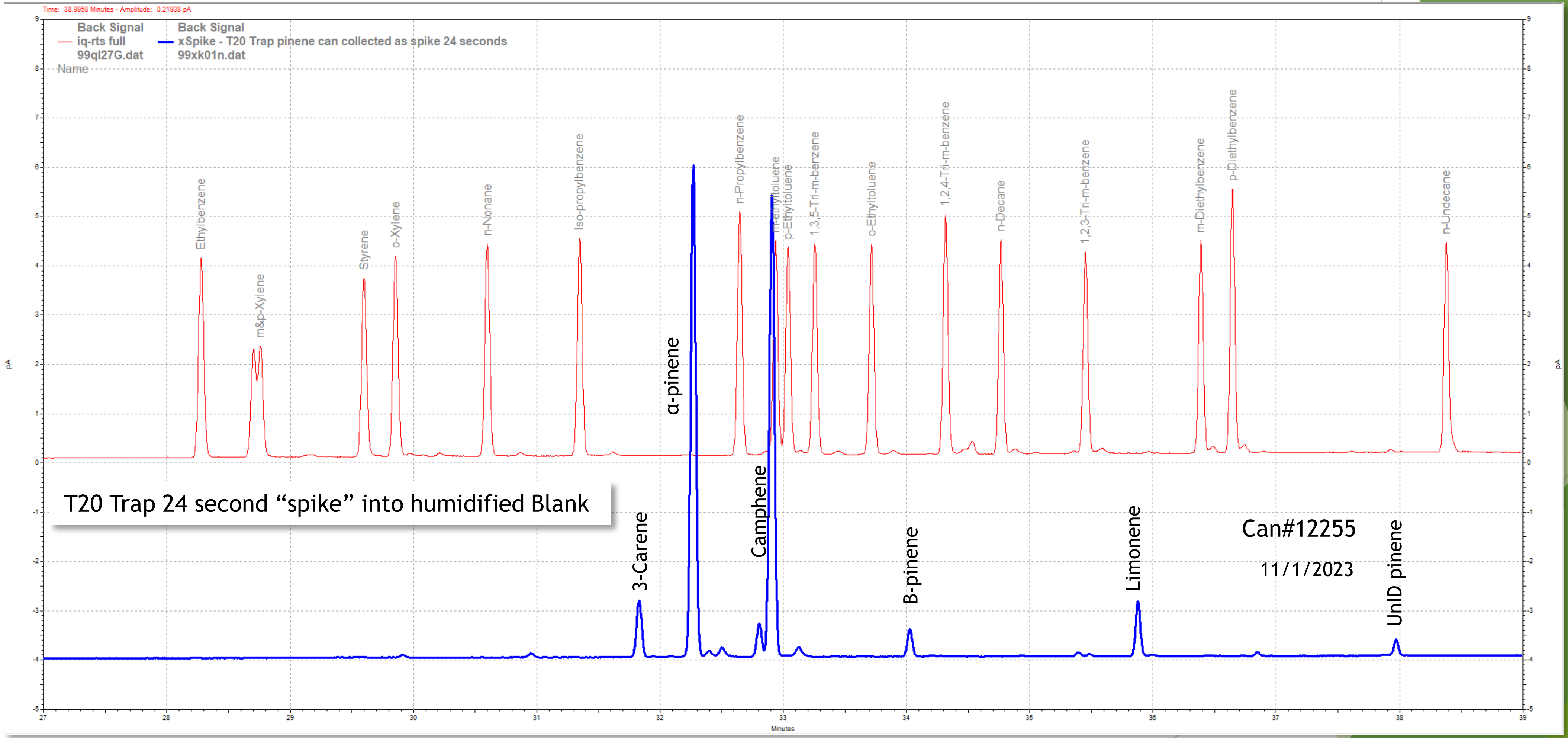
10/24/2023

9/20/2022

8/17/2022

6/21/2022

AutoGC Systems: Pinenes

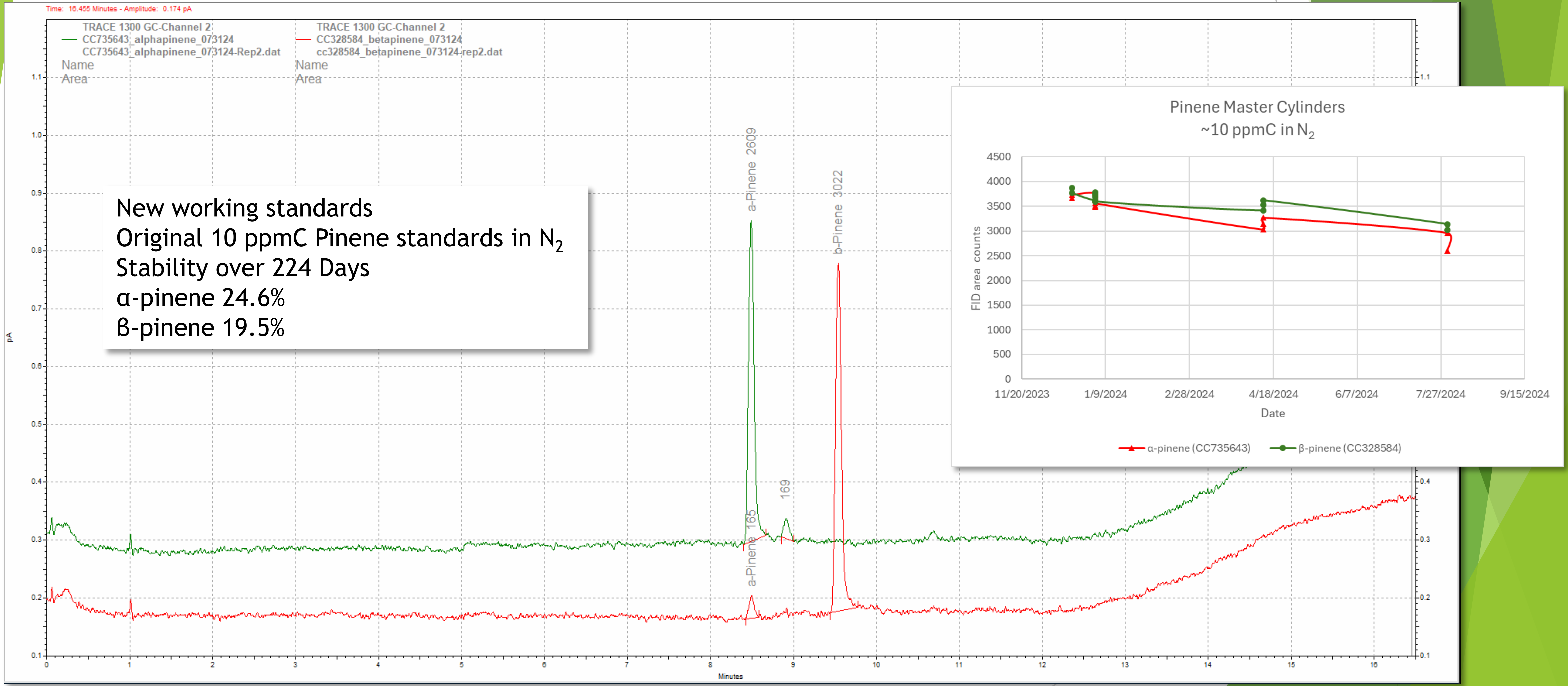


T20 Trap 24 second “spike” into humidified Blank

Can#12255

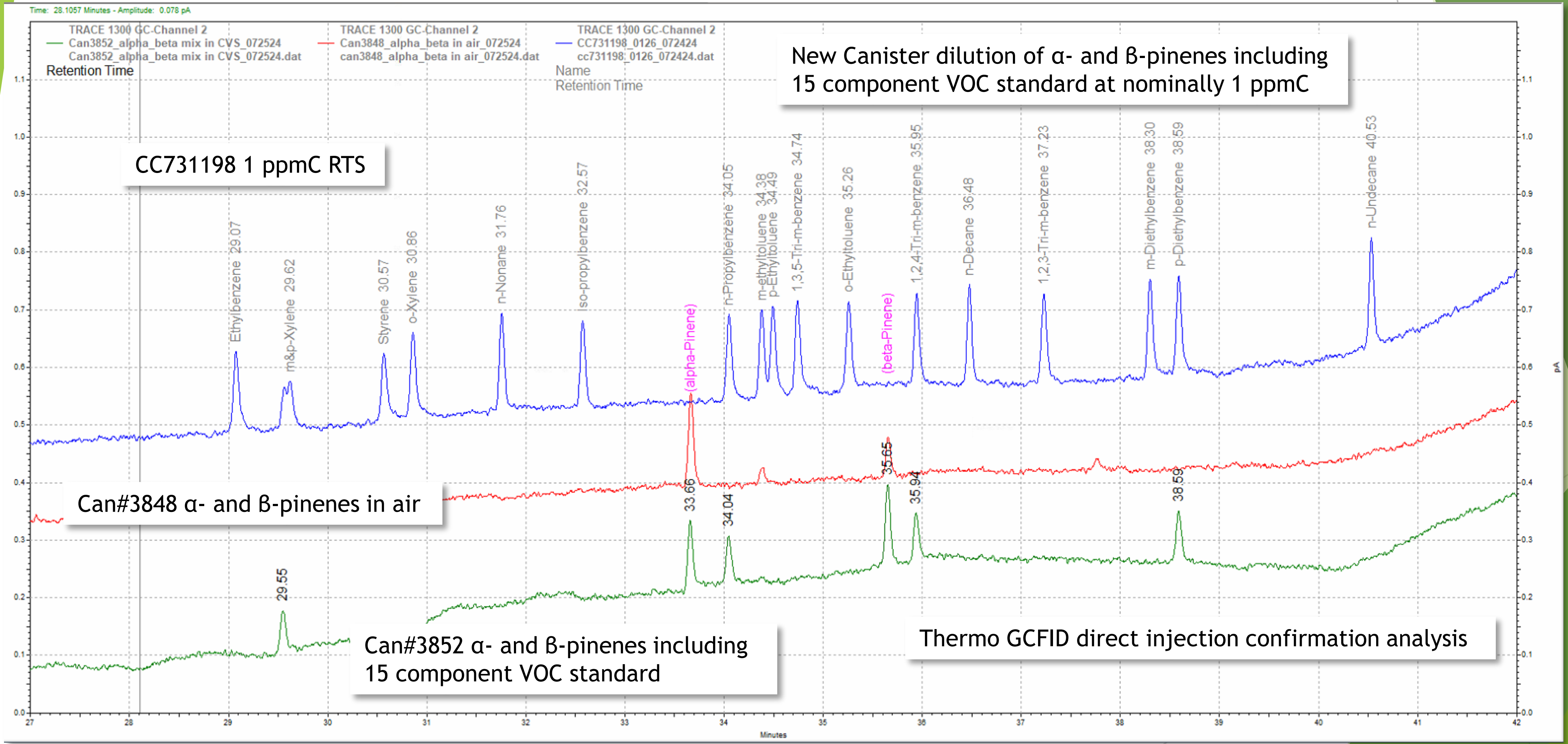
11/1/2023

AutoGC Systems: Pinenes



New working standards
Original 10 ppmC Pinene standards in N_2
Stability over 224 Days
α-pinene 24.6%
ß-pinene 19.5%

AutoGC Systems: Pinenes



New Canister dilution of α- and ß-pinenes including 15 component VOC standard at nominally 1 ppmC

