

Detailed Hydrocarbon Analysis of a PIONA Sample Using Vacuum Ultra-violet Spectroscopy

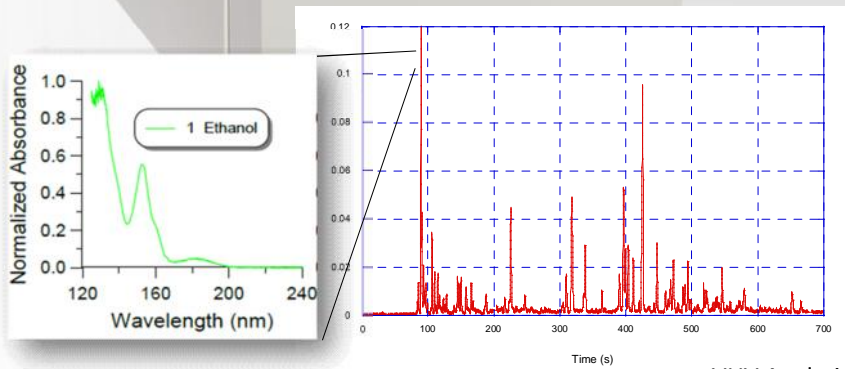
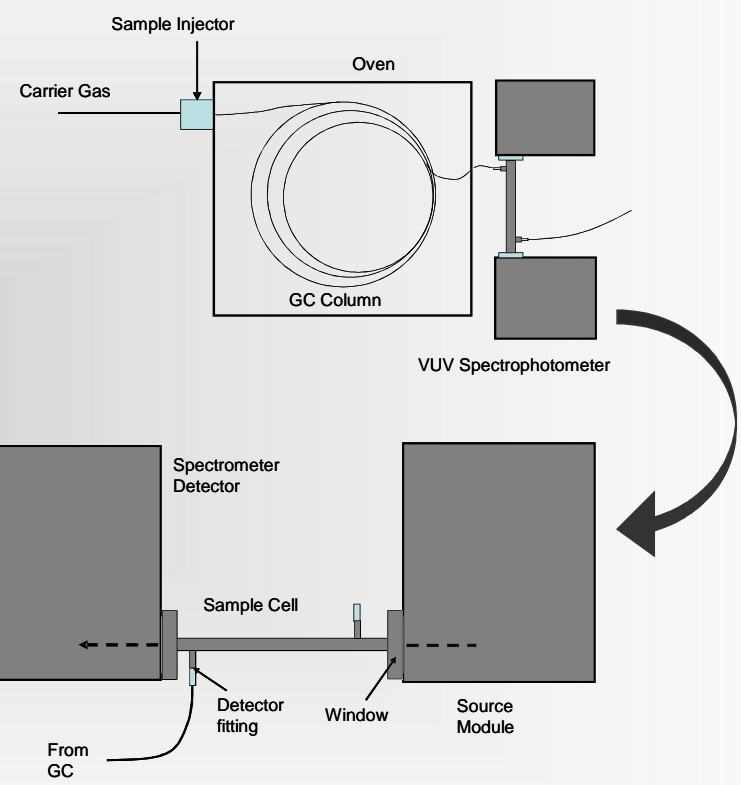
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VUV Analytics, Inc.

