Hourly Monitoring of NMHCs by AutoGC for Photochemical Assessment Monitoring Stations (PAMS)

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National Ambient Air Quality Standards (NAAQS) Rule

"Following the directives of the Clean Air Act (CAA), on October 1, 2015, Administrator McCarthy signed a rulemaking action that revises the current national ambient air quality standards (NAAQS) for ozone to a new, more protective level of 0.070 parts per million (70 parts per billion)."

-From EPA Memorandum re: Implementing the 2015 Ozone National Ambient Air Quality Standards, 1 Oct 2015

Changes to PAMS VOC monitoring requirements:

- Redistribution of sites – NCore sites in CBSA > 1 million
  - Additional monitors based on State EMPs for non-attainment areas
- Continuous Monitoring – canister samples only on waivers
- Hourly sampling only for ozone season

NMHC Monitoring Strategies: Sampling

- Sample field collection → Analysis in the Laboratory
  - Collection in canisters
  - Collection on sorbent tubes
  - Analysis by either GC-FID or GC-MS
  - Less frequent sampling 3 hour or 8 hour composite samples
  - Delay in results
- Continuous field sampling and analysis
  - Collection and analysis by AutoGC
  - Generally GC-FID
  - Hourly samples
  - Immediate results

NMHC Monitoring Strategies: Analytical Choices

GC-FID

- Less expensive
- Stable < 2% drift over 1 month
- Response relative to carbon
  a. carbon-based calibration
  b. relative carbon reactivity
- Linear detector response
- Not sensitive to O_2, N_2 or H_2O
- Possible interferences

GC-MS

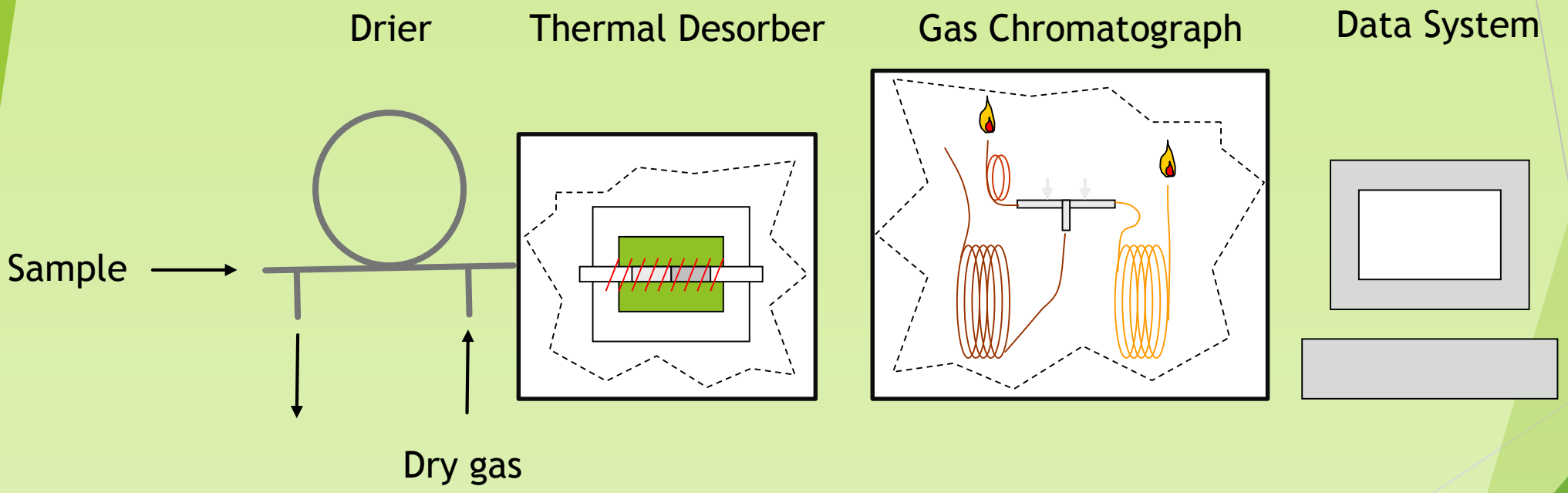
- More complex data
- More complex operation
- Requires more frequent calibration
  a. requires target specific calibration
  b. non-linear response
- Non-uniform detector response
- Sensitive to O_2, N_2 or H_2O interference
- Not sensitive to interferences

NMHC Monitoring Strategies: AutoGC

- Continuous field sampling and analysis
  - Collection multiple bed sorbent trap
    - 40 minutes minimum each hour
    - Cryogenic collection temperature for C2 NMHCs
    - Requires humidity control generally via permeable membrane
    - Overlapping collection and analysis
  - Separation via multi-dimensional gas chromatographic system
    - Sample injected to boiling point column for C6 – C12 analysis
    - C2-C6 NMHCs elute to second PLOT column
    - Dual FID system
  - Analysis via Chromatographic Data system
    - Identification and quantitation complete each hour

AutoGC Systems: Hourly Sample Collection and Separation

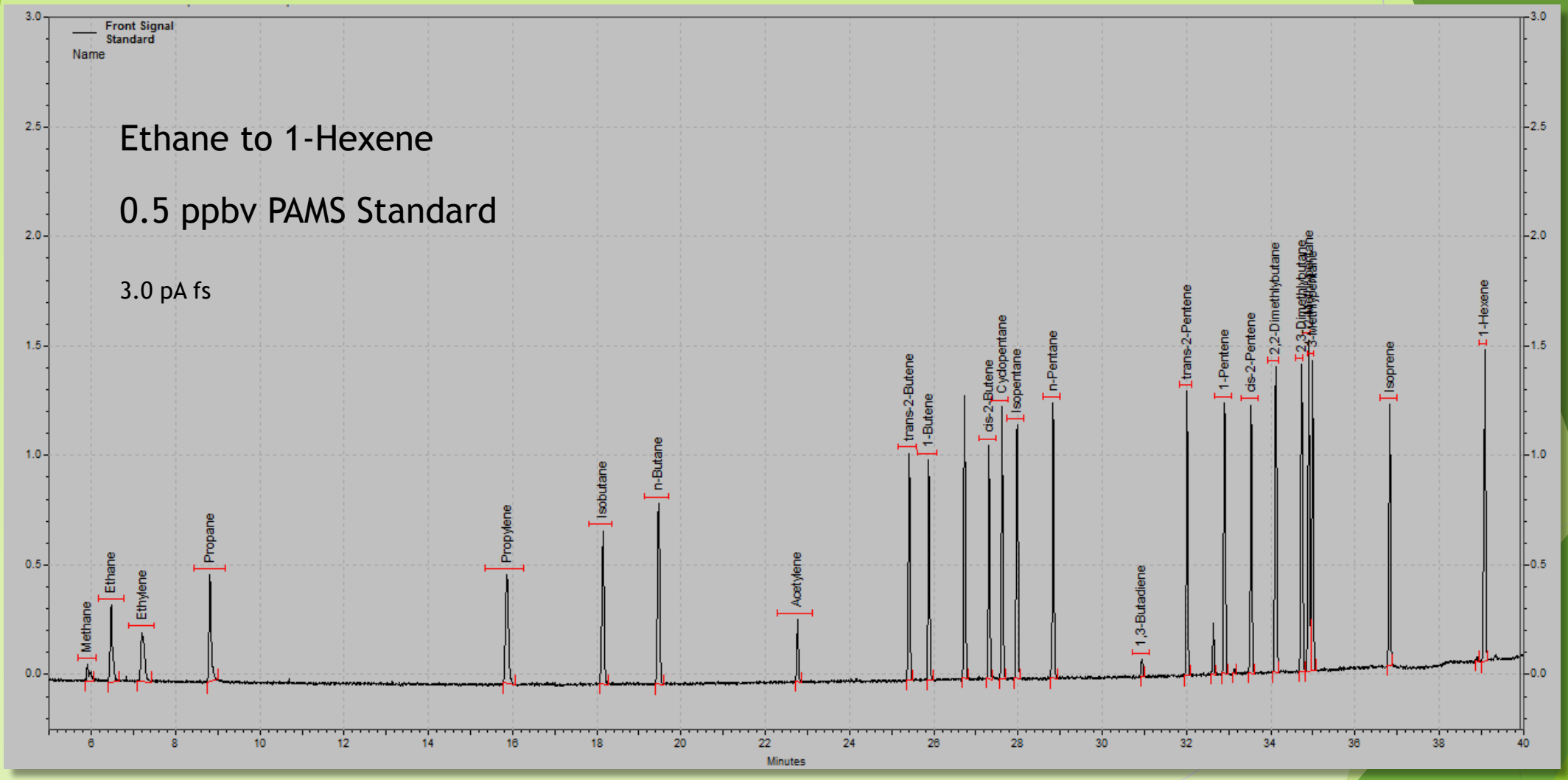
Basic System for the Separation of NMHCs from Ambient Air



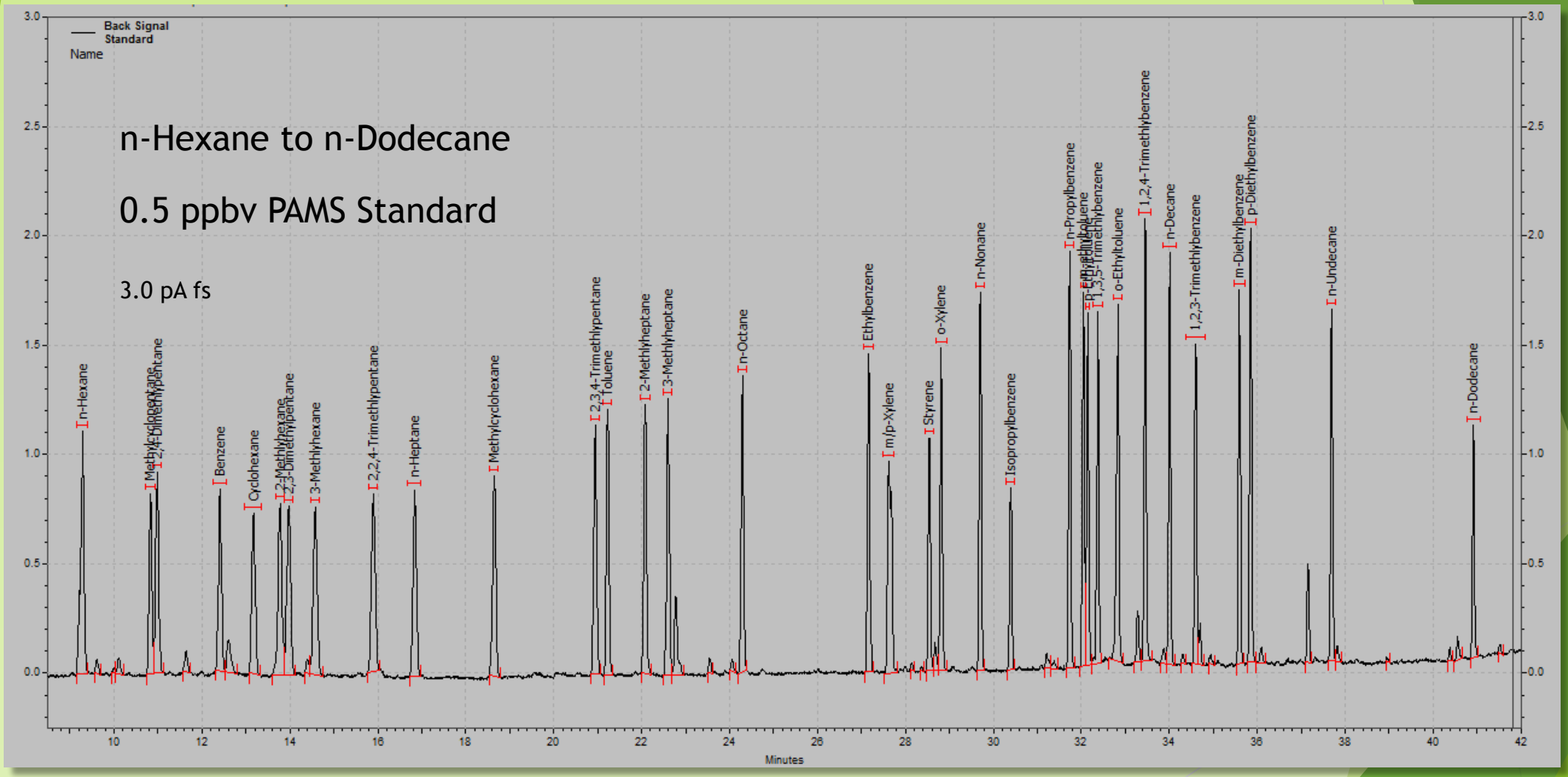
Ancillary Equipment Requirements

- Air supply – Compressor
  - Purification Systems to supply
    - Dry air < 1ppm moisture for Peltier cooler and nafion drier ~ 350 mL/min
    - Hydrocarbon-free air for FID support gas ~ 800 mL/min
    - Dilution gas for dilution system ~150 – 300 mL/min
- Hydrogen
  - Cylinder gas or Hydrogen generator ~80 mL/min
- Carrier gas – Helium ~10-15 mL/min
- Sample manifold and pump
- Canisters and dilution system
  - Calibration curves
  - Check standards