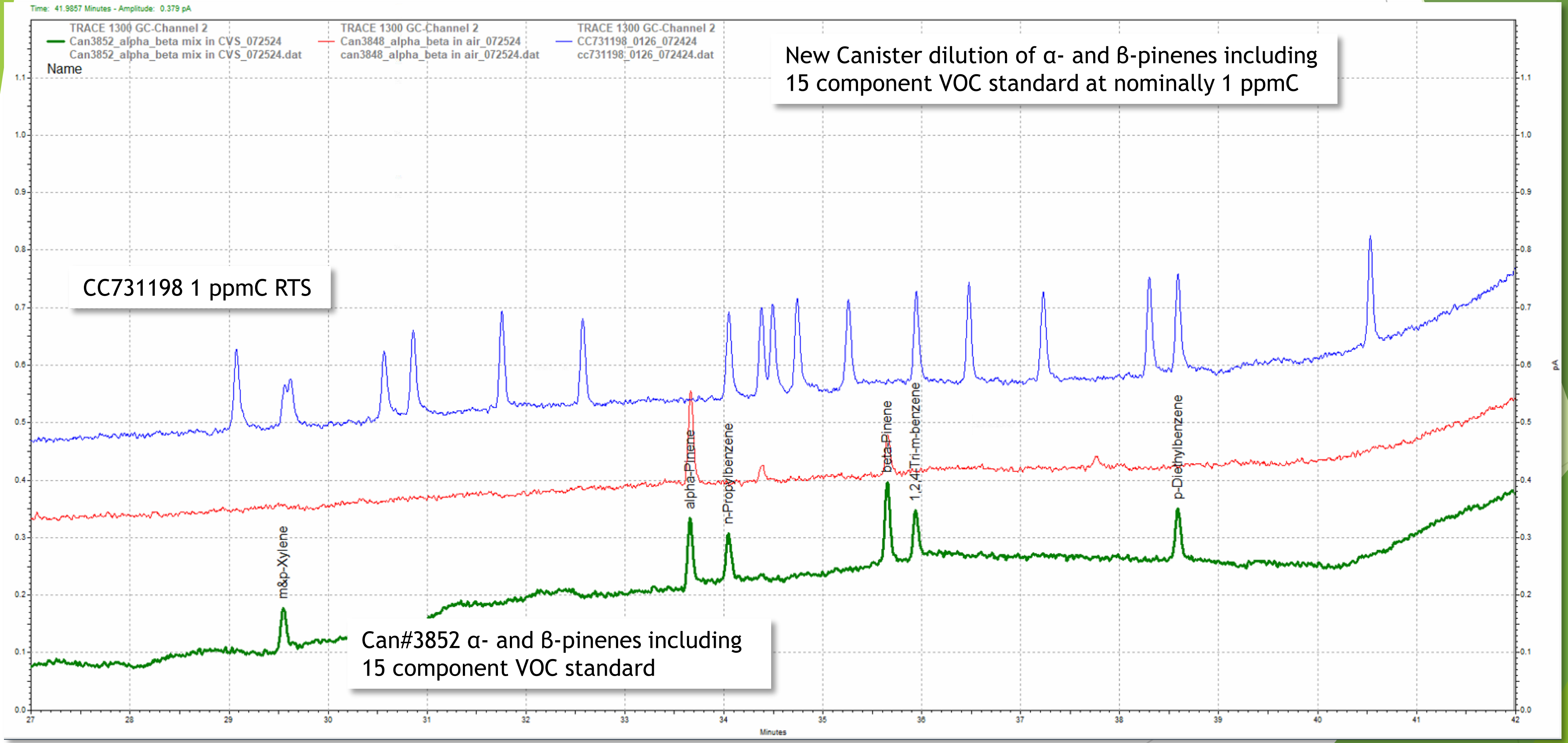
CC731198 1 ppmC RTS

Can#3848 α- and ß-pinenes in air

Can#3852 α- and ß-pinenes including 15 component VOC standard

Thermo GCFID direct injection confirmation analysis

AutoGC Systems: Pinenes



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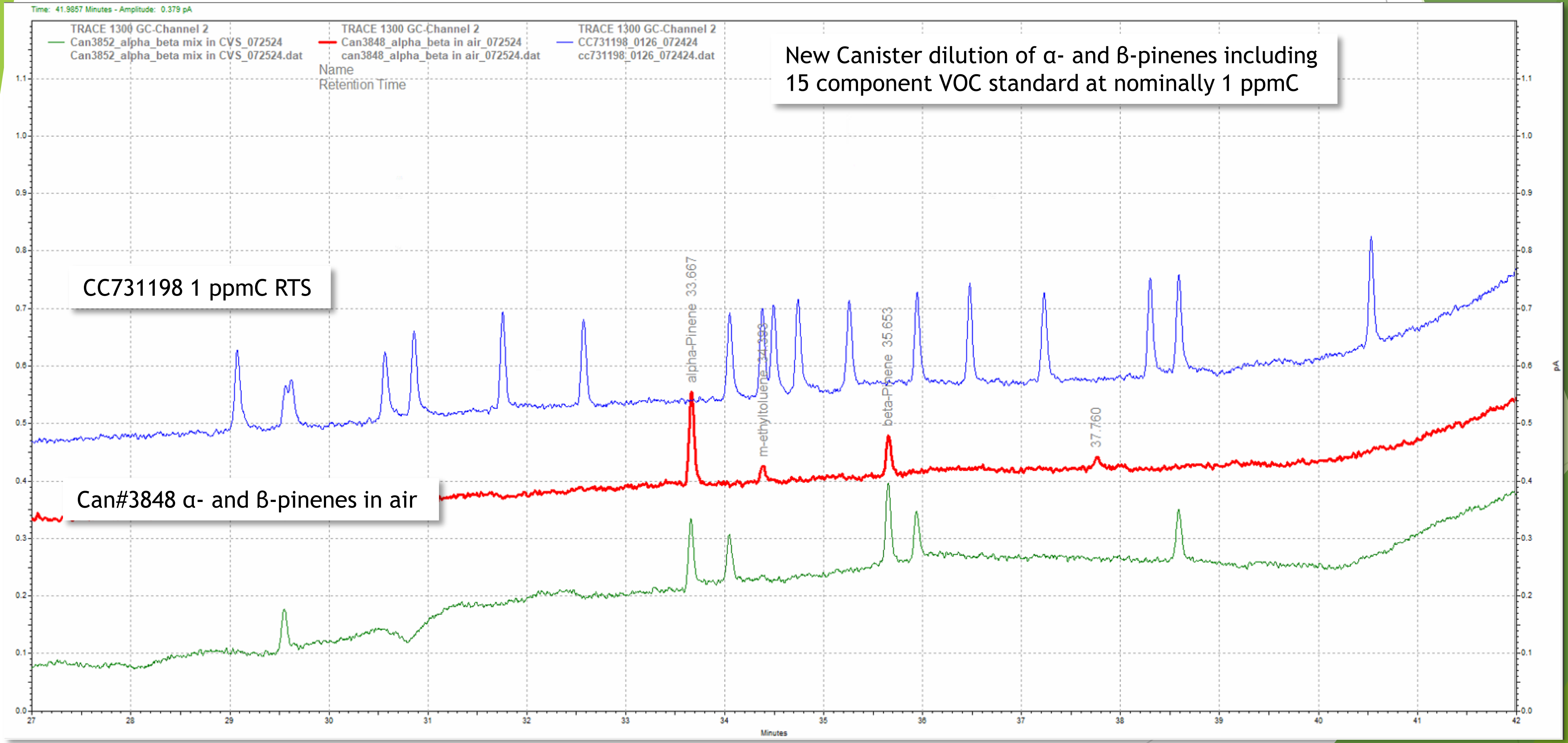