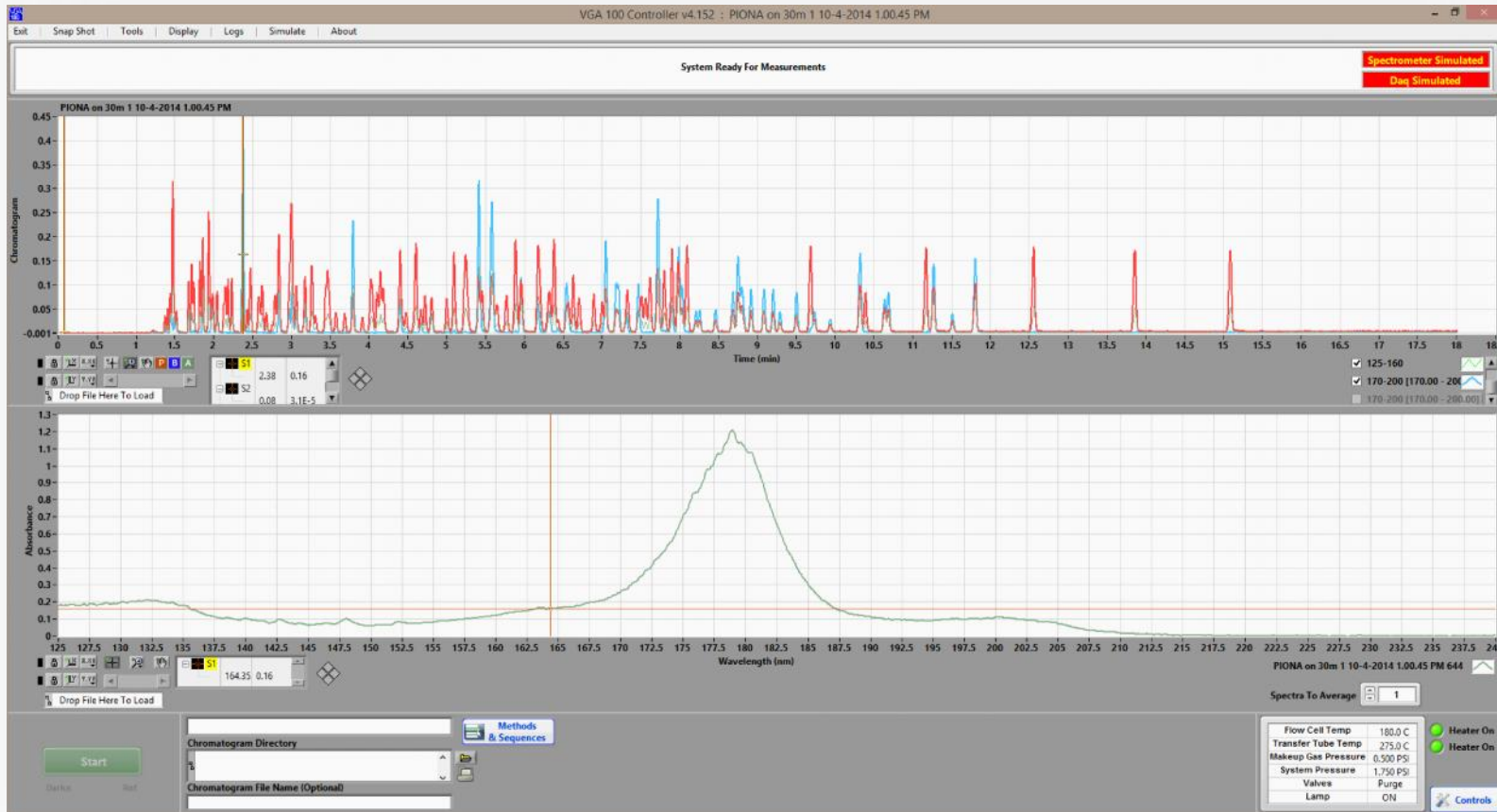
Austin, TX



VGA-100



VGA-100 Controller Screen



Unambiguous Compound Identification



Analyte Spectra llb Search llb

	Chi^2	Name (right-click for options)
1	1.0892E-5	1-Methyl-3-ethylbenzene
2	5.8569E-5	1-Methyl-3-isopropylbenzene
3	7.8800E-5	m-Xylene
4	1.1618E-4	1-Methyl-2-isopropylbenzene
5	1.3529E-4	1-Methyl-3-n-propylbenzene
6	1.3769E-4	1-Methyl-2-n-propylbenzene
7	1.6438E-4	m-Xylene (200C)
8	2.2360E-4	tert-1-Butyl-2-methylbenzene
9	2.2996E-4	1-Methyl-2-ethylbenzene
10	2.3750E-4	1,2-Diethylbenzene
11	2.6925E-4	t-1-Butyl-4-ethylbenzene
12	3.2314E-4	1-Methyl-4-isopropylbenzene
13	3.4078E-4	1-Methyl-4-ethylbenzene
14	3.8248E-4	1-Methyl-4-isopropylbenzene
15	4.2493E-4	1-Methyl-4-ethylbenzene (200C)
16	5.0014E-4	1,2,4-Trimethylbenzene (200C)
17	6.6011E-4	p-Xylene
18	7.1426E-4	1,2,4-Trimethylbenzene
19	7.1531E-4	Lilial
20	7.2300E-4	1-Methyl-3-ethylbenzene
21	7.4892E-4	1,2-Dimethyl-4-ethylbenzene
22	8.2641E-4	p-Xylene (200C)