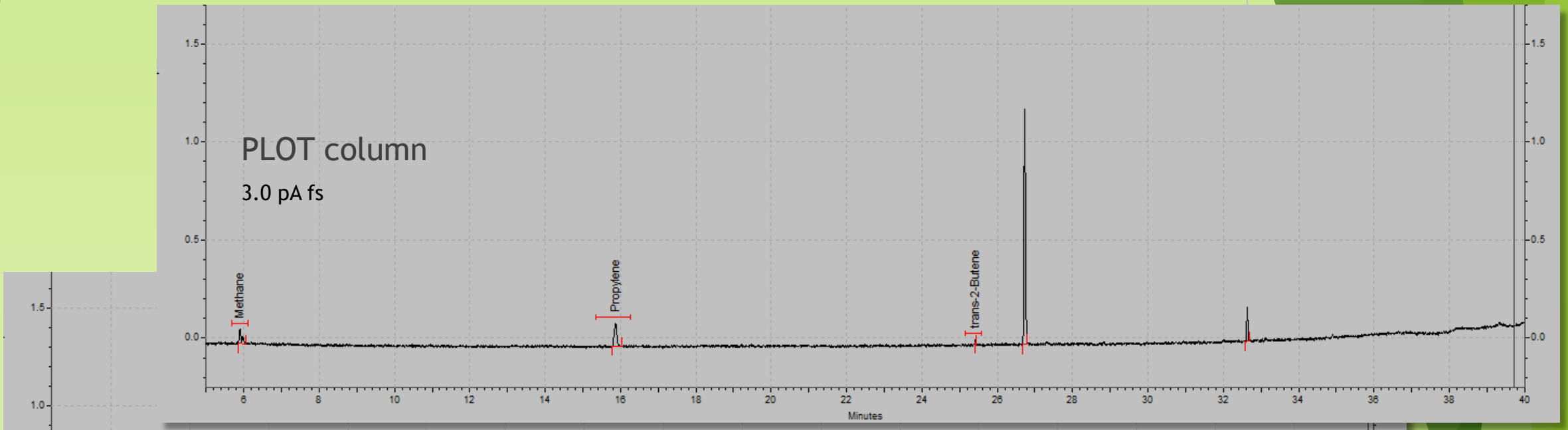
C2-C6 Alumina PLOT Separation

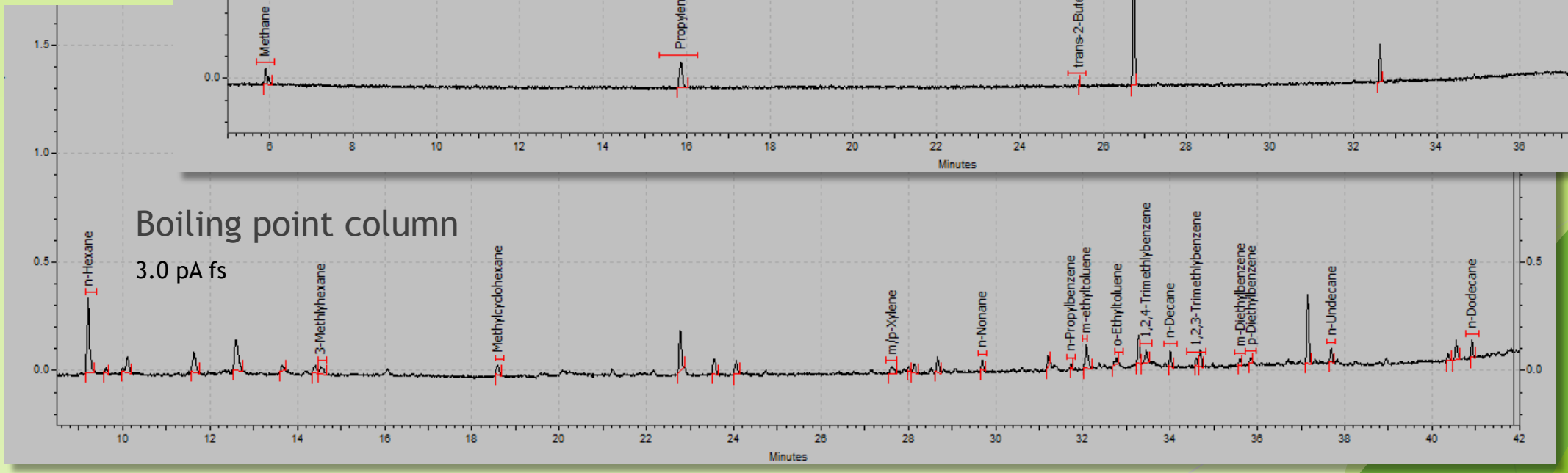


C6+ Dimethylsiloxane (Boiling Point) Separation

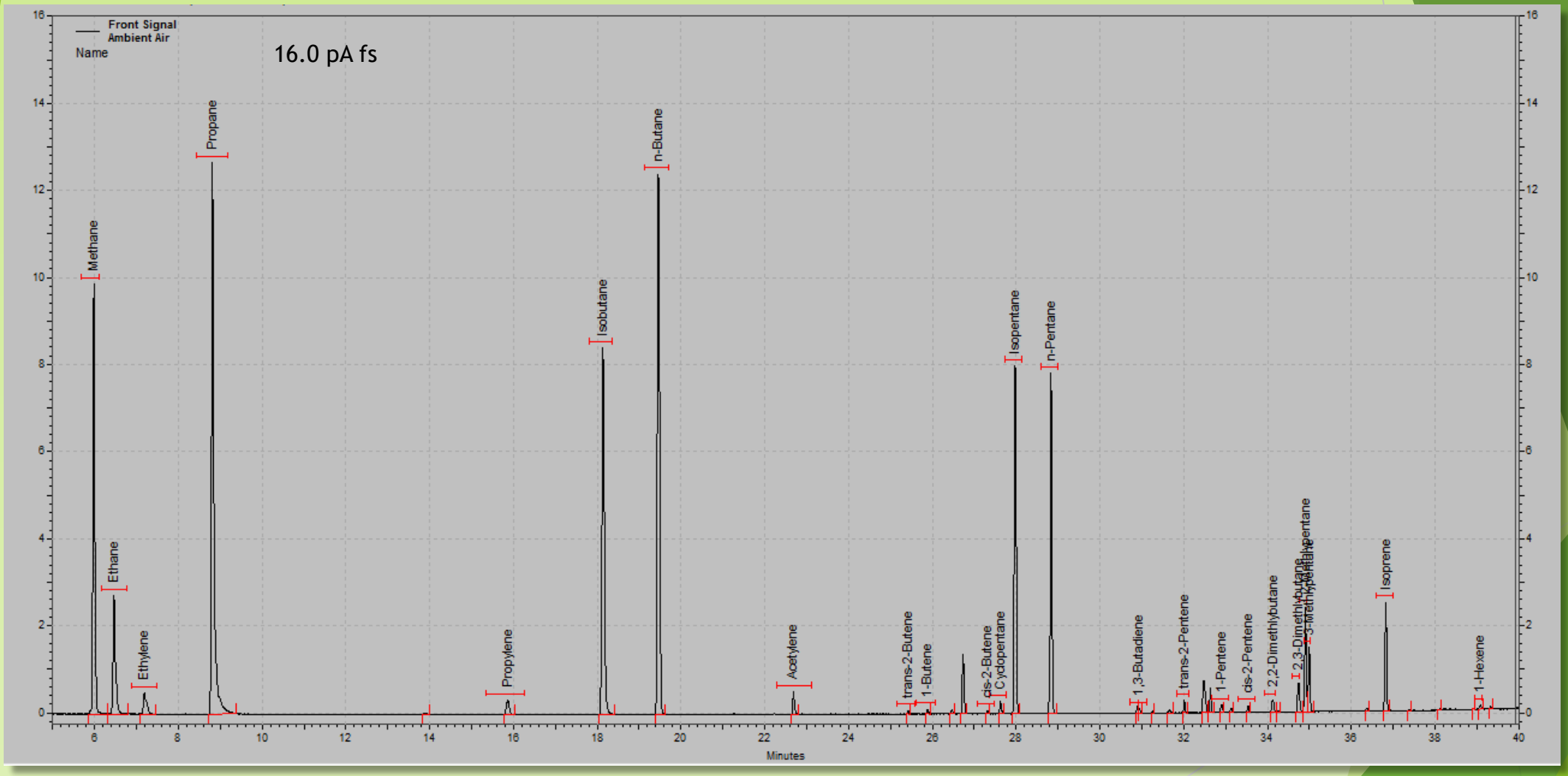


Analytical Blank

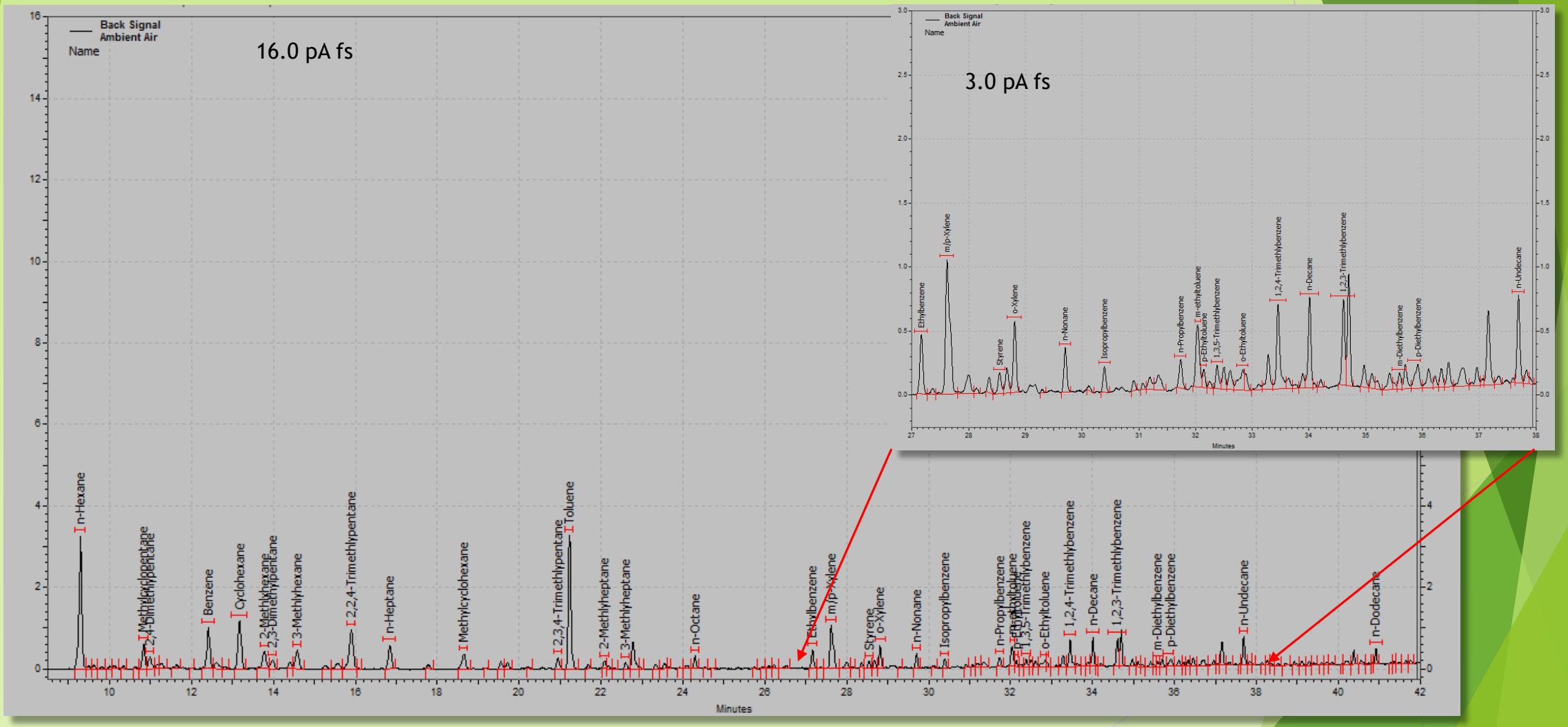




Ambient Air – PLOT Column



Ambient Air – Boiling Point Column

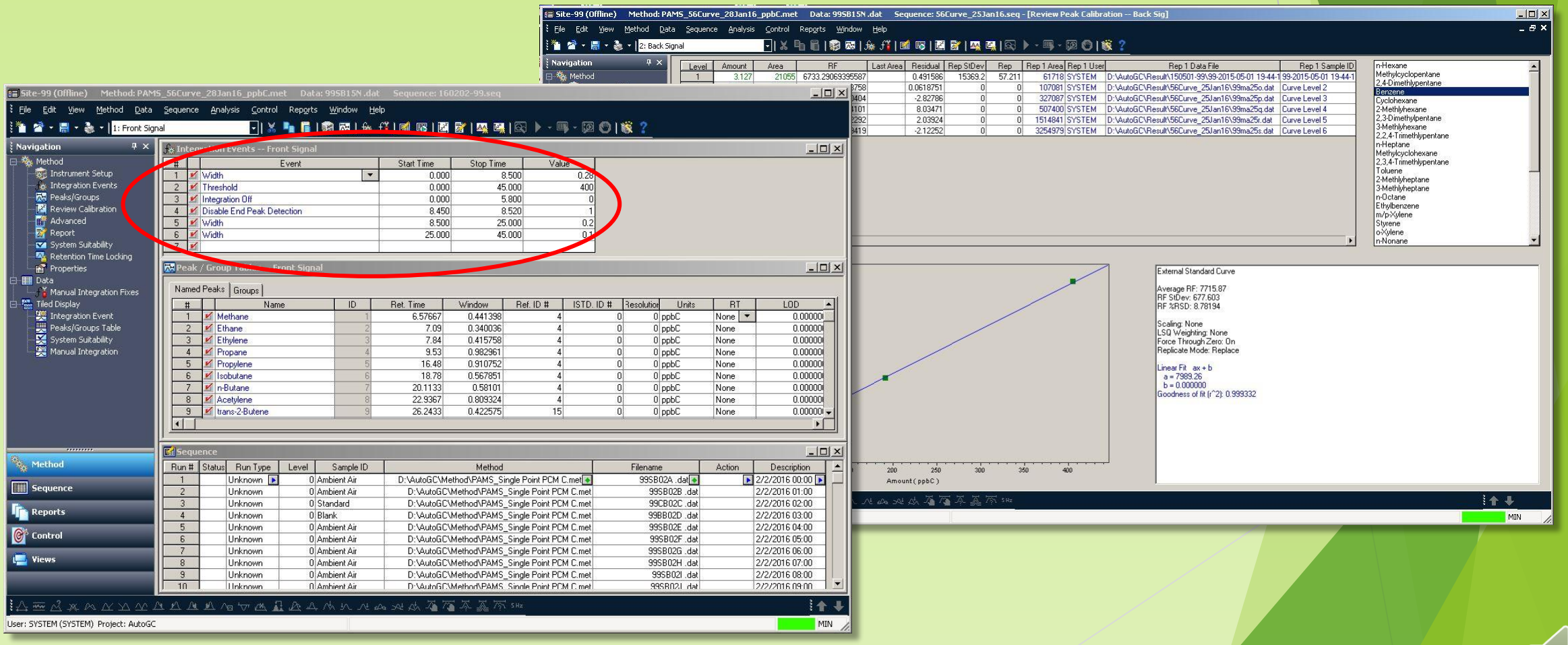


Chromatography Data Systems

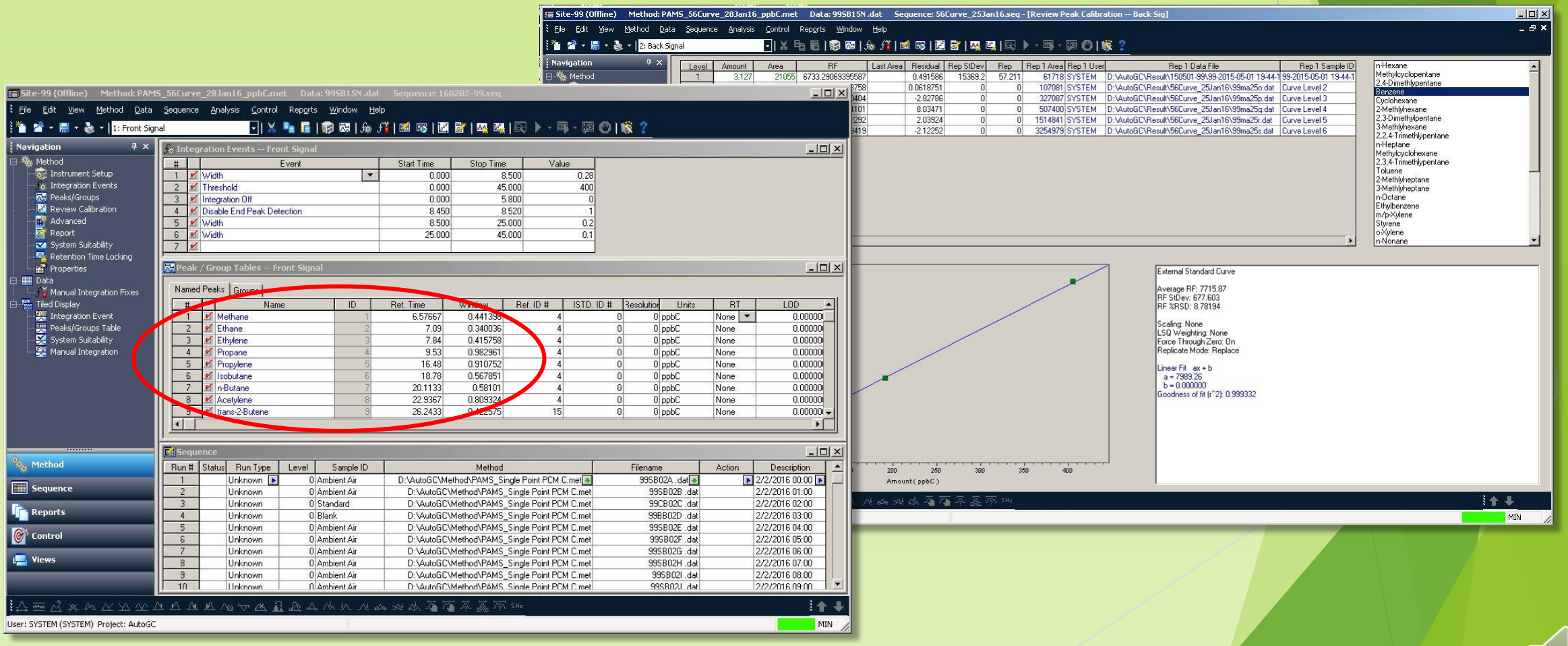
Requirements:

- Data portability
- Ability to reconstruct the original processing method from result
- Use of Retention time references to accommodate diurnal shifts
- Use of response factors and calibration by reference for unidentified HCs
- Ability to name files for easy identification of site, date, time, hour and sample type