New Canister dilution of α- and β-pinenes including 15 component VOC standard at nominally 1 ppmC

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Can#3848 α- and β-pinenes in air

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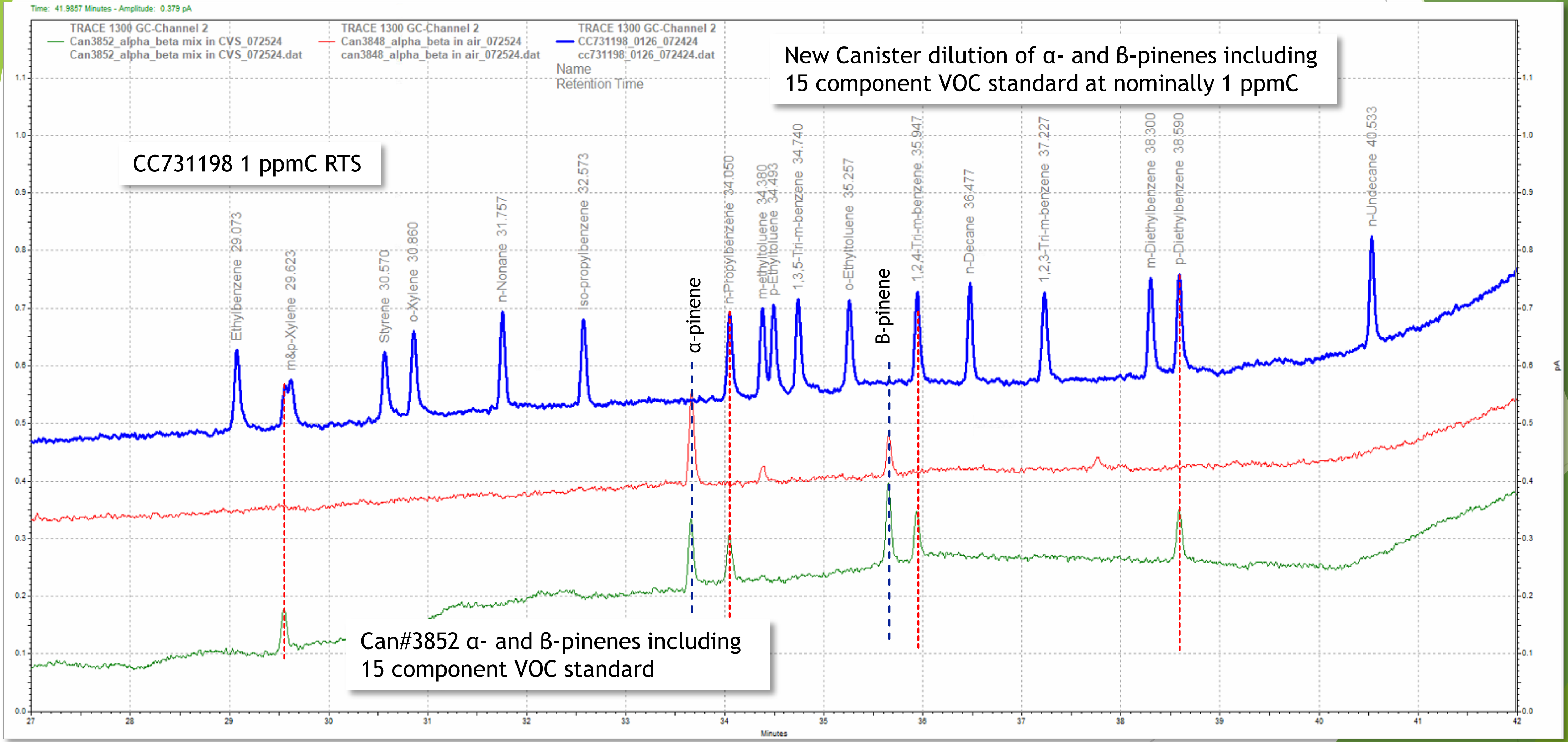