Library search shows clear class similarities

Search Spectra Search Restrictions Weighting Function Search Restrictions Off

Gasoline 9-22-2014 12:34:16 PM 16734

Gasoline 9-22-2014 12:34:16 PM 16734
1-Methyl-3-ethylbenzene

Unlock llb Search Exit

PIONA Standard



One background sample for each of five analyte classes:

- 11 Paraffins
- 35 Isoparaffins
- 25 Olefins
- 30 Naphthenes
- 38 Aromatics

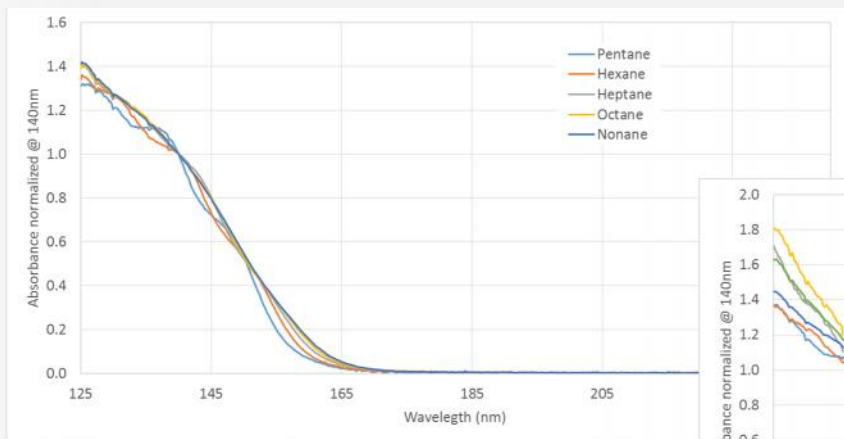
One sample consisting of a mixture of all five classes (139 analytes in all)

The study of this sample set is meant to:

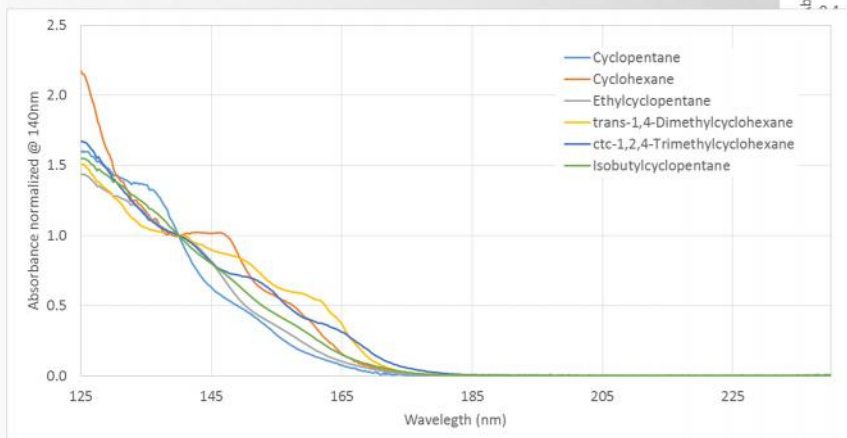
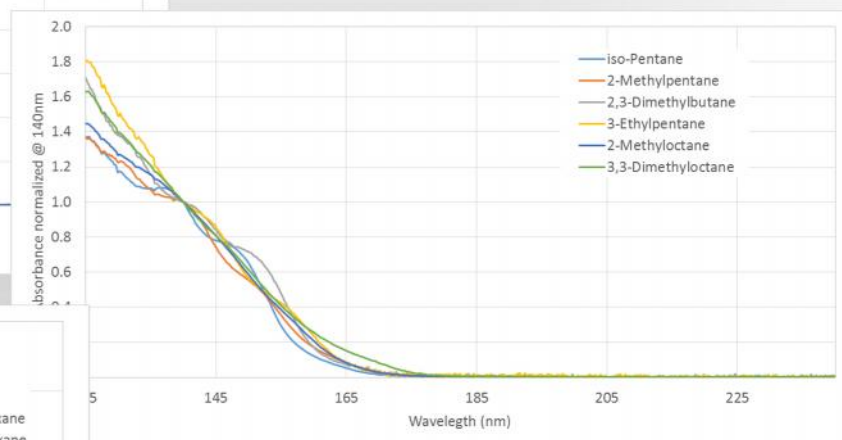
- Provide a reference set of analytes useful for analysis of fuel samples, guided by ASTM methods 6730 and 6839.
- Help develop methodology for automated analysis of complex separations involving many coeluting species.
- Serve as a stepping stone toward analysis of real fuel samples.