- Ability to schedule and control introduction of routine quality control samples
- Ability to recover from simple power failures and continue hourly sampling

Method Development
EZChrom Chromatography Data System



Method Development
EZChrom Chromatography Data System



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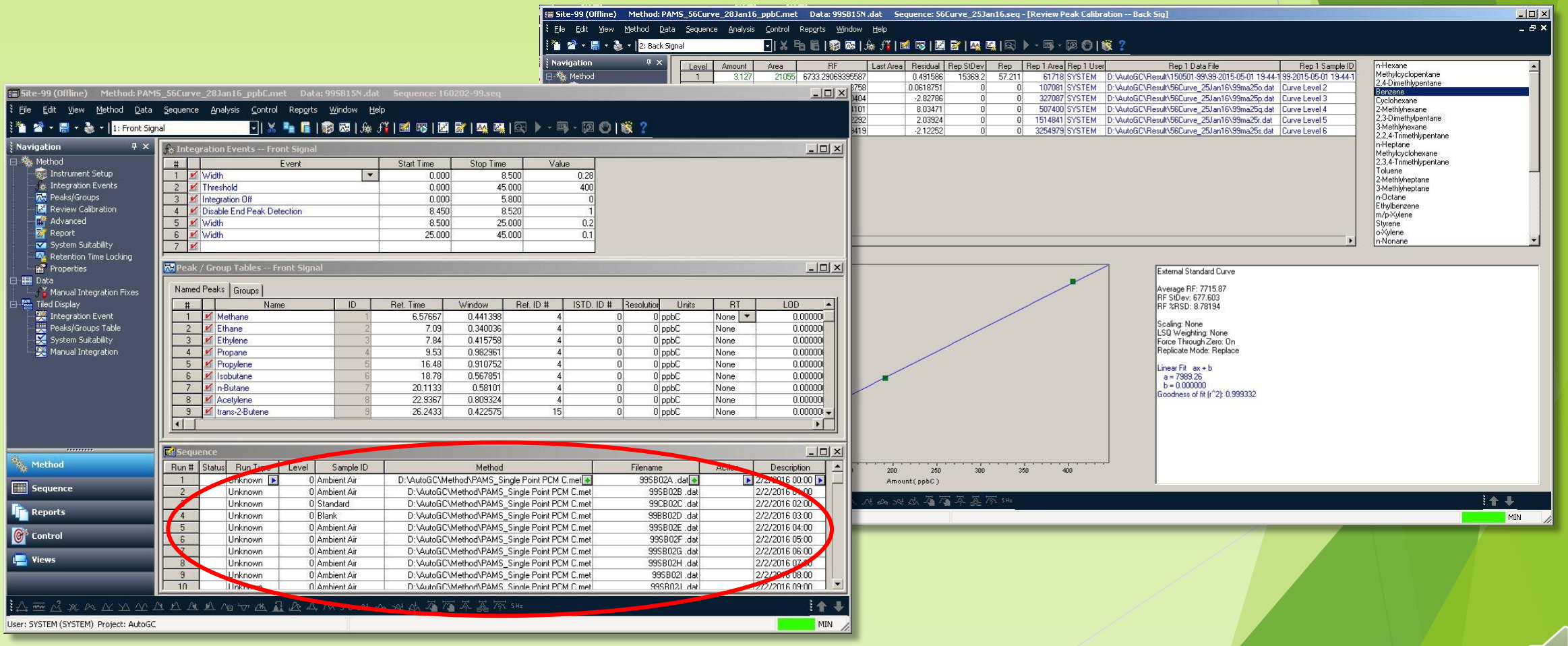
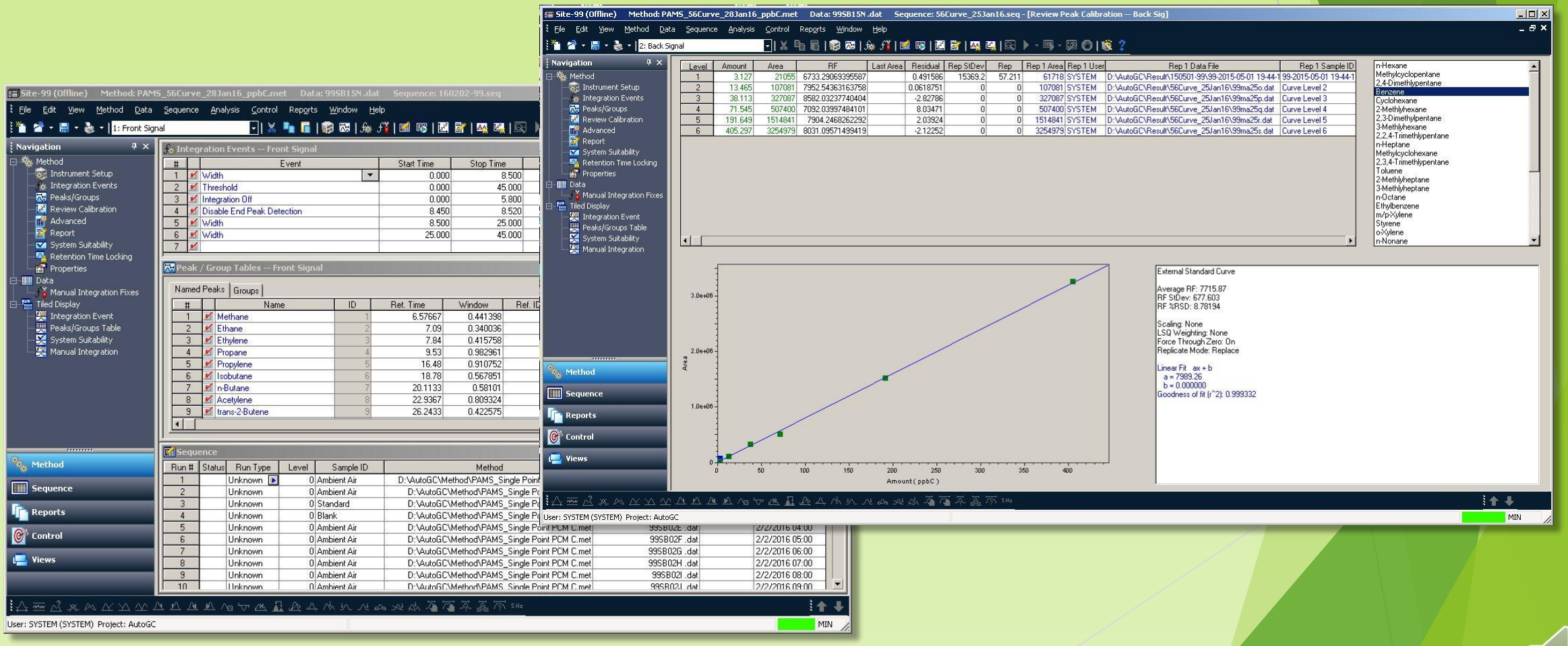


Method Development
EZChrom Chromatography Data System



Calibration Considerations

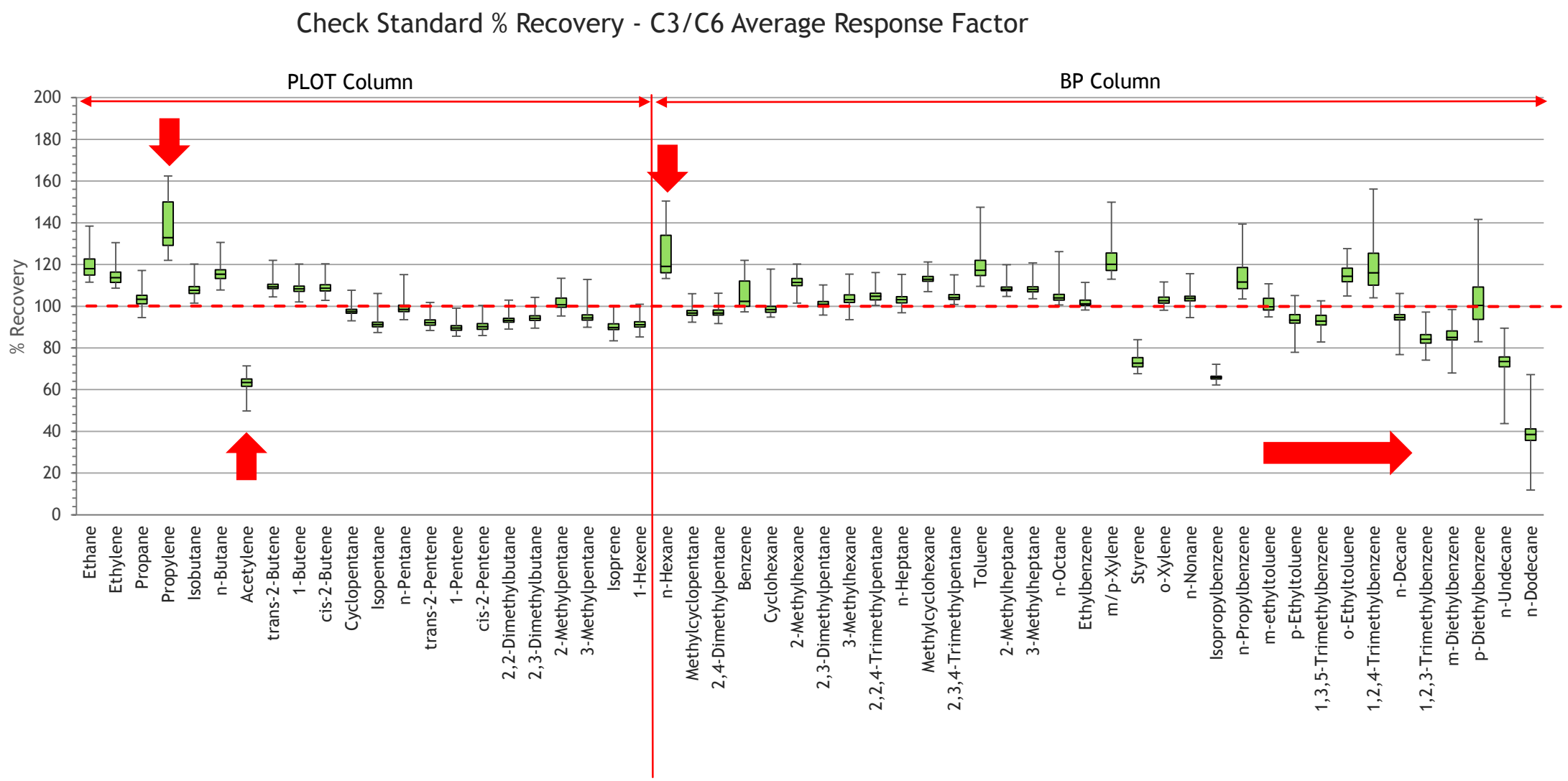
Target Specific Linear Regression

- Requires standard containing all targets
- Requires vigilant calibration validation procedures to insure all targets are calibrated correctly
- Typical for GC-MS systems which require target specific calibration