New Canister dilution of α- and Β-pinenes including 15 component VOC standard at nominally 1 ppmC

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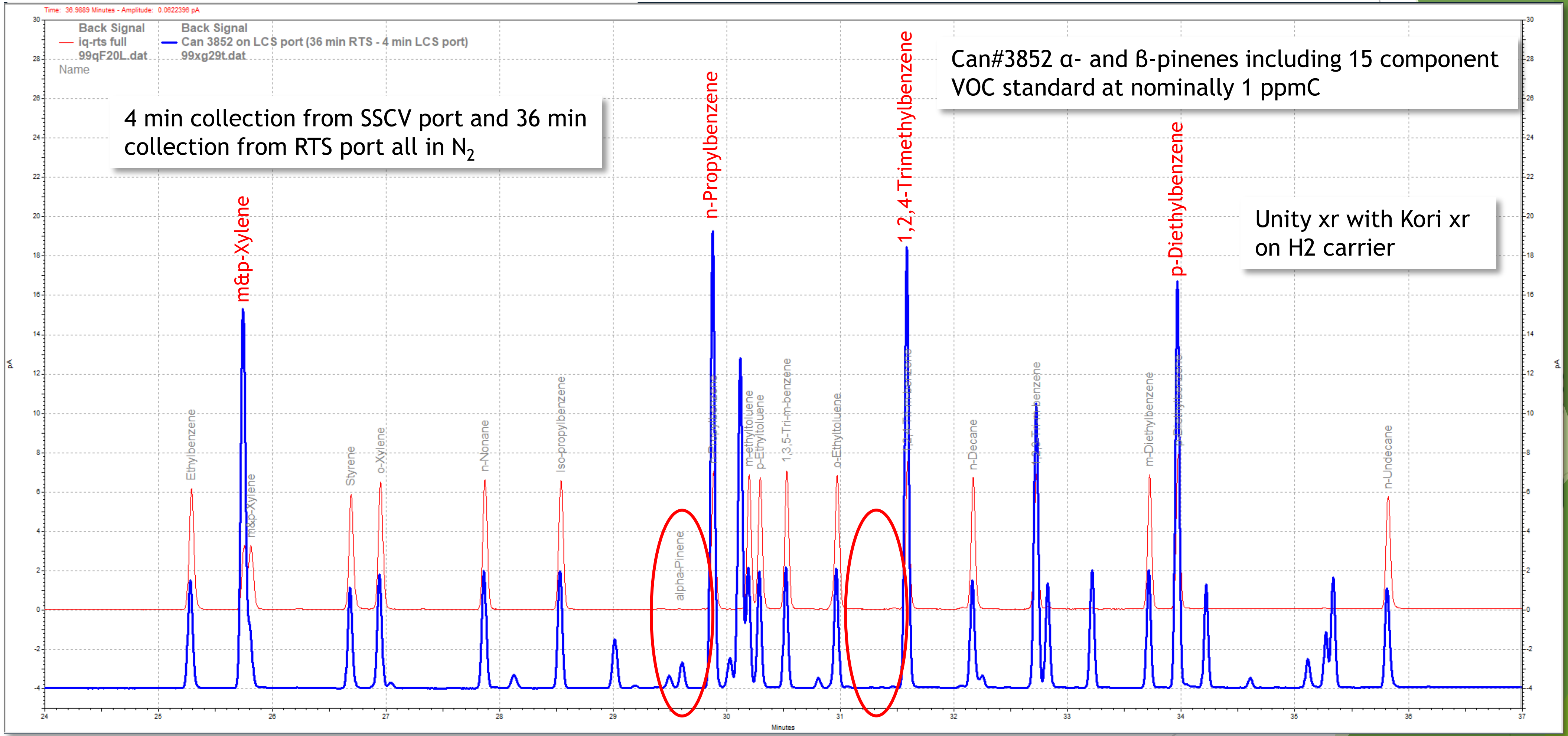
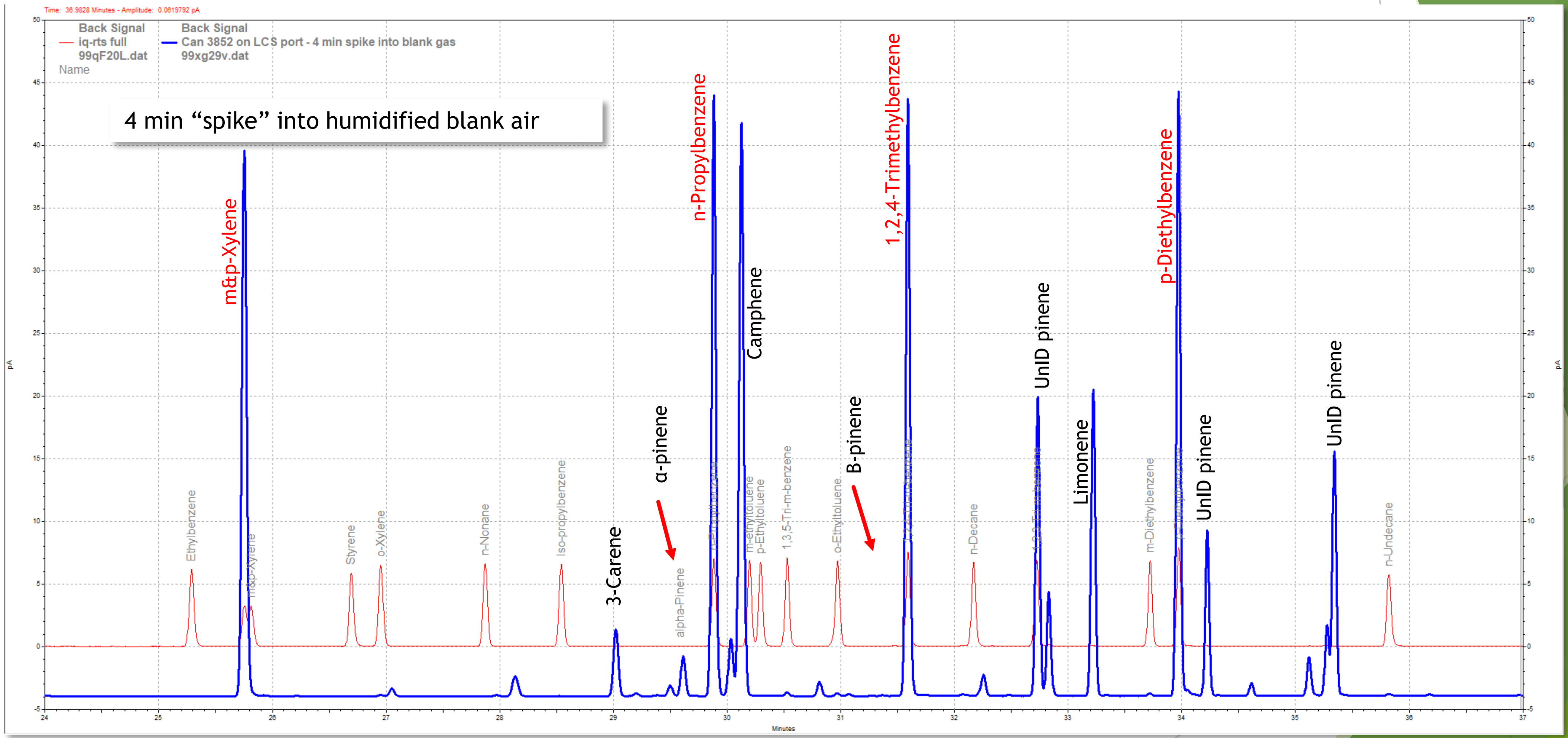