Saturated Hydrocarbons

Paraffins



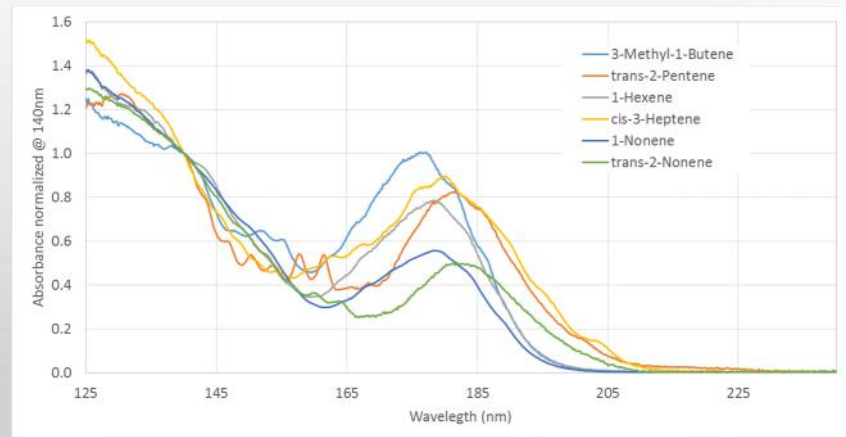
Isoparaffins



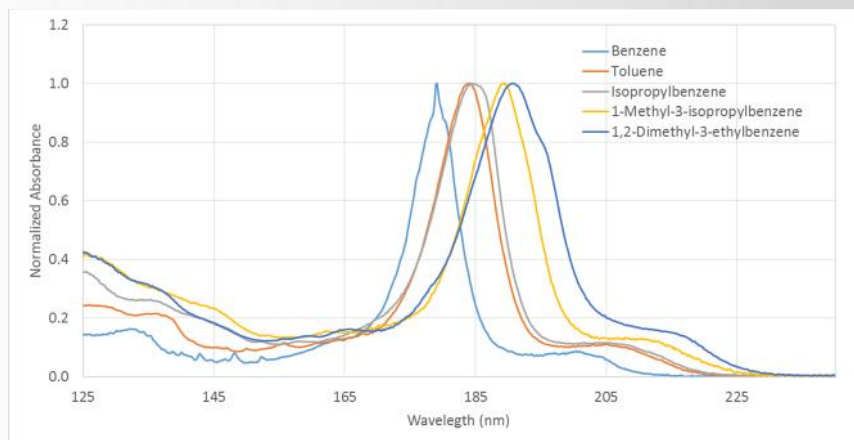
Naphthenes

Olefins and Aromatics

Olefins



Aromatics