Carbon Based Response Factors

- Only requires certified standards for reference components
- Uses simple average Response Factor
- Easily applied and confirmed for all targets
- Specific to GC-FID systems with carbon based response

Recoveries in Daily Check Standard at 0.5 ppbv



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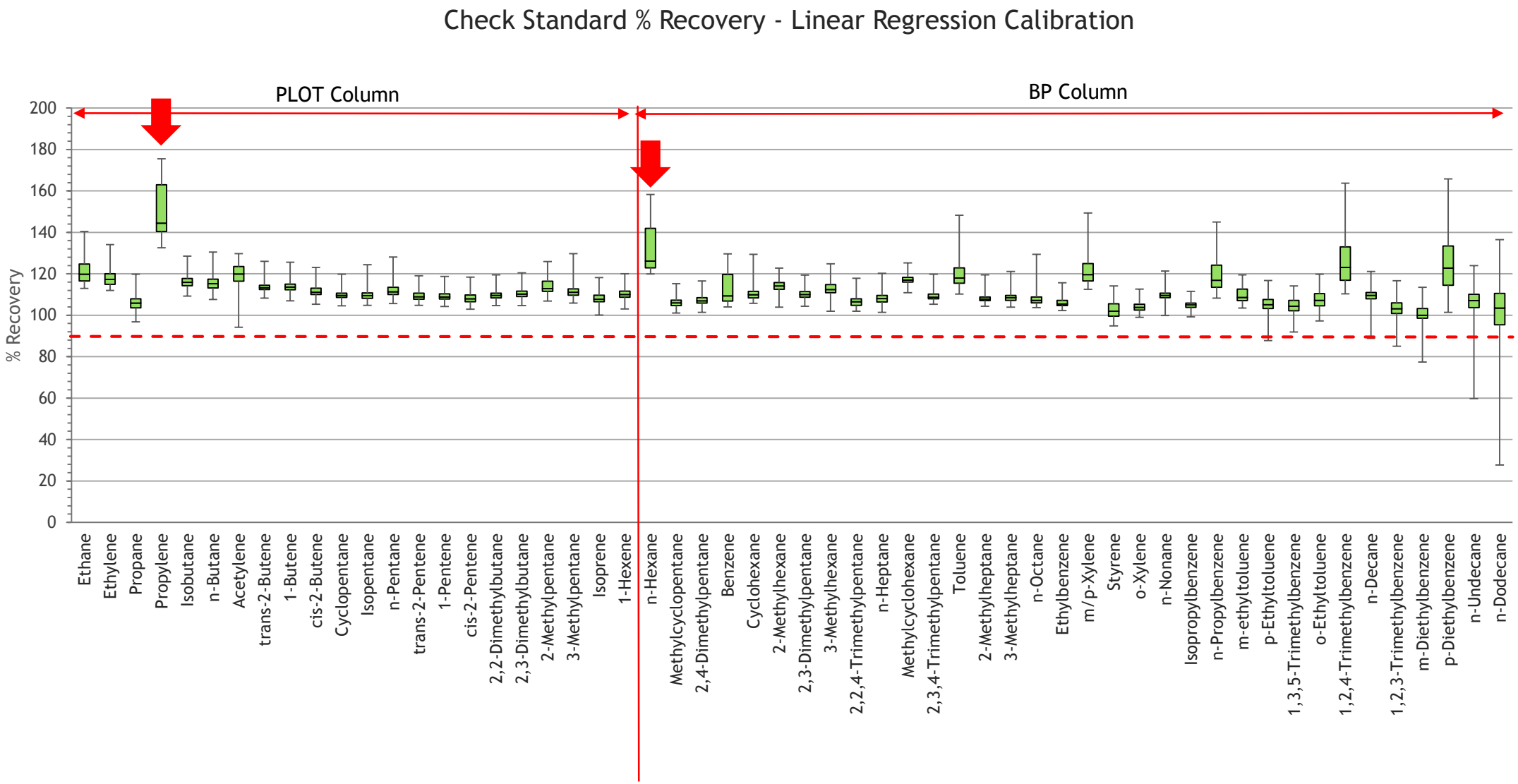
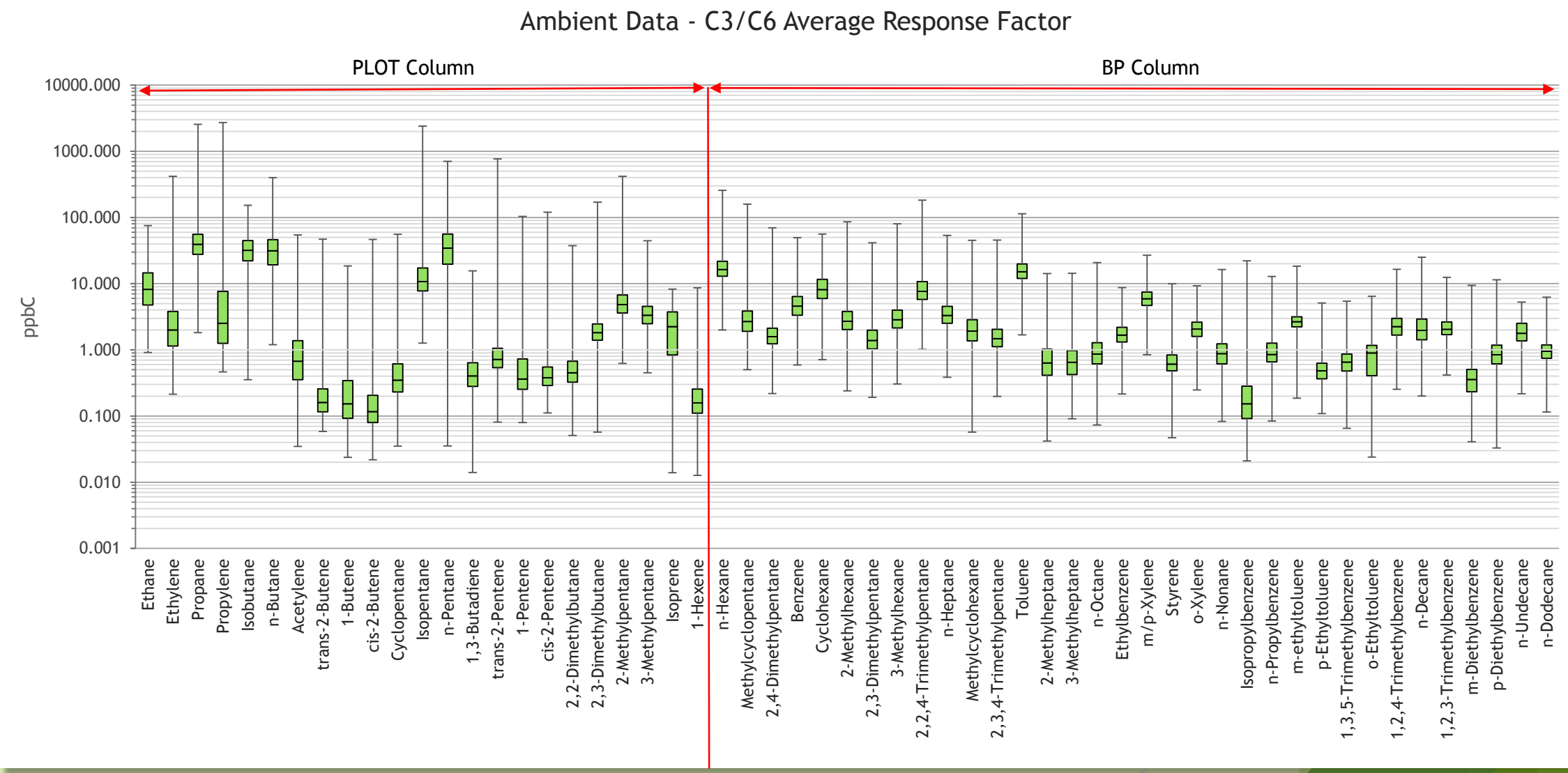
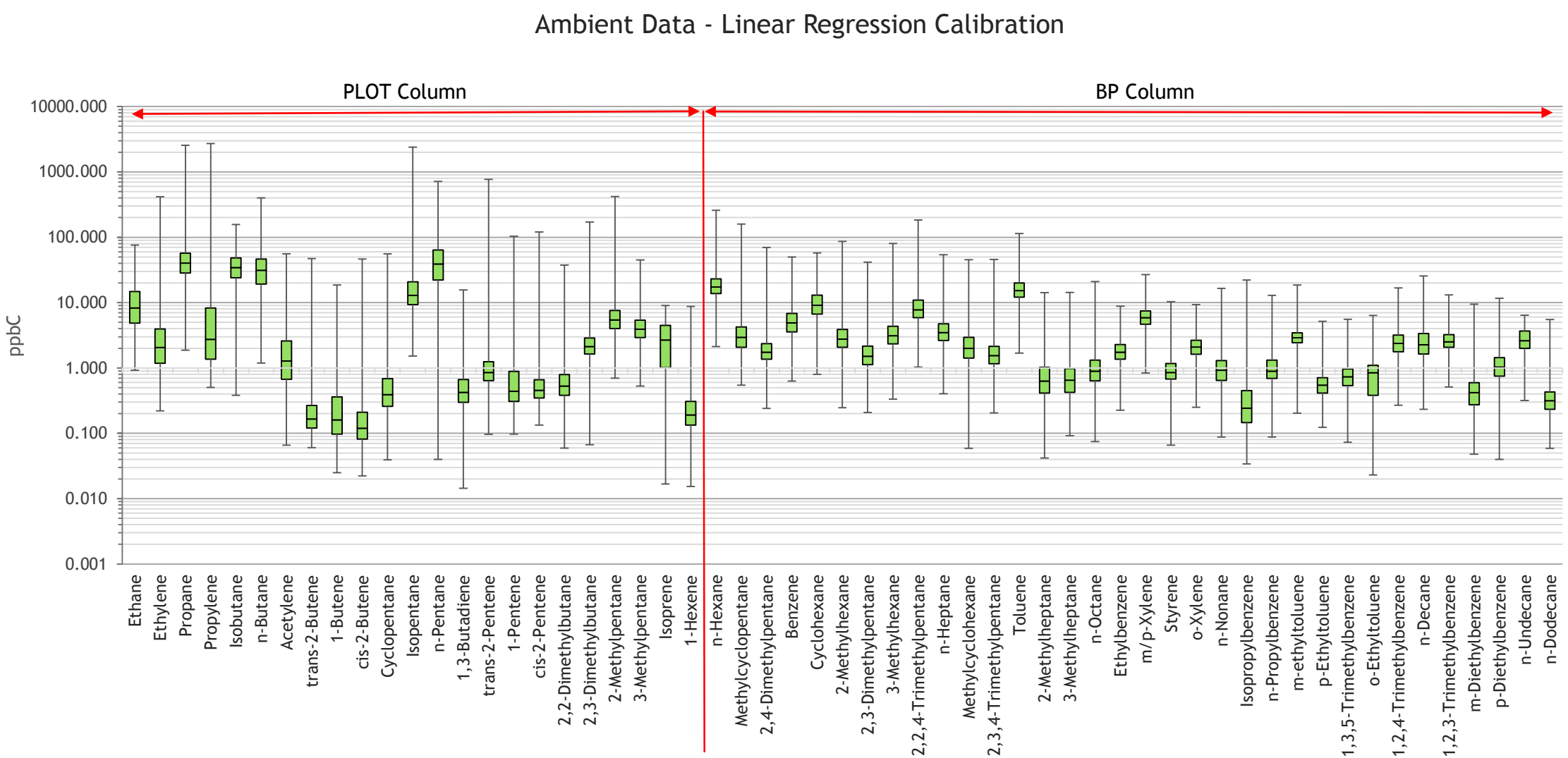