4 min collection from SSCV port and 36 min collection from RTS port all in N_2

Can#3852 α- and ß-pinenes including 15 component VOC standard at nominally 1 ppmC

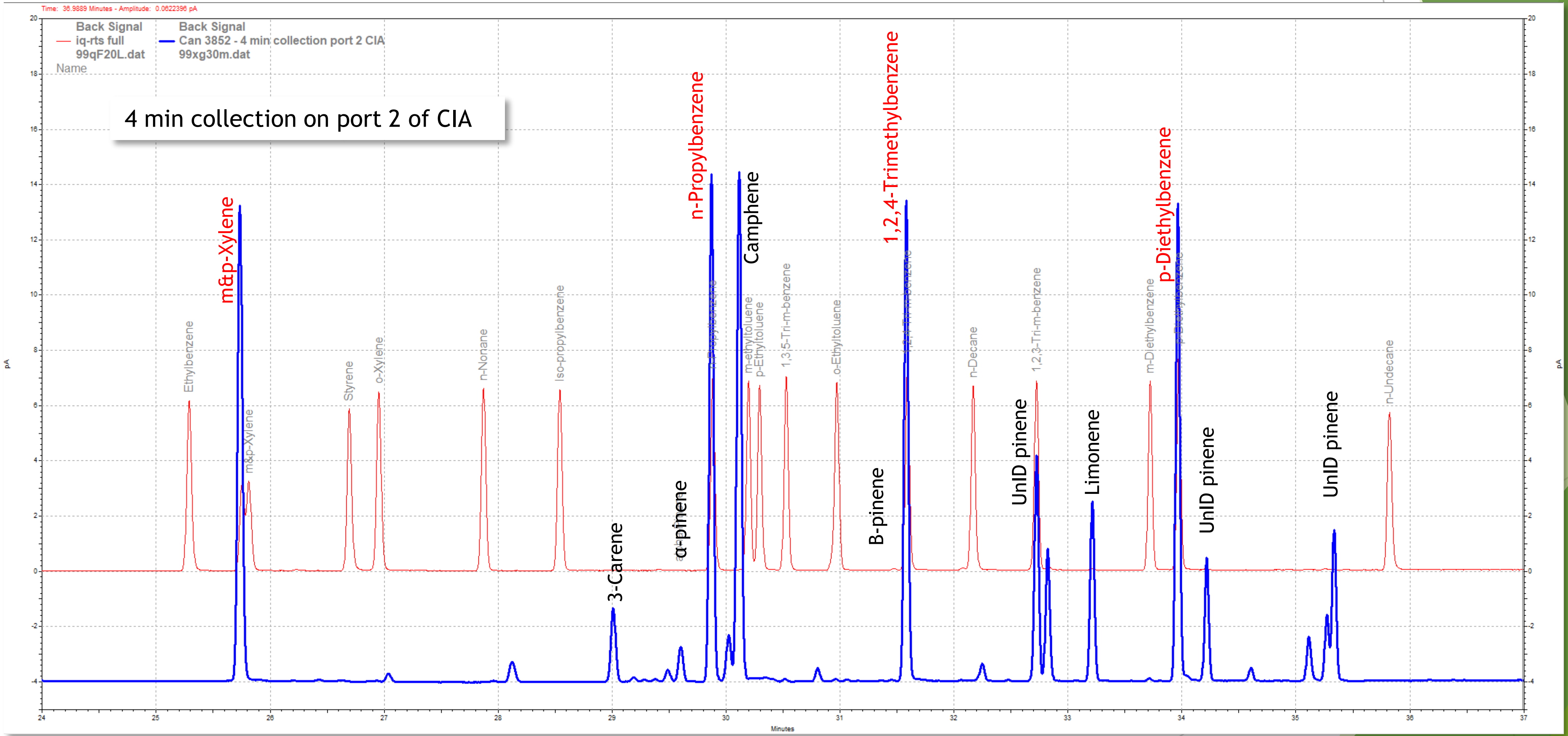
Unity xr with Kori xr on H2 carrier

AutoGC Systems: Pinenes



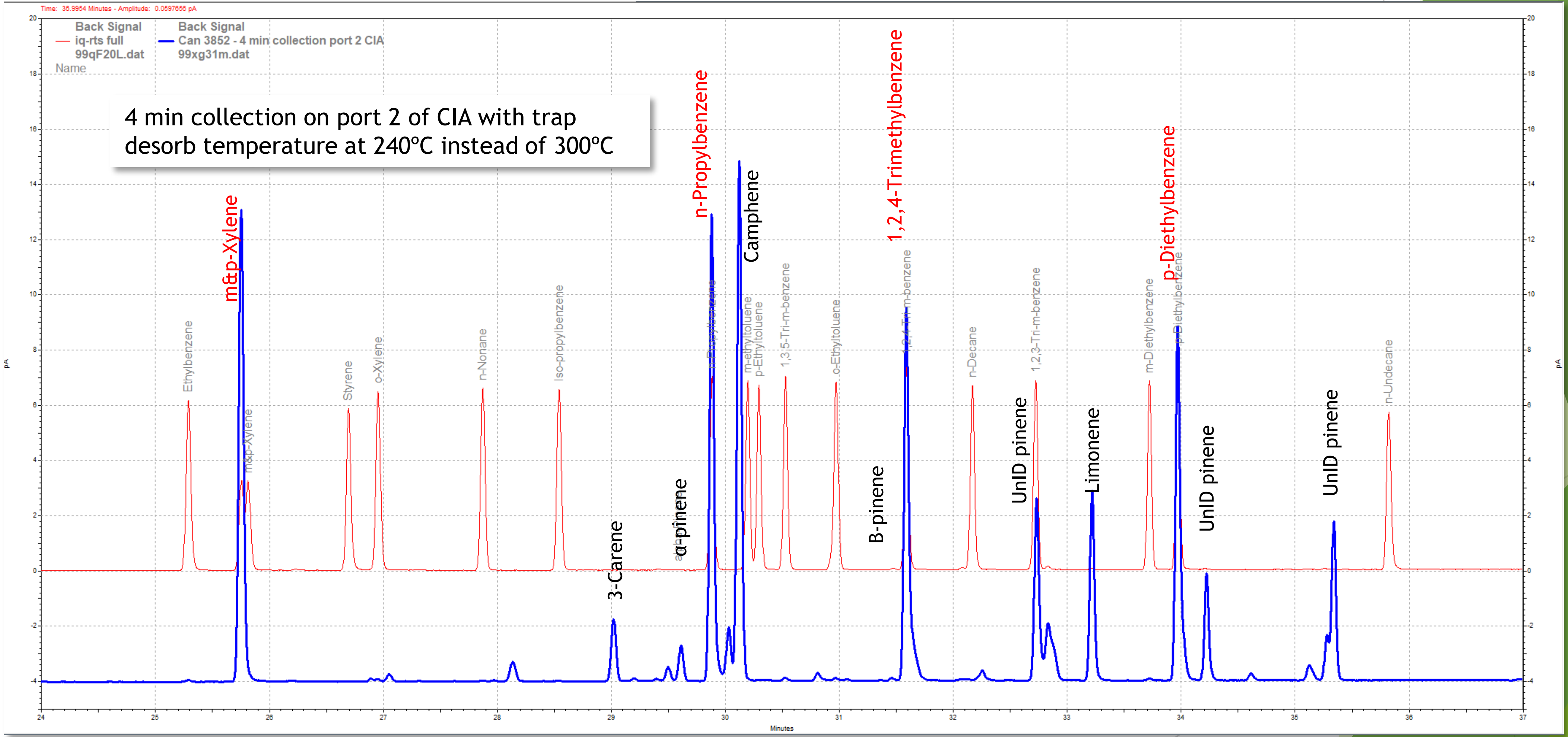