Preliminary Class Identification Experiment



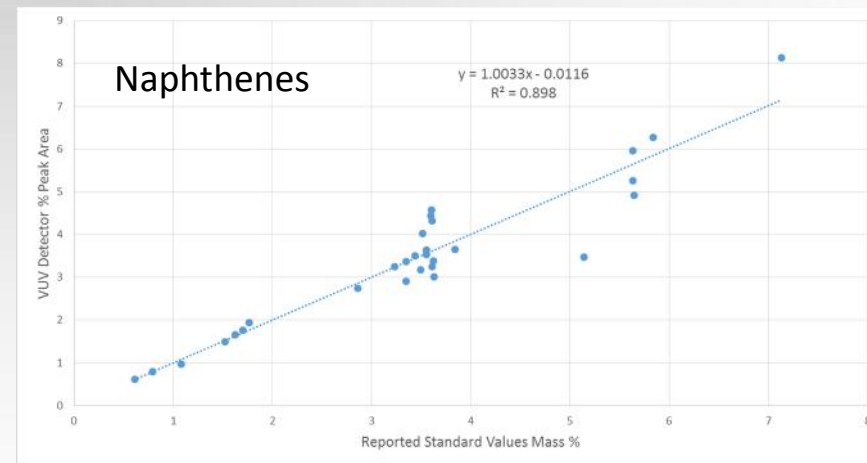
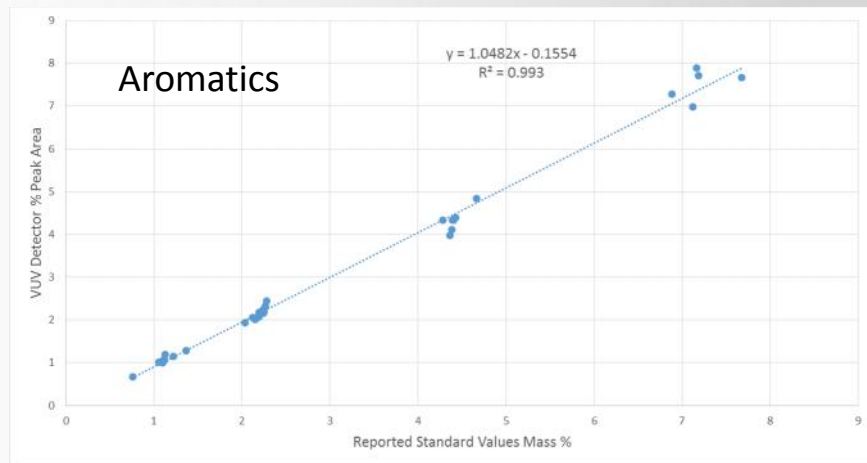
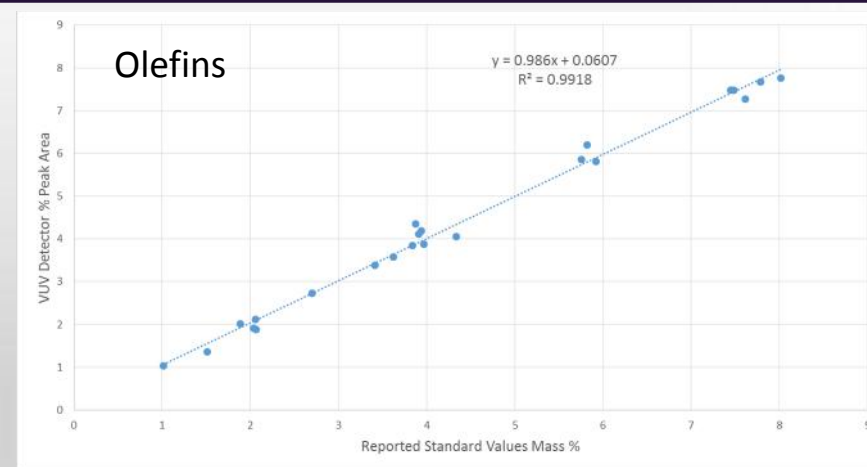
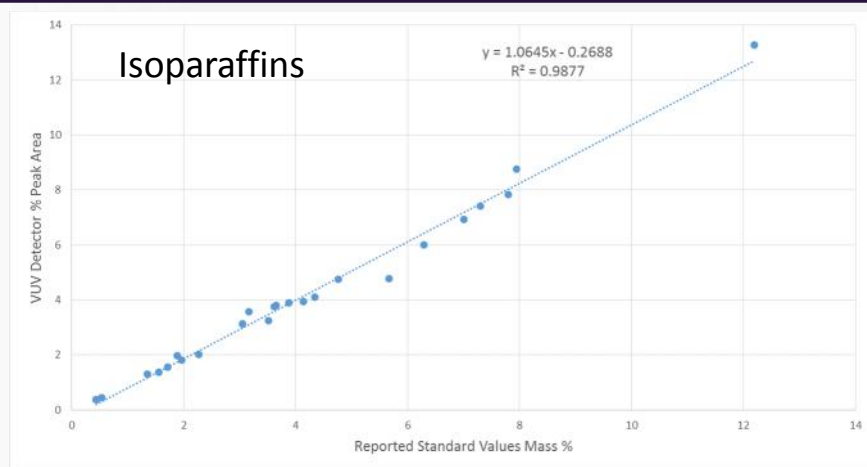
For each analyte class:

- The five analyte background samples were run using a 100m Petrocol column and on two separate occasions.
- Reference spectra were created from one run of the background samples.
- A library search was performed on the second run.
- The number of successful matches were recorded, as well as the number of cases where the first hit was at least in the correct analyte class.
- The result was 100% classification of the PIONA reference analytes.

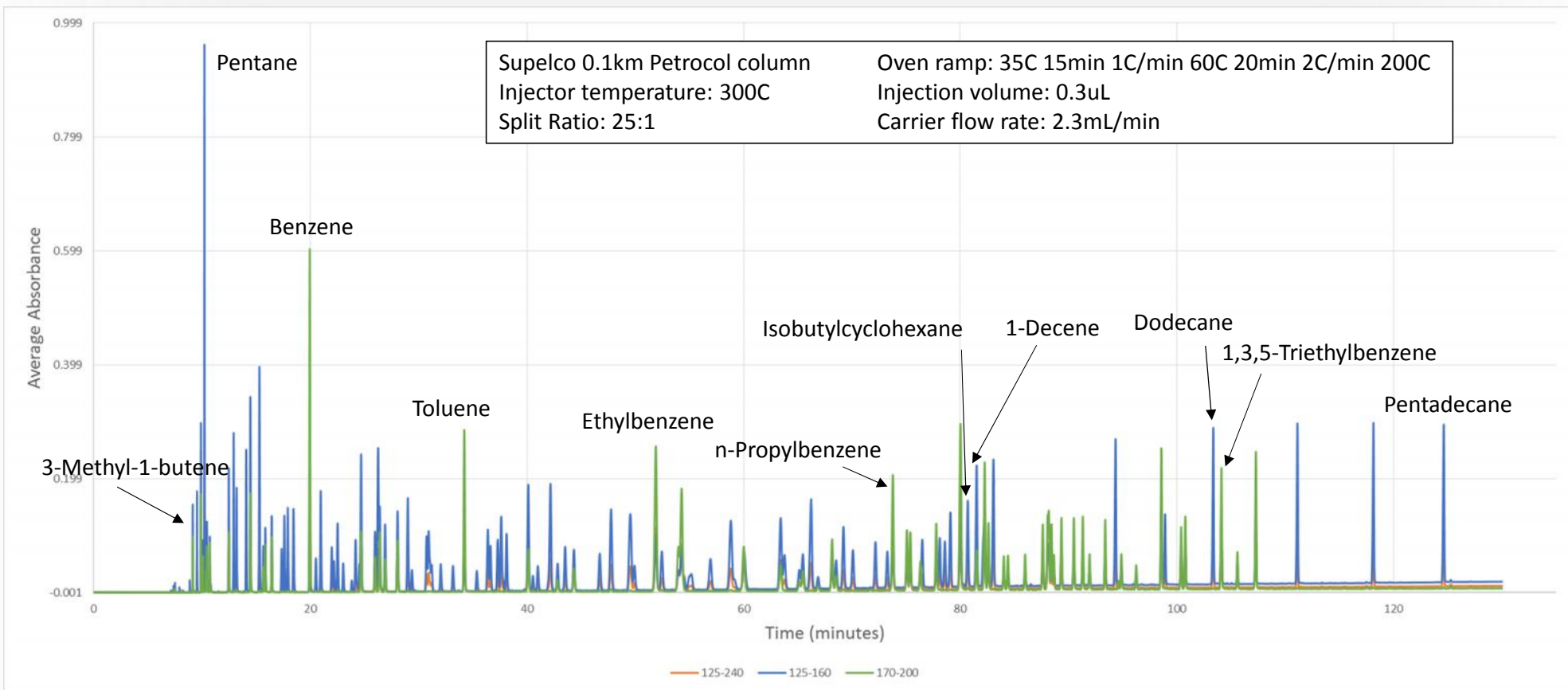
	Paraffins	Isoparaffins	Naphthenes	Aromatics	Olefins
Total number of analytes	11	35	30	38	25
Exact matches	9	31	29	36	25
Exact match and/or correct class	11	35	30	38	25