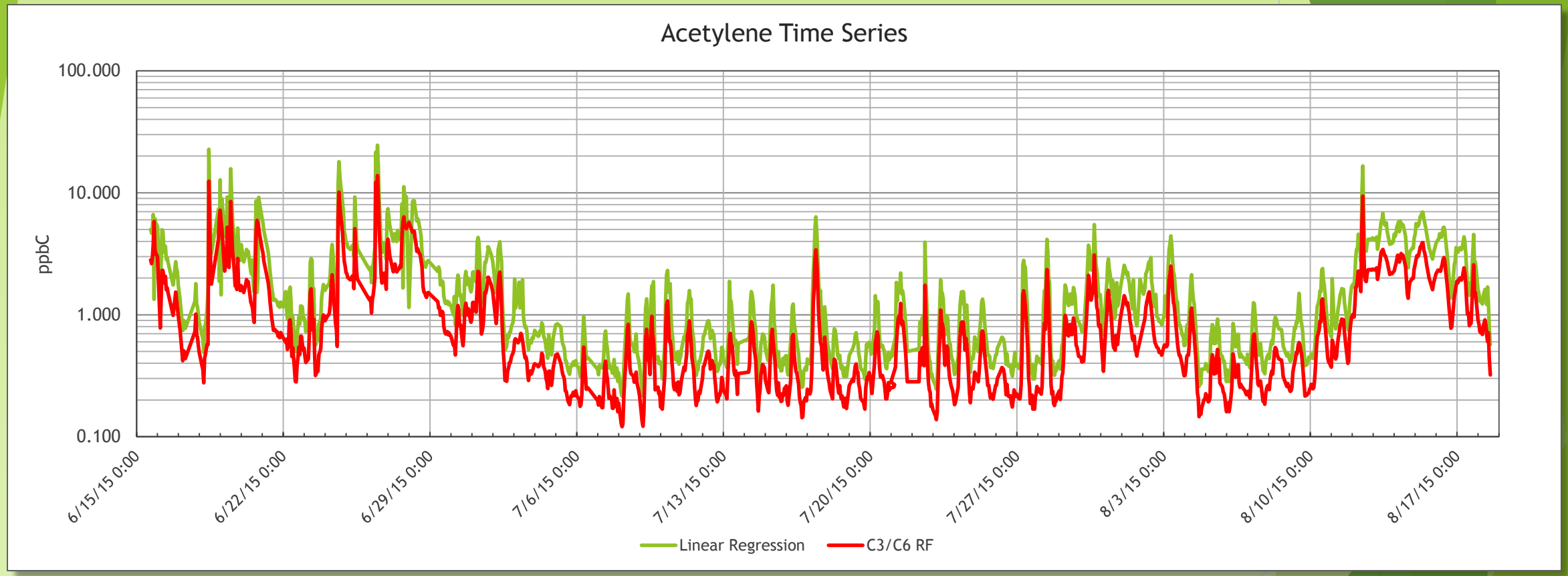
Ambient Data – Carbon Response Factor Calibration



Ambient Data – Linear Regression Calibration



Linear Regression vs. Carbon Response Calibration Effect on Measured Concentrations



Data Quality Objectives

Operations

- Well defined Operating Procedures
- Well documented instrumental parameters
- Fully automated system to reduce errors in operator activities
- Easily identifiable and transportable data files
- Fully automated Quality Checks

Data Validation

- Well defined Data Quality Objectives
- Real-time data transfer and review
- Well defined validation operating procedures
- Good annual audits to review instrument performance across network.

Network Quality Control

Quality Control Check	Composition	Purpose	Frequency	Acceptance Criteria
Retention Time Standard (RTS)	Mixture containing all target compounds ideally between 1-5 ppbC	To help assess retention time shifts and optimize processing methods	Twice a month or weekly	100% of the compounds are identified correctly in the multicomponent RTS
Calibration Verification Standard (CVS)	Mixture of 15 reference compounds including Propane and Benzene used for calibration	To assess the instrument drift and ensure continued instrument calibration	Daily	1) Propane and Benzene % recoveries within 75% - 125% and all other calibrants within 55 - 145%
				2) Data must be bracketed by valid CVS
Method (Analytical) Blank	Humidified, clean air	To assess system contribution to the measurement	Daily	1) All target compounds < 2.0 ppbC
				2) TNMHC < 20 ppbC
				3) Data must be bracketed by valid blanks
Precision Check	Mixture used for CVS	To assess analytical precision	Weekly	Propane and Benzene %RPD < 20% in two consecutive CVS runs
Laboratory Calibration Standard (LCS)	Mixture of 15 reference compounds including Propane and Benzene used for calibration	Second source standard, statically blended 5 ppbv	Twice a month or weekly	Propane and Benzene % recoveries within 70-130%

Data Review – Data Validation

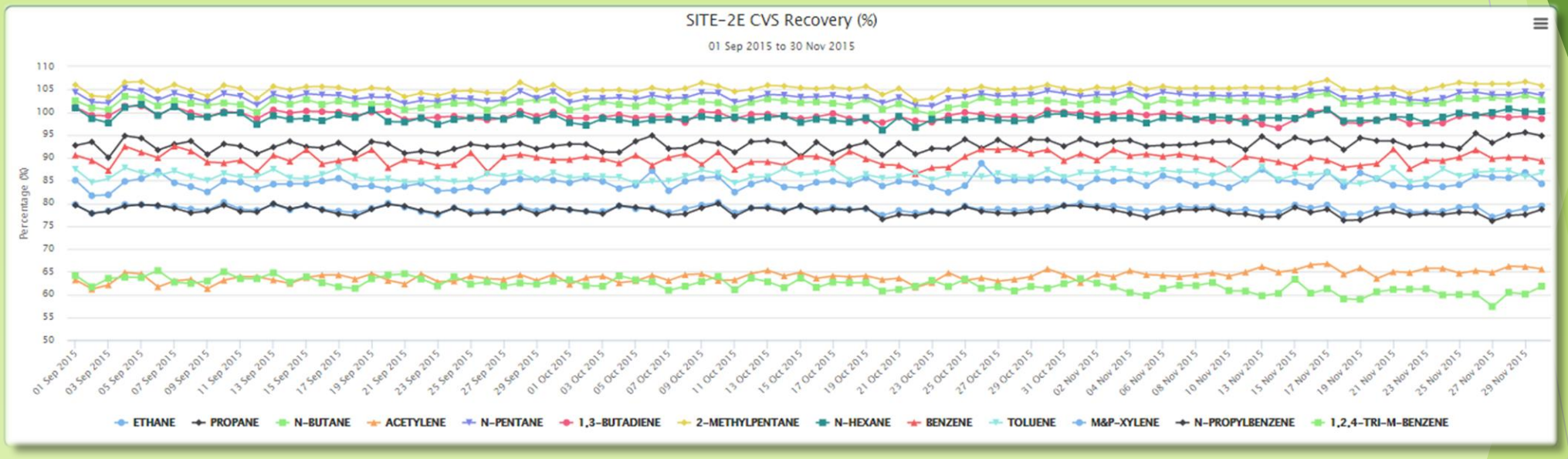
Data Review - Daily

- Site Operations
  - On-time collection
  - Correct identification
  - Equipment parameters
- Quality Controls
  - Passing Blanks
  - Passing check standard recovery

Data Validation - Monthly

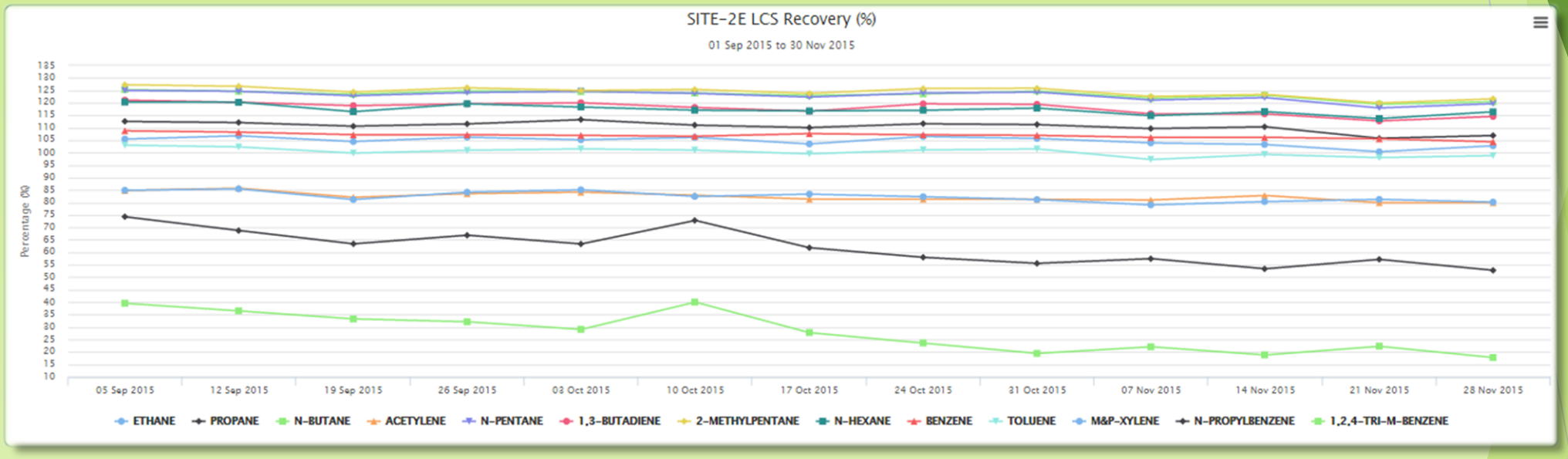
- Review of Quality Controls
  - Passing check standard recoveries – flagging
  - Passing blanks – flagging failed targets
  - Retention time checks
- Chromatography review
  - Review of high hours or other issues

Calibration Verification Standard (CVS) Dynamically Diluted Daily Check Standard



Recoveries based on carbon response for Propane or Benzene

Laboratory Control Standard (LCS)
Weekly Static Dilution Canister Sample



QuickLook Email Report

Galena Park **CONCENTRATION PPB-C** **CURRENT SEQUENCE/IDX NAME** **SEQUENCE (DAYS IN USE)**
05/30/15 **150515-53.seq** **15**

file	date	time	methane	ethane	ethylene	propane	propylene	ic4	nc4	acetylene	t-2-butene	1-butene	cis-2-butene	cyc5	ic5	nc5	1,3-butadiene	t-2-pentene	2m2butene	1-pentene	-2-pentene	2,2dmc4	2mc5	isoprene	total plot	rget plot tot	file
Ce30a	30-May	132		10.6		16.3			25.4	9.6					1.3	30.9	23.3		n/a				35.0		162.0	153.2	Ce30a
Be30b	30-May	232																	n/a						2.4	1.0	Be30b
Se30c	30-May	332	21.8	28.5	3.2	8.3	0.8	5.3	9.5	0.9		0.4		1.2	16.9	13.1		0.6	n/a				4.2		125.2	116.2	Se30c
Se30d	30-May	432	20.3	23.7	3.6	8.8	2.3	6.7	9.7	1.0		0.4		1.0	15.9	12.3		0.5	n/a				3.7		119.7	111.5	Se30d
Se30e	30-May	532	21.1	20.3	2.3	7.0	2.4	5.3	7.7	0.5	0.5	1.3		0.8	15.0	10.5		0.5	n/a				3.2		108.0	99.9	Se30e
Se30f	30-May	632	24.1	25.6	3.9	12.7	7.4	18.4	11.4	1.6	2.0	2.5	1.3	0.9	13.5	6.5	3.6	1.0	n/a	0.5	0.5		4.4		155.3	142.5	Se30f
Se30g	30-May	732	22.0	14.9	2.9	8.6	2.9	5.6	8.7	1.1	0.5	1.6		0.9	19.4	12.6		0.5	n/a				3.3	0.5	116.3	107.4	Se30g
Se30h	30-May	832	19.9	17.0	3.9	10.2	4.9	14.0	9.7	1.0	1.8	2.7	1.1	0.6	10.6	5.6	2.2	0.7	n/a				3.0	1.1	121.9	110.8	Se30h
Se30i	30-May	932	19.5	6.5	1.4	4.6	1.8	2.0	4.5	0.6					5.9	2.2			n/a				1.4	1.7	58.5	54.0	Se30i
Se30j	30-May	1032	20.2	6.5	1.4	4.4	1.0	1.0	2.8	0.5					3.9	1.4			n/a				1.0	1.8	50.7	47.2	Se30j
Se30k	30-May	1132	19.7	4.9	1.0	2.0	0.5	0.7	1.8	0.5					2.6	1.2			n/a				0.7	1.3	40.1	37.5	Se30k
Se30l	30-May	1232	19.3	6.4	1.3	5.4	0.6	2.9	8.1	0.6				0.6	20.9	13.9			n/a				2.5	1.3	90.3	84.9	Se30l
Se30m	30-May	1332	19.4	8.7	1.8	8.6	1.7	10.4	35.9	0.9	1.0	1.4	1.0	4.6	159.7	105.1		1.8	n/a	2.3	1.0	2.8	18.3	1.4	419.3	388.0	Se30m
Se30n	30-May	1432	19.1	7.0	1.0	2.8	0.9	3.6	17.9	0.6	0.4			4.3	189.7	129.4		1.2	n/a	2.3	0.5	2.0	14.0	1.3	427.2	399.3	Se30n
Se30o	30-May	1532	18.9	12.7	2.1	7.4	2.3	9.8	49.8	0.6	1.2	0.8	1.1	10.4	462.4	312.1	0.9	4.8	n/a	10.9	2.2	5.4	35.7	2.7	1025.0	954.2	Se30o
Se30p	30-May	1632	18.8	20.6	3.2	12.3	4.7	15.2	103.8	0.8	2.1	1.4	2.0	26.4	1220.6	826.8		10.7	n/a		2.2	15.4	90.9	4.5	2585.8	2382.4	Se30p
Se30q	30-May	1732	18.7	5.2	0.9	2.7	1.7	1.3	3.2	0.4					11.1	6.7			n/a				1.5	0.4	62.8	55.4	Se30q
Se30r	30-May	1832	19.3	15.4	3.4	18.3	4.5	11.7	37.1	1.0	0.8	1.4	0.6	3.0	94.7	67.1	2.0	1.3	n/a	1.2	0.6	1.5	14.9		326.6	300.1	Se30r
Se30s	30-May	1932	20.5	18.6	2.5	17.2	2.2	17.3	58.4	1.5	1.2	1.4	1.0	4.7	158.9	109.6	1.8	3.2	n/a	2.7	1.4	2.5	22.0		488.4	449.0	Se30s
Se30t	30-May	2032	19.8	33.3	10.0	80.4	4.5	44.2	122.4	1.9	1.6	2.0	1.3	5.8	158.4	111.9	2.5	4.5	n/a	2.0	1.8	3.5	32.0		696.1	644.2	Se30t
Se30u	30-May	2132	19.6	14.2	2.6	9.4	2.9	3.2	6.9	0.9		0.5		0.5	9.5	4.7		0.5	n/a				2.5		90.2	79.5	Se30u
Ee30v	30-May	2232		12.0		17.5			23.7	11.0						30.0	21.1		n/a				35.8		158.3	152.0	Ee30v
Qe30w	30-May	2332		1.9	1.5	2.6	1.4	2.3	4.1		2.4	2.9	3.2	2.0	4.1	2.8		2.0	n/a	1.9	2.5		4.8	2.2	57.4	45.2	Qe30w
Se30x	30-May	32	26.3	11.4	1.5	6.7	1.2	2.9	4.6	0.7		0.4		0.5	6.7	3.7			n/a	0.5			1.6		77.9	69.9	Se30x