4 min “spike” into humidified blank air

AutoGC Systems: Pinenes



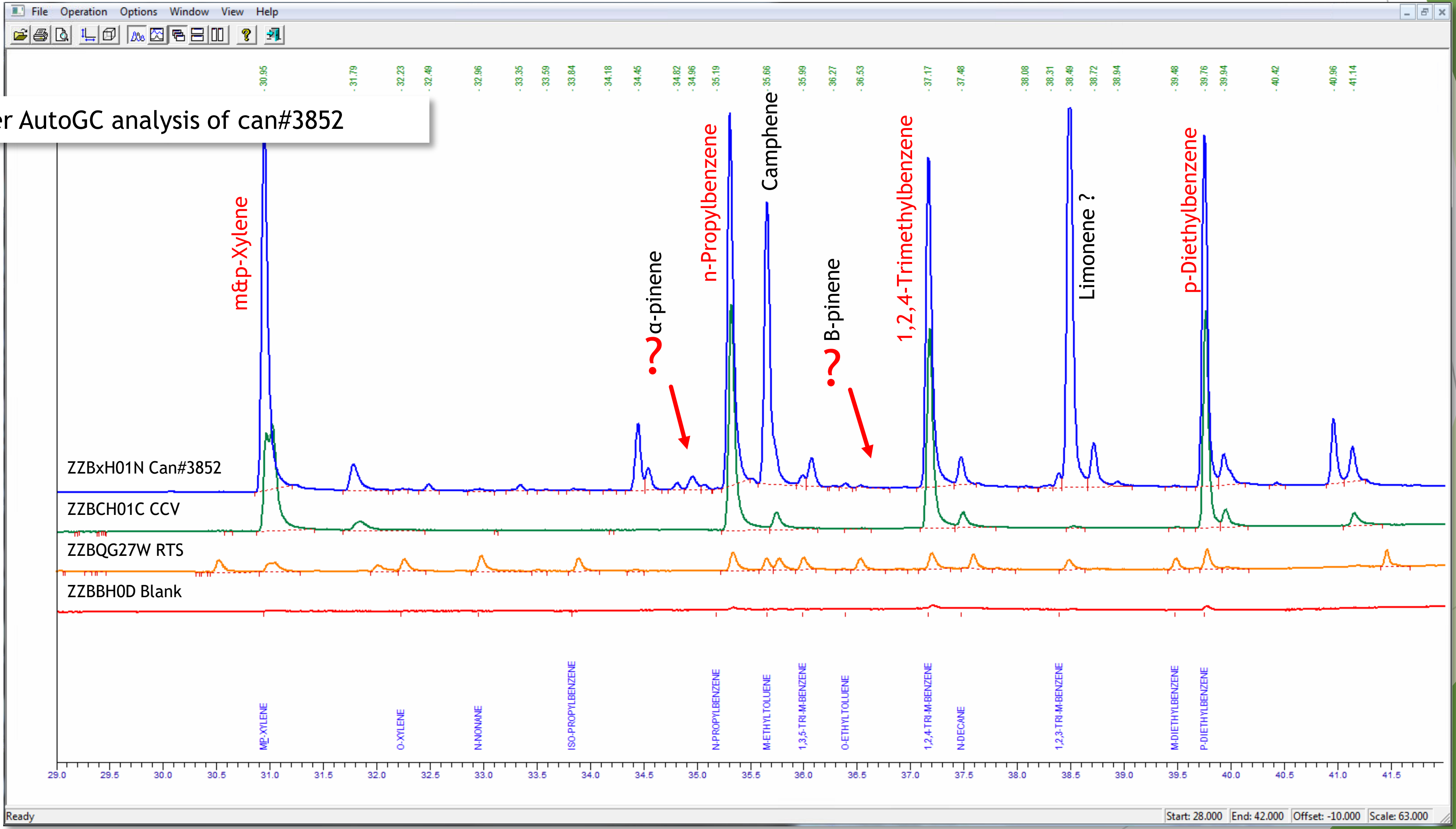
4 min collection on port 2 of CIA

AutoGC Systems: Pinenes



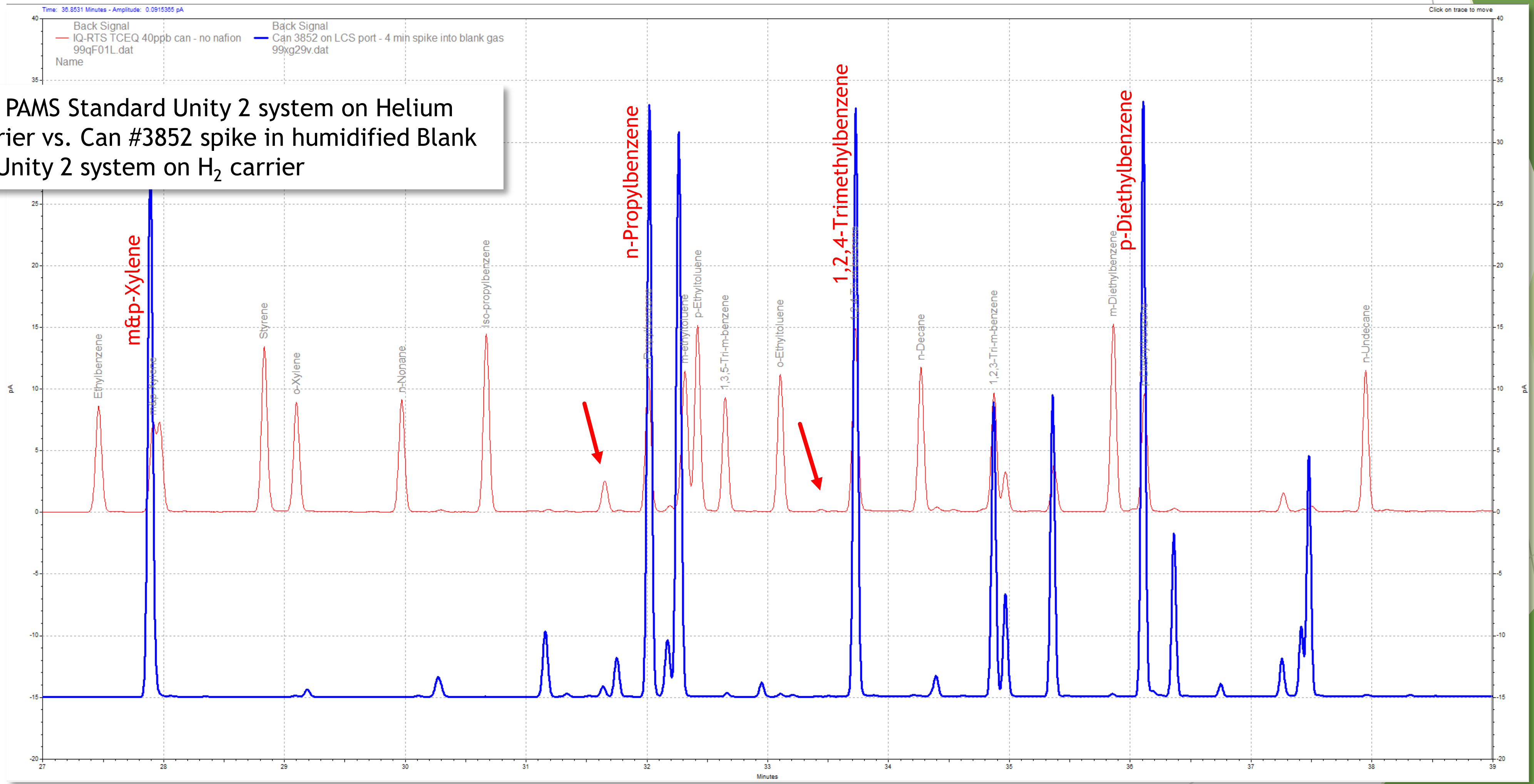
4 min collection on port 2 of CIA with trap desorb temperature at 240ºC instead of 300ºC