*Note: No attempt was made to account for coelutions in the Aromatics background sample

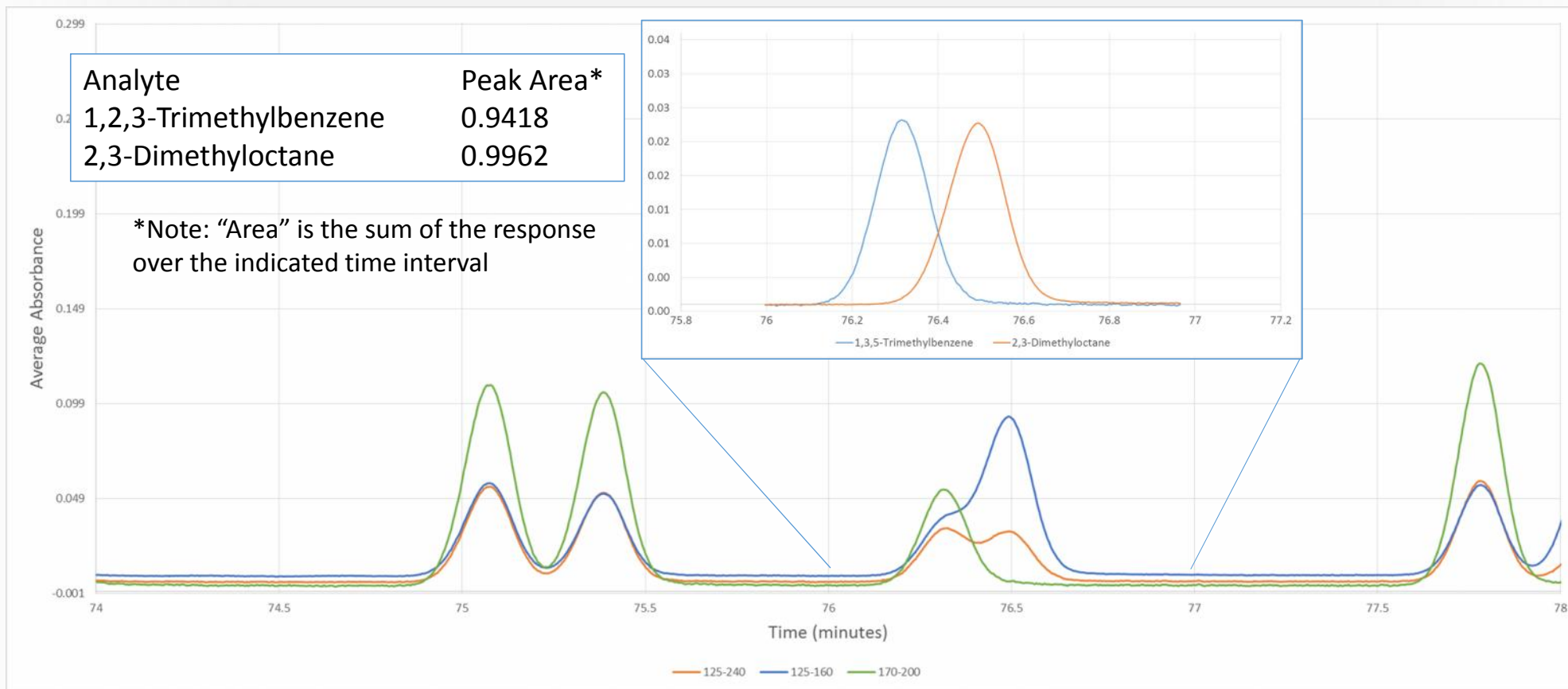
Peak Area % Vs. Mass %: Isoparaffins