file	nc6	mcyc5	2,4dmc5	benzene	cyc6	2-mc6	2,3-dmc5	3-mc6	2,2,4-tmc5	nc7	mcyc6	2,3,4,-tmc5	toluene	2mc7	3mc7	nc8	ethylbenzene	m&p-xylene	styrene	o-xylene	nc9	c3benzene	nc3bz	1,3,5-tmbz	1,2,4-tmbz	nc10	1,2,3-tmbz	nc11	db1 total	rget bp1 tot	file
Ce30a	34.0			32.5	1.0								35.8					40.9	2.6				45.9		41.4			n/a	263.4	235.2	Ce30a
Be30b																							0.5					n/a	3.6	1.9	Be30b
Se30c	5.3	2.0	0.5	2.1	1.2	1.0	0.5	1.2	2.8	1.9	1.4	0.4	4.3	0.4		0.8		1.5		0.4	0.4				0.4			n/a	35.9	29.9	Se30c
Se30d	4.0	2.0	0.8	2.0	1.3	1.0	0.6	1.0	2.4	1.6	1.3		3.7			0.7		1.4			0.4							n/a	30.5	26.6	Se30d
Se30e	3.9	2.0	0.6	1.5	1.2	1.2	0.7	1.5	2.4	2.1	2.0	0.5	4.9	0.7	0.5	1.0	0.5	2.2		0.5	0.6				0.6	0.6		n/a	39.7	32.6	Se30e
Se30f	4.9	3.0	0.9	1.4	1.8	1.7	0.8	1.9	3.1	1.9	3.8	0.7	5.9	0.7	0.8	1.0	1.4	4.6	2.8	2.0	0.8			0.7	1.5	0.8		n/a	69.1	49.3	Se30f
Se30g	3.7	2.3	1.1	1.4	1.9	1.2	0.8	1.5	5.1	1.8	3.0	1.3	6.9	0.8	0.7	1.0	0.9	3.6	0.4	1.1	0.9			0.5	0.9	0.7		n/a	56.2	44.0	Se30g
Se30h	3.4	2.1	0.6	1.3	1.6	1.2	0.6	1.2	2.2	1.5	3.5	0.5	4.4	0.7	0.8	1.0	0.9	3.1	1.7	0.9	0.9			0.5	0.9	0.8		n/a	52.4	37.1	Se30h
Se30i	1.2	0.8		0.6	0.6	0.6		0.6	1.5	0.6	0.9		2.9				0.5	1.7		0.5								n/a	19.5	16.3	Se30i
Se30j	0.8	0.6		0.5		0.4		0.5	1.3				5.2					1.5		0.6					0.4			n/a	16.8	14.9	Se30j
Se30k	0.7								1.0				1.7					0.6							0.4			n/a	8.8	7.5	Se30k
Se30l	2.4	0.9	0.8	0.7	0.5	0.5		0.6	1.4	0.6	0.5		1.8					0.7										n/a	13.9	13.0	Se30l
Se30m	13.8	7.0	8.1	3.7	3.3	2.7	1.5	3.6	5.2	2.8	2.9	0.7	6.8	0.6	0.8	1.0	2.8	9.8	0.7	3.4	0.7				0.6			n/a	97.3	83.4	Se30m
Se30n	11.7	5.5	10.0	3.0	2.8	1.3	0.8	1.7	2.6	1.3	1.5		3.4				0.5	2.1		0.8								n/a	62.0	51.1	Se30n
Se30o	28.2	12.9	22.7	10.3	6.5	2.7	1.6	4.3	9.2	2.9	3.3	0.7	6.6			0.5	0.5	1.6		0.5					1.1			n/a	142.2	117.7	Se30o
Se30p	76.5	33.7	58.8	21.9	24.8	7.2	4.3	10.3	20.4	6.6	8.5	1.2	10.4	0.6	0.5	0.9	0.8	2.6		0.7				0.5	1.8	0.6		n/a	377.7	294.6	Se30p
Se30q	1.4	0.6		0.7		0.5		0.5	1.4				1.9					1.0										n/a	14.3	12.3	Se30q
Se30r	15.2	5.7	5.1	3.2	3.4	2.7	1.5	2.8	8.1	3.6	3.5	1.1	7.0	0.9	0.9	1.4	1.4	5.1	1.2	1.6	0.9			0.5	1.1	0.8		n/a	96.9	78.9	Se30r
Se30s	19.6	7.8	9.1	5.0	4.0	3.7	2.2	4.8	13.2	4.4	4.3	2.8	11.8	1.0	1.3	2.0	1.6	5.4	2.1	1.5	1.8			0.8	1.6	1.4		n/a	146.1	113.9	Se30s
Se30t	30.6	12.0	8.7	5.5	7.2	7.8	3.9	9.7	12.8	12.3	12.8	2.6	19.8	4.2	3.9	6.3	4.9	17.1	1.6	5.5	4.8		1.0	2.3	4.2	2.8	1.0	n/a	277.9	205.6	Se30t
Se30u	2.5	1.4	0.7	1.1	0.7	1.0	0.6	1.2	3.1	1.0	1.1	0.8	4.9			0.6	0.8	2.8	0.6	0.9	0.5			0.4	0.7	0.6		n/a	35.5	29.1	Se30u
Ee30v	34.1			32.0				0.9					37.3					43.3	2.6				47.3		42.5		0.5	n/a	272.6	240.9	Ee30v
Qe30w	3.2	2.4	3.9	2.9	4.3	2.0	4.8	2.3	2.9	1.9	2.6	2.1	3.4	1.8	1.9	2.4	1.5	3.0	2.1	1.7	1.9	2.5	2.4	1.8	2.9	2.1	1.6	n/a	78.0	68.4	Qe30w
Se30x	2.4	0.9	0.7	0.8	0.5	0.7	0.5	0.7	3.7	0.5	0.6	1.0	3.4				0.5	1.7		0.5					0.6			n/a	28.2	22.2	Se30x

		DAILY Certif Con'c ppmV	DATE Calc Dilute ppbC	5/30/2015 Measur Con'c ppbC	RUN A %Recov			5 PPB Carbon Number	Certif Con'c ppmV	DATE Calc Dilute ppbC	5/30/2015 Measur Con'c ppbC	RUN V %Recov
	Carbon Number											
Ethane	2.00	1.06	11.39	10.57	92.8		Ethane	2.00	1.03	11.29	11.99	106.2
Propane	3.00	1.01	16.28	16.27	99.9		Propane	3.00	1.02	16.77	17.49	104.3
n-Butane	4.00	1.02	21.92	25.38	115.8		n-Butane	4.00	1.04	22.80	23.71	104.0
Acetylene	2.00	1.06	11.39	9.62	84.5		Acetylene	2.00	1.07	11.73	11.01	93.9
n-pentane	5.00	0.99	26.59	30.95	116.4		n-pentane	5.00	1.08	29.59	30.02	101.5
1,3-butadiene	4.00	1.03	22.13	23.34	105.5		1,3-butadiene	4.00	0.99	21.70	21.10	97.2
2-methylpentane	6.00	1.00	32.23	34.95	108.4		2-methylpentane	6.00	1.01	33.21	35.76	107.7
PLOT BLANK	RUN	B		2.43								
Hexane	6.00	1.03	33.20	34.05	102.6		Hexane	6.00	1.00	32.88	34.09	103.7
Benzene	6.00	1.03	33.23	32.47	97.7		Benzene	6.00	1.01	33.21	32.03	96.5
Toluene	7.00	1.05	39.48	35.84	90.8		Toluene	7.00	1.01	38.74	37.28	96.2
m-Xylene	8.00	1.06	45.55	40.95	89.9		m-Xylene	8.00	0.97	42.52	43.28	101.8
n-Propylbenzene	9.00	1.02	49.31	45.93	93.1		n-Propylbenzene	9.00	1.00	49.32	47.31	95.9
l,2,4-Trimethylbenzene	9.00	1.04	50.28	41.42	82.4		l,2,4-Trimethylbenzene	9.00	1.02	50.31	42.52	84.5
BP1 BLANK	RUN	B		3.64								
BLEND RATIO		0.00537										
RF PLOT		5144		NT PLOT		15		AT PLOT		30		
RF BP1		4723		NT BP1		15		AT BP1		60		
DATE		5/27/2015										
BY		0.00		** NOTE: ppbC levels < 0.4 are not listed								

QuickLook Email Report

Galena Park	CONCENTRATION PPB-C	CURRENT SEQUENCE/IDX NAME	SEQUENCE (DAYS IN USE
05/30/15		150515-53.seq	15

file	date	time	methane	ethane	ethylene	propane	propylene	ic4	nc4	acetylene	t-2-butene	1-butene	cis-2-butene	cyc5	ic5	nc5	1,3-butadiene	t-2-pentene	2m2butene
Ce30a	30-May	132		10.6		16.3			25.4	9.6					1.3	30.9	23.3		n/a
Be30b	30-May	232																	n/a
Se30c	30-May	332	21.8	28.5	3.2	8.3	0.8	5.3	9.5	0.9		0.4		1.2	16.9	13.1		0.6	n/a
Se30d	30-May	432	20.3	23.7	3.6	8.8	2.3	6.7	9.7	1.0		0.4		1.0	15.9	12.3		0.5	n/a
Se30e	30-May	532	21.1	20.3	2.3	7.0	2.4	5.3	7.7	0.5	0.5	1.3		0.8	15.0	10.5		0.5	n/a
Se30f	30-May	632	24.1	25.6	3.9	12.7	7.4	18.4	11.4	1.6	2.0	2.5	1.3	0.9	13.5	6.5	3.6	1.0	n/a
Se30g	30-May	732	22.0	14.9	2.9	8.6	2.9	5.6	8.7	1.1	0.5	1.6		0.9	19.4	12.6		0.5	n/a
Se30h	30-May	832	19.9	17.0	3.9	10.2	4.9	14.0	9.7	1.0	1.8	2.7	1.1	0.6	10.6	5.6	2.2	0.7	n/a
Se30i	30-May	932	19.5	6.5	1.4	4.6	1.8	2.0	4.5	0.6					5.9	2.2			n/a
Se30j	30-May	1032	20.2	6.5	1.4	4.4	1.0	1.0	2.8	0.5					3.9	1.4			n/a
Se30k	30-May	1132	19.7	4.9	1.0	2.0	0.5	0.7	1.8	0.5					2.6	1.2			n/a
Se30l	30-May	1232	19.3	6.4	1.3	5.4	0.6	2.9	8.1	0.6				0.6	20.9	13.9			n/a
Se30m	30-May	1332	19.4	8.7	1.8	8.6	1.7	10.4	35.9	0.9	1.0	1.4	1.0	4.6	159.7	105.1		1.8	n/a
Se30n	30-May	1432	19.1	7.0	1.0	2.8	0.9	3.6	17.9	0.6	0.4			4.3	189.7	129.4		1.2	n/a
Se30o	30-May	1532	18.9	12.7	2.1	7.4	2.3	9.8	49.8	0.6	1.2	0.8	1.1	10.4	462.4	312.1	0.9	4.8	n/a
Se30p	30-May	1632	18.8	20.6	3.2	12.3	4.7	15.2	103.8	0.8	2.1	1.4	2.0	26.4	1220.6	826.8		10.7	n/a
Se30q	30-May	1732	18.7	5.2	0.9	2.7	1.7	1.3	3.2	0.4					11.1	6.7			n/a
Se30r	30-May	1832	19.3	15.4	3.4	18.3	4.5	11.7	37.1	1.0	0.8	1.4	0.6	3.0	94.7	67.1	2.0	1.3	n/a
Se30s	30-May	1932	20.5	18.6	2.5	17.2	2.2	17.3	58.4	1.5	1.2	1.4	1.0	4.7	158.9	109.6	1.8	3.2	n/a
Se30t	30-May	2032	19.8	33.3	10.0	80.4	4.5	44.2	122.4	1.9	1.6	2.0	1.3	5.8	158.4	111.9	2.5	4.5	n/a
Se30u	30-May	2132	19.6	14.2	2.6	9.4	2.9	3.2	6.9	0.9		0.5		0.5	9.5	4.7		0.5	n/a
Ee30v	30-May	2232		12.0		17.5			23.7	11.0						30.0	21.1		n/a
Qe30w	30-May	2332		1.9	1.5	2.6	1.4	2.3	4.1		2.4	2.9	3.2	2.0	4.1	2.8		2.0	n/a
Se30x	30-May	32	26.3	11.4	1.5	6.7	1.2	2.9	4.6	0.7		0.4		0.5	6.7	3.7			n/a