AutoGC Systems: Pinenes



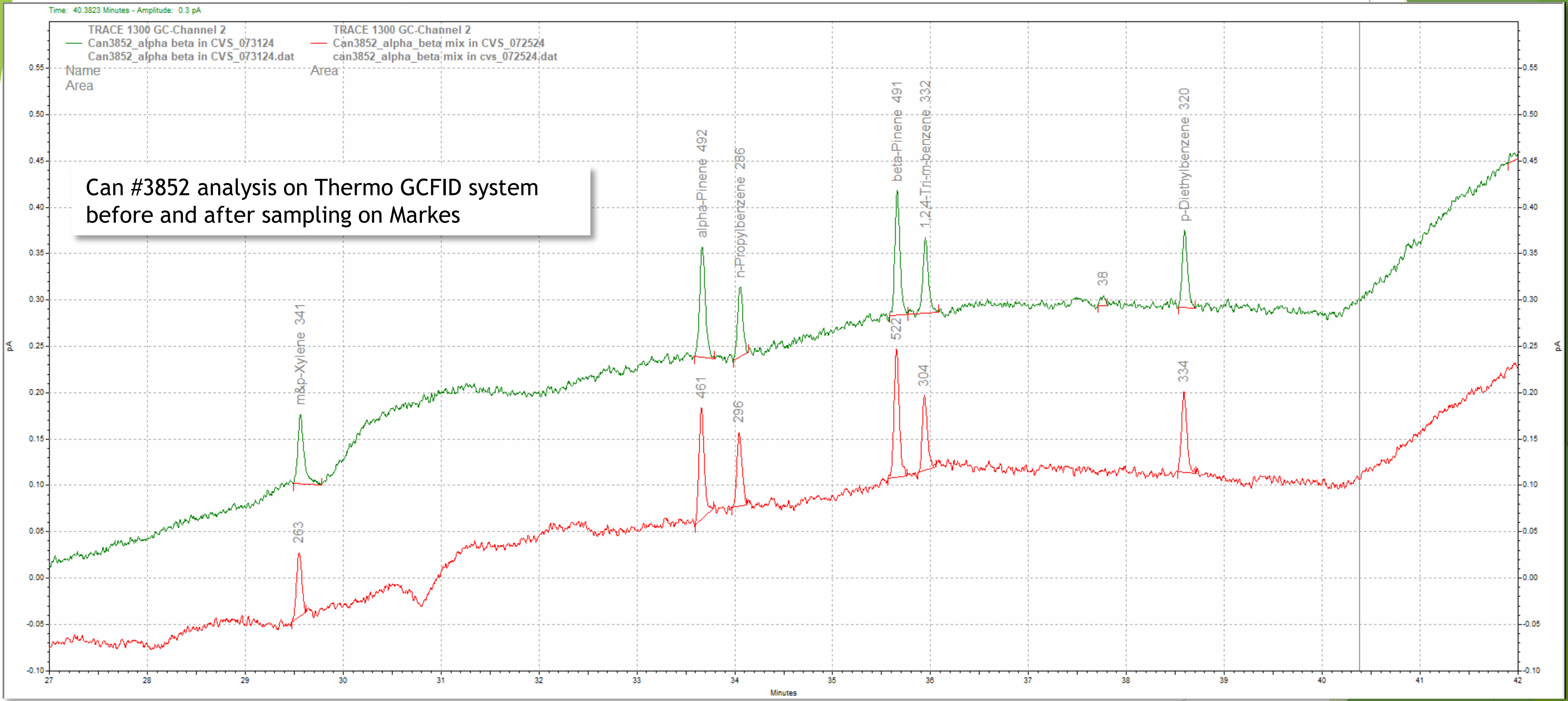
Perkin Elmer AutoGC analysis of can#3852

AutoGC Systems: Pinenes



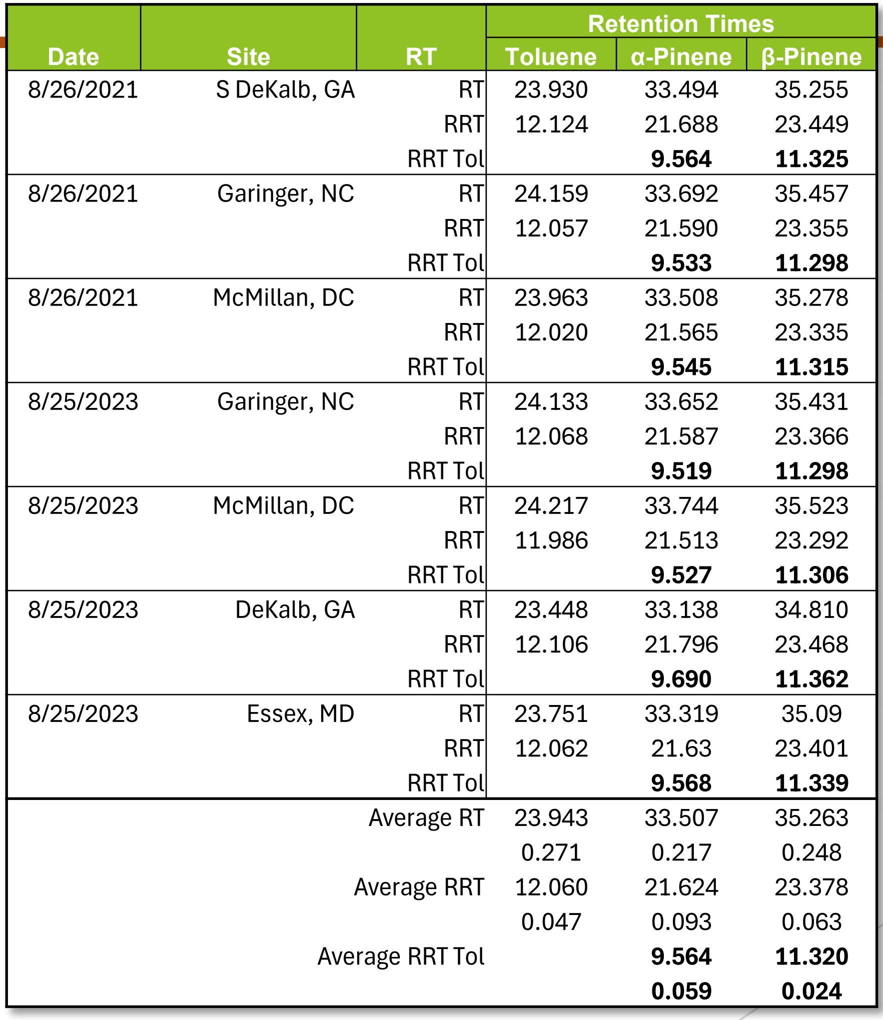
EPA PAMS Standard Unity 2 system on Helium carrier vs. Can #3852 spike in humidified Blank on Unity 2 system on H_2 carrier