file	nc6	mcyc5	2,4dmc5	benzene	cyc6	2-mc6	2,3-dmc5	3-mc6	2,2,4-tmc5	nc7	mcyc6	2,3,4,-tmc5	toluene	2mc7	3mc7	nc8	ethylbenzene	m&p-xylene	styrene
Ce30a	34.0			32.5	1.0								35.8					40.9	2.6
Be30b																			
Se30c	5.3	2.0	0.5	2.1	1.2	1.0	0.5	1.2	2.8	1.9	1.4	0.4	4.3	0.4		0.8		1.5	
Se30d	4.0	2.0	0.8	2.0	1.3	1.0	0.6	1.0	2.4	1.6	1.3		3.7			0.7		1.4	
Se30e	3.9	2.0	0.6	1.5	1.2	1.2	0.7	1.5	2.4	2.1	2.0	0.5	4.9	0.7	0.5	1.0	0.5	2.2	
Se30f	4.9	3.0	0.9	1.4	1.8	1.7	0.8	1.9	3.1	1.9	3.8	0.7	5.9	0.7	0.8	1.0	1.4	4.6	2.8
Se30g	3.7	2.3	1.1	1.4	1.9	1.2	0.8	1.5	5.1	1.8	3.0	1.3	6.9	0.8	0.7	1.0	0.9	3.6	0.4
Se30h	3.4	2.1	0.6	1.3	1.6	1.2	0.6	1.2	2.2	1.5	3.5	0.5	4.4	0.7	0.8	1.0	0.9	3.1	1.7
Se30i	1.2	0.8		0.6	0.6	0.6		0.6	1.5	0.6	0.9		2.9				0.5	1.7	
Se30j	0.8	0.6		0.5		0.4		0.5	1.3				5.2					1.5	
Se30k	0.7								1.0				1.7					0.6	
Se30l	2.4	0.9	0.8	0.7	0.5	0.5		0.6	1.4	0.6	0.5		1.8					0.7	
Se30m	13.8	7.0	8.1	3.7	3.3	2.7	1.5	3.6	5.2	2.8	2.9	0.7	6.8	0.6	0.8	1.0	2.8	9.8	0.7
Se30n	11.7	5.5	10.0	3.0	2.8	1.3	0.8	1.7	2.6	1.3	1.5		3.4				0.5	2.1	
Se30o	28.2	12.9	22.7	10.3	6.5	2.7	1.6	4.3	9.2	2.9	3.3	0.7	6.6			0.5	0.5	1.6	
Se30p	76.5	33.7	58.8	21.9	24.8	7.2	4.3	10.3	20.4	6.6	8.5	1.2	10.4	0.6	0.5	0.9	0.8	2.6	
Se30q	1.4	0.6		0.7		0.5		0.5	1.4				1.9					1.0	
Se30r	15.2	5.7	5.1	3.2	3.4	2.7	1.5	2.8	8.1	3.6	3.5	1.1	7.0	0.9	0.9	1.4	1.4	5.1	1.2
Se30s	19.6	7.8	9.1	5.0	4.0	3.7	2.2	4.8	13.2	4.4	4.3	2.8	11.8	1.0	1.3	2.0	1.6	5.4	2.1
Se30t	30.6	12.0	8.7	5.5	7.2	7.8	3.9	9.7	12.8	12.3	12.8	2.6	19.8	4.2	3.9	6.3	4.9	17.1	1.6
Se30u	2.5	1.4	0.7	1.1	0.7	1.0	0.6	1.2	3.1	1.0	1.1	0.8	4.9			0.6	0.8	2.8	0.6
Ee30v	34.1			32.0				0.9					37.3					43.3	2.6
Qe30w	3.2	2.4	3.9	2.9	4.3	2.0	4.8	2.3	2.9	1.9	2.6	2.1	3.4	1.8	1.9	2.4	1.5	3.0	2.1
Se30x	2.4	0.9	0.7	0.8	0.5	0.7	0.5	0.7	3.7	0.5	0.6	1.0	3.4				0.5	1.7	

0.5					1.1			n/a	142.2	117.7	Se30o
0.7				0.5	1.8	0.6		n/a	377.7	294.6	Se30p
								n/a	14.3	12.3	Se30q
1.6	0.9			0.5	1.1	0.8		n/a	96.9	78.9	Se30r
1.5	1.8			0.8	1.6	1.4		n/a	146.1	113.9	Se30s
3.3	4.8		1.0	2.3	4.2	2.8	1.0	n/a	277.9	205.6	Se30t
0.9	0.5			0.4	0.7	0.6		n/a	35.5	29.1	Se30u
			47.3		42.5		0.5	n/a	272.6	240.9	Ee30v
1.7	1.9	2.5	2.4	1.8	2.9	2.1	1.6	n/a	78.0	68.4	Qe30w
0.5					0.6			n/a	28.2	22.2	Se30x

	Carbon Number	DAILY Certif Con'c ppmV	DATE Calc Dilute ppbC	5/30/2015 Measur Con'c ppbC	RUN A %Recov		5 PPB Carbon Number	Certif Con'c ppmV	DATE Calc Dilute ppbC	5/30/2015 Measur Con'c ppbC	RUN V %Recov
Ethane	2.00	1.06	11.39	10.57	92.8	Ethane	2.00	1.03	11.29	11.99	106.2
Propane	3.00	1.01	16.28	16.27	99.9	Propane	3.00	1.02	16.77	17.49	104.3
n-Butane	4.00	1.02	21.92	25.38	115.8	n-Butane	4.00	1.04	22.80	23.71	104.0
Acetylene	2.00	1.06	11.39	9.62	84.5	Acetylene	2.00	1.07	11.73	11.01	93.9
n-pentane	5.00	0.99	26.59	30.95	116.4	n-pentane	5.00	1.08	29.59	30.02	101.5
1,3-butadiene	4.00	1.03	22.13	23.34	105.5	1,3-butadiene	4.00	0.99	21.70	21.10	97.2
2-methylpentane	6.00	1.00	32.23	34.95	108.4	2-methylpentane	6.00	1.01	33.21	35.76	107.7
PLOT BLANK	RUN	B		2.43							
Hexane	6.00	1.03	33.20	34.05	102.6	Hexane	6.00	1.00	32.88	34.09	103.7
Benzene	6.00	1.03	33.23	32.47	97.7	Benzene	6.00	1.01	33.21	32.03	96.5
Toluene	7.00	1.05	39.48	35.84	90.8	Toluene	7.00	1.01	38.74	37.28	96.2
m-Xylene	8.00	1.06	45.55	40.95	89.9	m-Xylene	8.00	0.97	42.52	43.28	101.8
n-Propylbenzene	9.00	1.02	49.31	45.93	93.1	n-Propylbenzene	9.00	1.00	49.32	47.31	95.9
l,2,4-Trimethylbenzene	9.00	1.04	50.28	41.42	82.4	l,2,4-Trimethylbenzene	9.00	1.02	50.31	42.52	84.5
BP1 BLANK	RUN	B		3.64							

BLEND RATIO	0.00537				
RF PLOT	5144	NT PLOT	15	AT PLOT	30
RF BP1	4723	NT BP1	15	AT BP1	60
DATE	5/27/2015				
BY	0.00				

** NOTE: ppbC levels < 0.4 are not listed

file	nc6	mcyc5	2,4dmc5	benzene	cyc6	2-mc6
Ce30a	34.0			32.5	1.0	
Be30b						
Se30c	5.3	2.0	0.5	2.1	1.2	1.0
Se30d	4.0	2.0	0.8	2.0	1.3	1.0
Se30e	3.9	2.0	0.6	1.5	1.2	1.2
Se30f	4.9	3.0	0.9	1.4	1.8	1.7
Se30g	3.7	2.3	1.1	1.4	1.9	1.2
Se30h	3.4	2.1	0.6	1.3	1.6	1.2
Se30i	1.2	0.8		0.6	0.6	0.6
Se30j	0.8	0.6		0.5		0.4
Se30k	0.7					
Se30l	2.4	0.9	0.8	0.7	0.5	0.5
Se30m	13.8	7.0	8.1	3.7	3.3	2.7
Se30n	11.7	5.5	10.0	3.0	2.8	1.3
Se30o	28.2	12.9	22.7	10.3	6.5	2.7
Se30p	76.5	33.7	58.8	21.9	24.8	7.2
Se30q	1.4	0.6		0.7		0.5
Se30r	15.2	5.7	5.1	3.2	3.4	2.7
Se30s	19.6	7.8	9.1	5.0	4.0	3.7
Se30t	30.6	12.0	8.7	5.5	7.2	7.8
Se30u	2.5	1.4	0.7	1.1	0.7	1.0
Ee30v	34.1			32.0		
Qe30w	3.2	2.4	3.9	2.9	4.3	2.0
Se30x	2.4	0.9	0.7	0.8	0.5	0.7

QuickLook Email Report

Galena Park — **CONCENTRATION PPB-C** — **CURRENT SEQUENCE/IDX**

05/30/15 — **150515-53.seq**

file	date	time	methane	ethane	ethylene	propane	propylene	ic4	nc4	acetylene	t2-butene
Ce30a	30-May	132		10.6		16.3			25.4	9.6	
Be30b	30-May	232									
Se30c	30-May	332	21.8	28.5	3.2	8.3	0.8	5.3	9.5	0.9	
Se30d	30-May	432	20.3	23.7	3.6	8.8	2.3	6.7	9.7	1.0	
Se30e	30-May	532	21.1	20.3	2.3	7.0	2.4	5.3	7.7	0.5	0.5
Se30f	30-May	632	24.1	25.6	3.9	12.7	7.4	18.4	11.4	1.6	2.0
Se30g	30-May	732	22.0	14.9	2.9	8.6	2.9	5.6	8.7	1.1	0.5
Se30h	30-May	832	19.9	17.0	3.9	10.2	4.9	14.0	9.[illegible]	1.0	1.8
Se30i	30-May	932	19.5	6.5	1.4	4.6	1.8	2.0	[illegible].5	0.6	
Se30j	30-May	1032	20.2	6.5	1.4	4.4	1.0	1.0	2.8	0.5	
Se30k	30-May	1132	19.7	4.9	1.0	2.0	0.5	0.7	1.8	0.5	
Se30l	30-May	1232	19.3	6.4	1.3	5.4	0.6	2.9	8.1	0.6	
Se30m	30-May	1332	19.4	8.7	1.8	8.6	1.7	10.4	35.9	0.9	1.0
Se30n	30-May	1432	19.1	7.0	1.0	2.8	0.9	3.[illegible]	17.9	0.6	0.4
Se30o	30-May	1532	18.9	12.7	2.1	7.4	2.3	[illegible].8	49.8	0.6	1.2
Se30p	30-May	1632	18.8	20.6	3.2	12.3	4.7	15.2	103.8	0.8	2.1
Se30q	30-May	1732	18.7	5.2	0.9	2.7	1.7	1.3	3.2	0.4	
Se30r	30-May	1832	19.3	15.4	3.4	18.3	4.5	11.7	37.1	1.0	0.8
Se30s	30-May	1932	20.5	18.6	2.5	17.2	2.2	17.3	58.4	1.5	1.2
Se30t	30-May	2032	19.8	33.3	10.0	80.4	4.[illegible]	44.2	122.4	1.9	1.6
Se30u	30-May	2132	19.6	14.2	2.6	9.4	[illegible].9	3.2	6.9	0.9	
Ee30v	30-May	2232		12.0		17.5			23.7	11.0	
Qe30w	30-May	2332		1.9	1.5	2.6	1.4	2.3	4.1		2.4
Se30x	30-May	32	26.3	11.4	1.5	6.7	1.2	2.9	4.6	0.7	

file	nc6	mcyc5	2,4dmc5	benzene	cyc6	2-mc6	2,3-dmc5	3-mc6	2,2,4-tmc5	nc7	mcyc6
Ce30a	34.0			32.5	1.0						
Be30b											
Se30c	5.3	2.0	0.5	2.1	1.[illegible]	1.0	0.5	1.2	2.8	1.9	1.4
Se30d	4.0	2.0	0.8	2.0	[illegible].3	1.0	0.6	1.0	2.4	1.6	1.3
Se30e	3.9	2.0	0.6	1.5	1.2	1.2	0.7	1.5	2.4	2.1	2.0
Se30f	4.9	3.0	0.9	1.4	1.8	1.7	0.8	1.9	3.1	1.9	3.8
Se30g	3.7	2.3	1.1	1.4	1.9	1.2	0.8	1.5	5.1	1.8	3.0
Se30h	3.4	2.1	0.6	1.3	1.6	1.2	0.6	1.2	2.2	1.5	3.5
Se30i	1.2	0.8		0.6	0.6	0.6		0.6	1.5	0.6	0.9
Se30j	0.8	0.6		0.5		0.4		0.5	1.3		
Se30k	0.7								1.0		
Se30l	2.4	0.9	0.8	0.7	0.5	0.5		0.6	1.4	0.6	0.5
Se30m	13.8	7.0	8.1	3.7	3.3	2.7	1.5	3.6	5.2	2.8	2.9
Se30n	11.7	5.5	10.0	3.0	2.8	1.3	0.8	1.7	2.6	1.3	1.5
Se30o	28.2	12.9	[illegible]2.7	10.3	6.5	2.7	1.6	4.3	9.2	2.9	3.3
Se30p	76.5	33.7	58.8	21.9	24.8	7.2	4.3	10.3	20.4	6.6	8.5
Se30q	1.4	0.6		0.7		0.5		0.5	1.4		
Se30r	15.2	5.7	5.1	3.2	3.4	2.7	1.5	2.8	8.1	3.6	3.5
Se30s	19.6	7.[illegible]	9.1	5.0	4.0	3.7	2.2	4.8	13.2	4.4	4.3
Se30t	30.6	[illegible]2.0	8.7	5.5	7.2	7.8	3.9	9.7	12.8	12.3	12.8
Se30u	2.5	1.4	0.7	1.1	0.7	1.0	0.6	1.2	3.1	1.0	1.1
Ee30v	34.1			32.0				0.9			
Qe30w	3.2	2.4	3.9	2.9	4.3	2.0	4.8	2.3	2.9	1.9	2.6
Se30x	2.[illegible]	0.9	0.7	0.8	0.5	0.7	0.5	0.7	3.7	0.5	0.6