AutoGC Systems: Pinenes



Can #3852 analysis on Thermo GCFID system before and after sampling on Markes

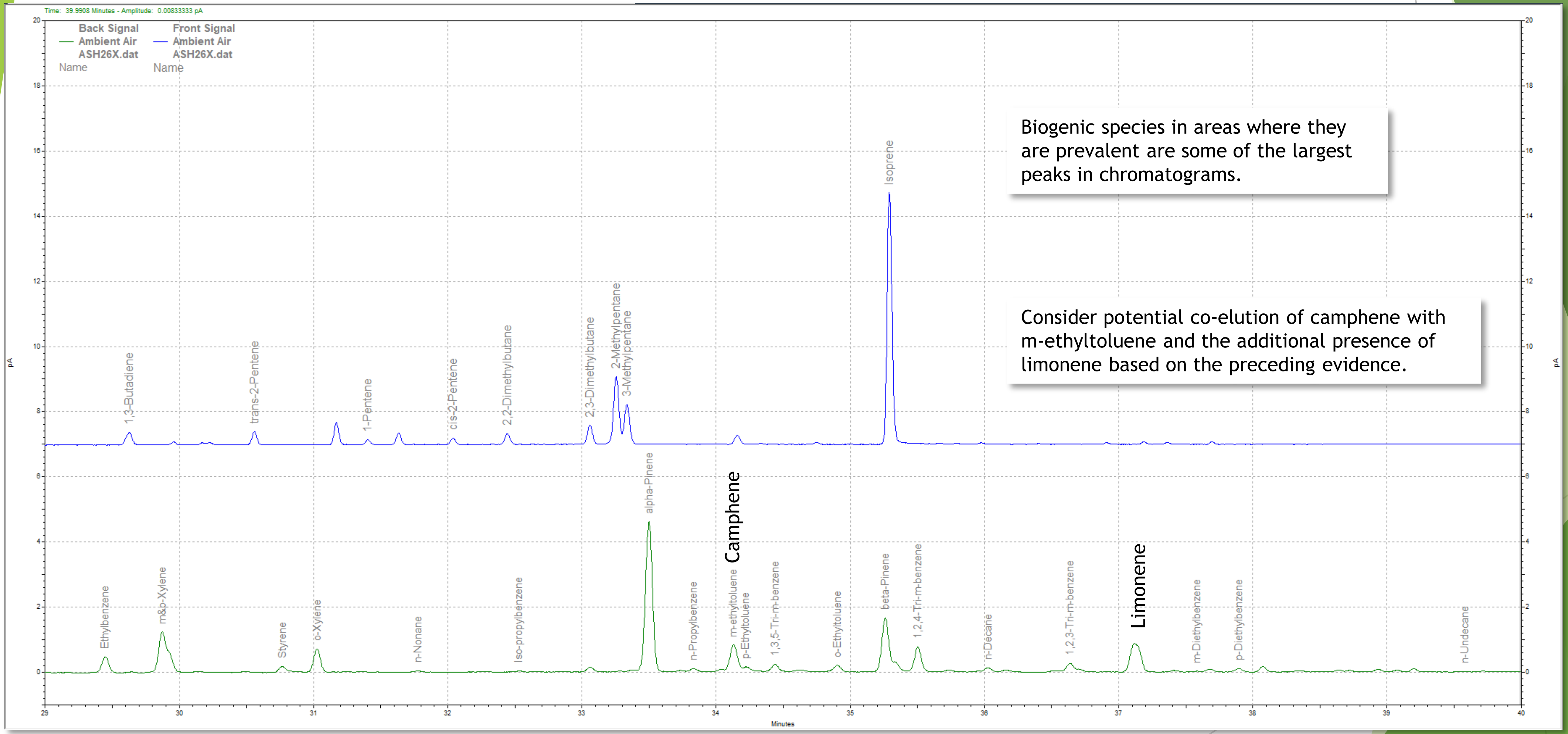
AutoGC Systems: Pinenes



Date	Site	RT	Retention Times		
			Toluene	**α-Pinene**	**β-Pinene**
8/26/2021	S DeKalb, GA	RT	23.930	33.494	35.255
		RRT	12.124	21.688	23.449
		RRT Tol		**9.564**	**11.325**
8/26/2021	Garinger, NC	RT	24.159	33.692	35.457
		RRT	12.057	21.590	23.355
		RRT Tol		**9.533**	**11.298**
8/26/2021	McMillan, DC	RT	23.963	33.508	35.278
		RRT	12.020	21.565	23.335
		RRT Tol		**9.545**	**11.315**
8/25/2023	Garinger, NC	RT	24.133	33.652	35.431
		RRT	12.068	21.587	23.366
		RRT Tol		**9.519**	**11.298**
8/25/2023	McMillan, DC	RT	24.217	33.744	35.523
		RRT	11.986	21.513	23.292
		RRT Tol		**9.527**	**11.306**
8/25/2023	DeKalb, GA	RT	23.448	33.138	34.810
		RRT	12.106	21.796	23.468
		RRT Tol		**9.690**	**11.362**
8/25/2023	Essex, MD	RT	23.751	33.319	35.09
		RRT	12.062	21.63	23.401
		RRT Tol		**9.568**	**11.339**
		Average RT	23.943	33.507	35.263
			0.271	0.217	0.248
		Average RRT	12.060	21.624	23.378
			0.047	0.093	0.063
		Average RRT Tol		**9.564**	**11.320**
				0.059	**0.024**

The use of Relative Retention Times may be useful to attempt to initially identify the presence of α- and β-pinenes. PAMS AutoGC systems are running a consistent GC method can produce robust retention times between sites and across years.

AutoGC Systems: Pinenes



Biogenic species in areas where they are prevalent are some of the largest peaks in chromatograms.

Consider potential co-elution of camphene with m-ethyltoluene and the additional presence of limonene based on the preceding evidence.

AutoGC Systems: Pinenes

- Summary
  - Pinenes appear to be somewhat stable in aluminum cylinders in dry N_2 for prolonged periods as single species and at ppmC concentrations.
  - Pinenes blends in dry N2 in Silco treated canisters are also stable for short periods of time at low ppmC levels.
  - However, injection either by short direct injection or by internal standard injection onto either T17 or T20 traps results in degradation using the PAMS AutoGC methods
  - Degradation does not appear to be related to GCFID performance since direct injection on similar systems without concentration appear to remain intact.
  - Breakdown appears to be similar between He or H_2 carrier.
  - Lowering trap desorb temperature does not appear to reduce pinene decomposition.
  - The determination of pinene retention times at sites with substantial forestation are easily demonstrated and confirmed by time series review.
  - Using relative retention time to Toluene in PAMS AutoGC standard methods results in reasonably accurate determination of predicted retention times based on data from sites with known pinene contributions.

AutoGC Systems: Pinenes References

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AutoGC Systems: Pinenes Acknowledgments

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Jonathan Meyer and Jesus Anguiano
for
blending a myriad of working standards and canisters

Amy Plummer
for
injecting these samples on the Markes and PE systems in every conceivable way attempting to get different results

All our valued customers from whom we always learn much and whose data has extended our knowledge of pinenes in AutoGC data

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The End

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