1.0 3.4 0.5 1.7 0.5 0.6 n/a 28.2 22.2 Se30x

	Carbon Number	DAILY Certif Con'c ppmV	DATE Calc Dilute ppbC	5/30/2015 Measur Con'c ppbC	RUN A %Recov	5 PPB	Carbon Number	Certif Con'c ppmV	DATE Calc Dilute ppbC	5/30/2015 Measur Con'c ppbC	RUN V %Recov
Ethane	2.00	1.06	11.39	10.57	92.8	Ethane	2.00	1.03	11.29	11.99	106.2
Propane	3.00	1.01	16.28	16.27	99.9	Propane	3.00	1.02	16.77	17.49	104.3
n-Butane	4.00	1.02	21.92	25.38	115.8	n-Butane	4.00	1.04	22.80	23.71	104.0
Acetylene	2.00	1.06	11.39	9.62	84.5	Acetylene	2.00	1.07	11.73	11.01	93.9
n-pentane	5.00	0.99	26.59	30.95	116.4	n-pentane	5.00	1.08	29.59	30.02	101.5
1,3-butadiene	4.00	1.03	22.13	23.34	105.5	1,3-butadiene	4.00	0.99	21.70	21.10	97.2
2-methylpentane	6.00	1.00	32.23	34.95	108.4	2-methylpentane	6.00	1.01	33.21	35.76	107.7
PLOT BLANK	RUN	B		2.43							
Hexane	6.00	1.03	33.20	34.05	102.6	Hexane	6.00	1.00	32.88	34.09	103.7
Benzene	6.00	1.03	33.23	32.47	97.7	Benzene	6.00	1.01	33.21	32.03	96.5
Toluene	7.00	1.05	39.48	35.84	90.8	Toluene	7.00	1.01	38.74	37.28	96.2
m-Xylene	8.00	1.06	45.55	40.95	89.9	m-Xylene	8.00	0.97	42.52	43.28	101.8
n-Propylbenzene	9.00	1.02	49.31	45.93	93.1	n-Propylbenzene	9.00	1.00	49.32	47.31	95.9
l,2,4-Trimethylbenzene	9.00	1.04	50.28	41.42	82.4	l,2,4-Trimethylbenzene	9.00	1.02	50.31	42.52	84.5
BP1 BLANK	RUN	B		3.64							

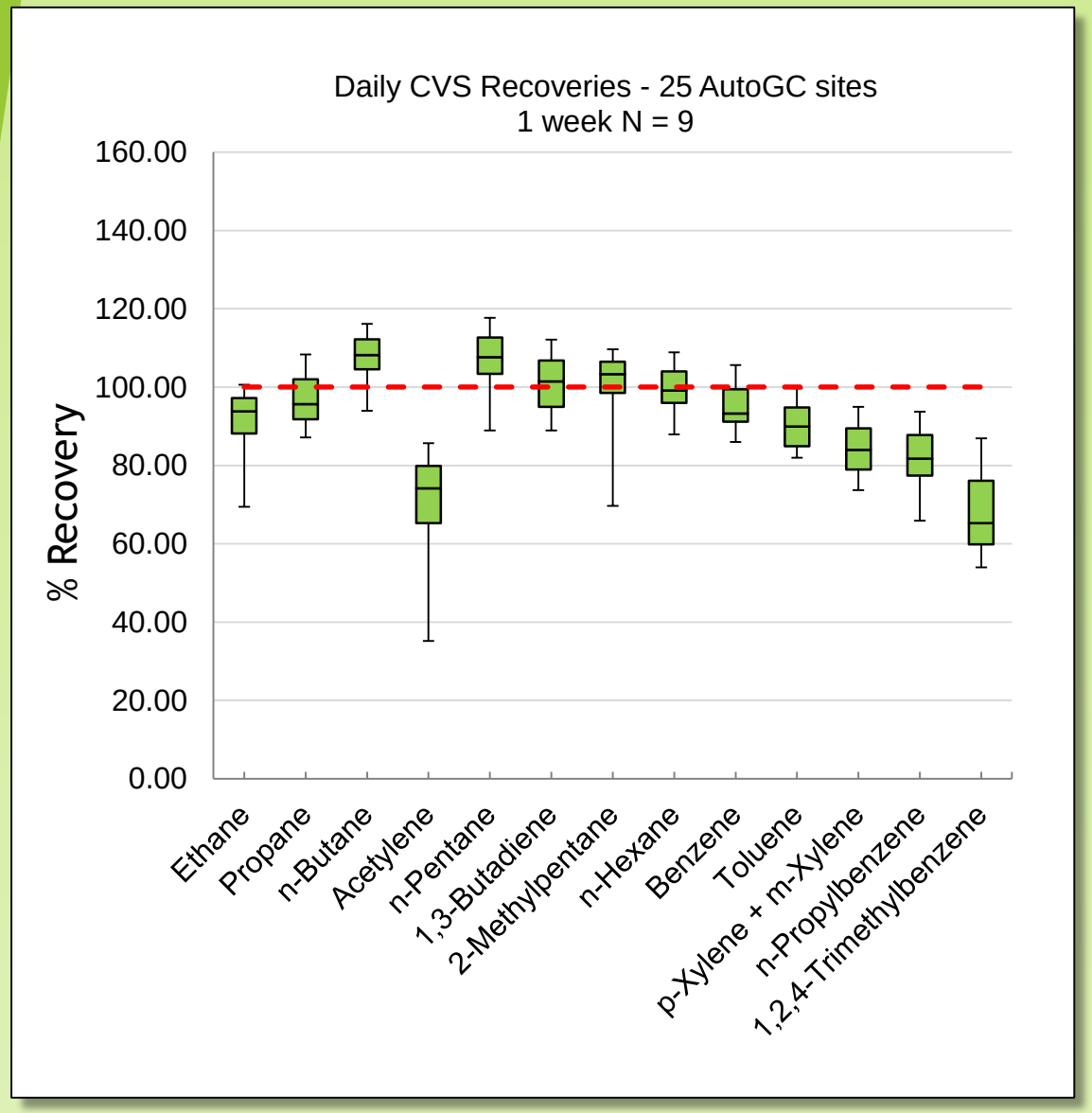
BLEND RATIO	0.00537		
RF PLOT	5144	NT PLOT 15	AT PLOT 30
RF BP1	4723	NT BP1 15	AT BP1 60
DATE	5/27/2015		
BY	0.00		

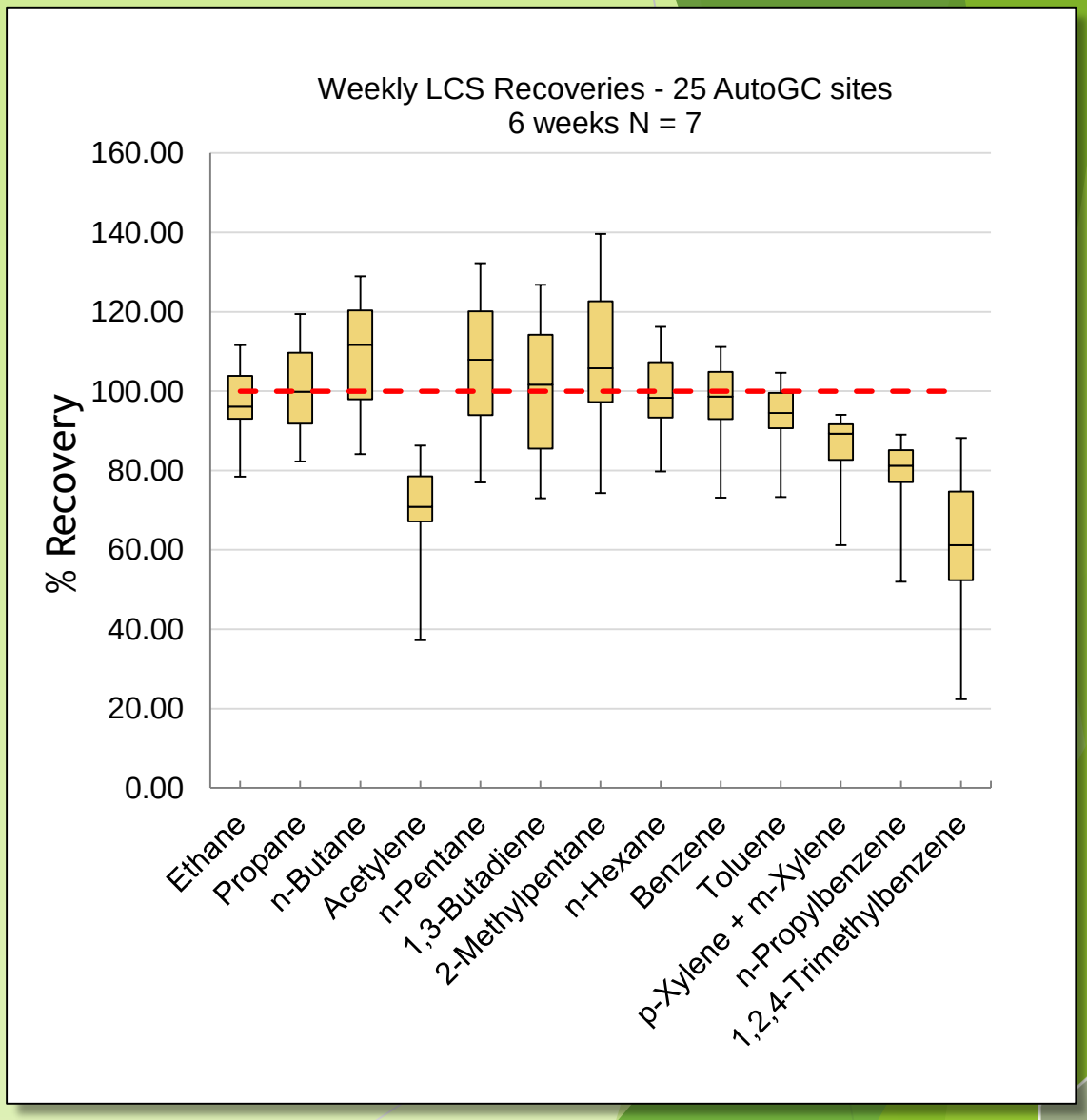
** NOTE: ppbC levels < 0.4 are not listed

	Carbon Number	DAILY Certif Con'c ppmV	DATE Calc Dilute ppbC	5/30/2015 Measur Con'c ppbC	RUN A %Recov	5 PPB	Carbon Number	Certif Con'c ppmV	DATE Calc Dilute ppbC	5/30/2015 Measur Con'c ppbC	RUN V %Recov
Ethane	2.00	1.06	11.39	10.57	92.8	Ethane	2.00	1.03	11.29	11.99	106.2
Propane	3.00	1.01	16.28	16.27	99.9	Propane	3.00	1.02	16.77	17.49	104.3
n-Butane	4.00	1.02	21.92	25.38	115.8	n-Butane	4.00	1.04	22.80	23.71	104.0
Acetylene	2.00	1.06	11.39	9.62	84.5	Acetylene	2.00	1.07	11.73	11.01	93.9
n-pentane	5.00	0.99	26.59	30.95	116.4	n-pentane	5.00	1.08	29.59	30.02	101.5
1,3-butadiene	4.00	1.03	22.13	23.34	105.5	1,3-butadiene	4.00	0.99	21.70	21.10	97.2
2-methylpentane	6.00	1.00	32.23	34.95	108.4	2-methylpentane	6.00	1.01	33.21	35.76	107.7
PLOT BLANK	RUN	B		2.43							
Hexane	6.00	1.03	33.20	34.05	102.6	Hexane	6.00	1.00	32.88	34.09	103.7
Benzene	6.00	1.03	33.23	32.47	97.7	Benzene	6.00	1.01	33.21	32.03	96.5
Toluene	7.00	1.05	39.48	35.84	90.8	Toluene	7.00	1.01	38.74	37.28	96.2
m-Xylene	8.00	1.06	45.55	40.95	89.9	m-Xylene	8.00	0.97	42.52	43.28	101.8
n-Propylbenzene	9.00	1.02	49.31	45.93	93.1	n-Propylbenzene	9.00	1.00	49.32	47.31	95.9
l,2,4-Trimethylbenzene	9.00	1.04	50.28	41.42	82.4	l,2,4-Trimethylbenzene	9.00	1.02	50.31	42.52	84.5
BP1 BLANK	RUN	B		3.64							

BLEND RATIO 0.00537
RF PLOT 5144 NT PLOT 15 AT PLOT 30
RF BP1 4723 NT BP1 15 AT BP1 60
DATE 5/27/2015
BY 0.00
** NOTE: ppbC levels < 0.4 are not listed

Network Quality Control – 25 AutoGC Sites





Requirements for Successful AutoGC

- Chromatographic Data System
  - Capable of identification and quantitation of complex samples
  - Robust and simple calibration strategy
  - Output format for easy review of data
  - Event control for automation of quality control checks
- Standard Operating Procedures
  - Daily operations for consistent data collection
  - Validation to handle deviations consistently
- Data Quality Objectives
  - Well defined control limits
  - System for identifying and correcting failures

FIFTY SIX
NON-METHANE
HYDROCARBONS
TWENTY FOUR
HOURS A DAY
SEVEN
DAYS A WEEK

Acknowledgements

"Without data you are just another person with an opinion." ---W. Edwards Deming

Nicola Watson, Markes International

Kelly Beard, Agilent Technologies

Texas Commission on Environmental Quality

Cory Chism

Cindy Maresh

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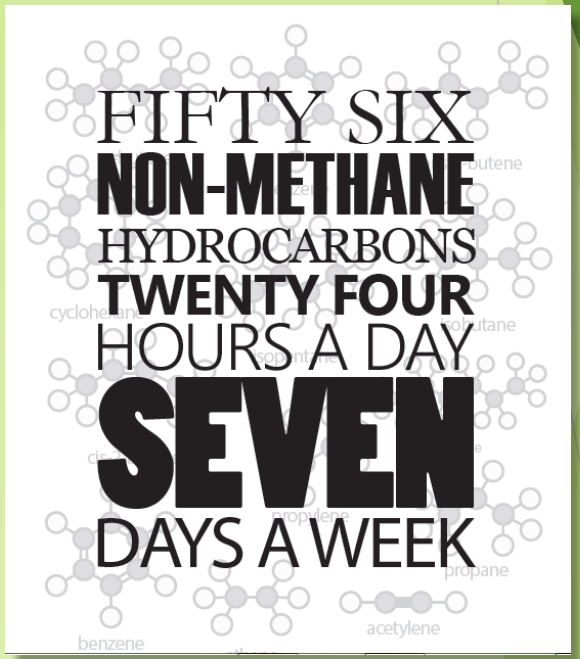
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