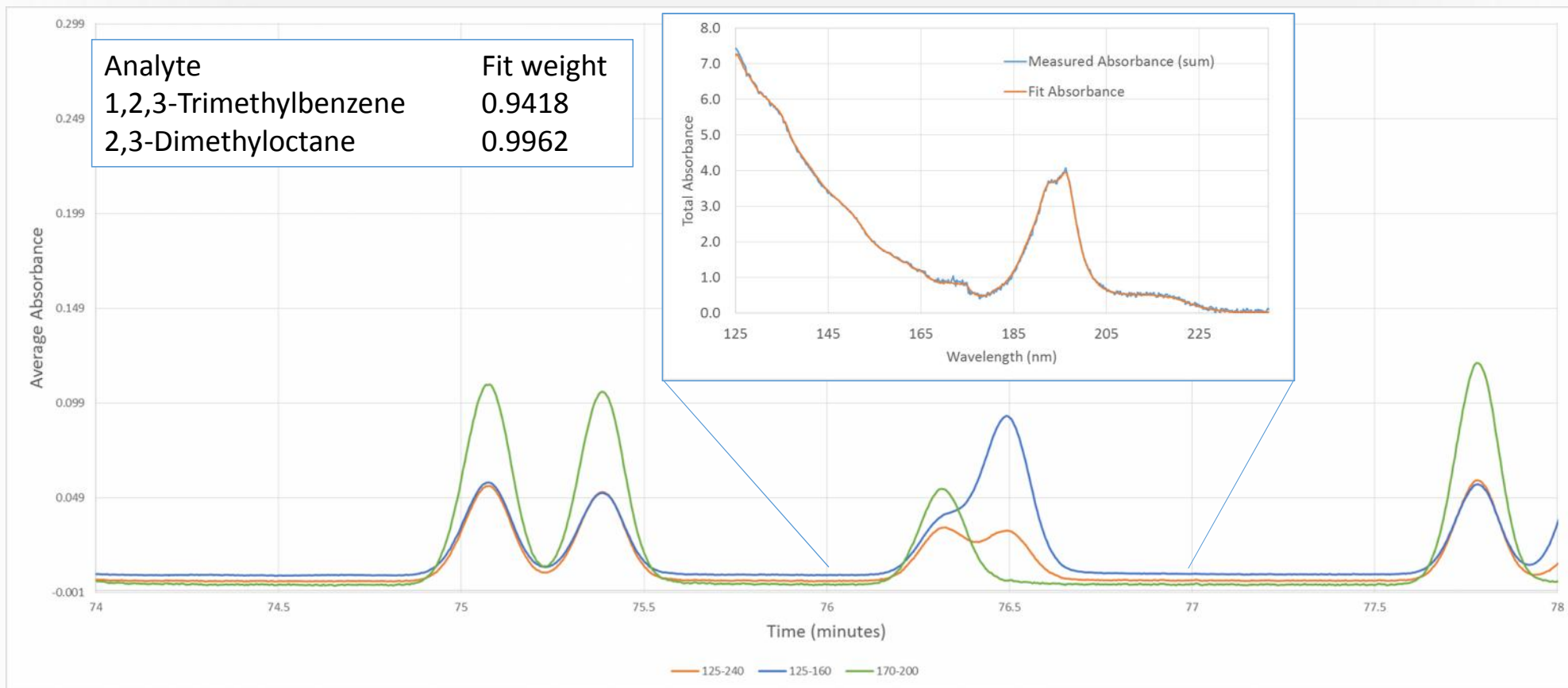
PIONA Sample Full Chromatogram



PIONA Sample 74 – 78 Minutes



PIONA Sample 74 – 78 Minutes



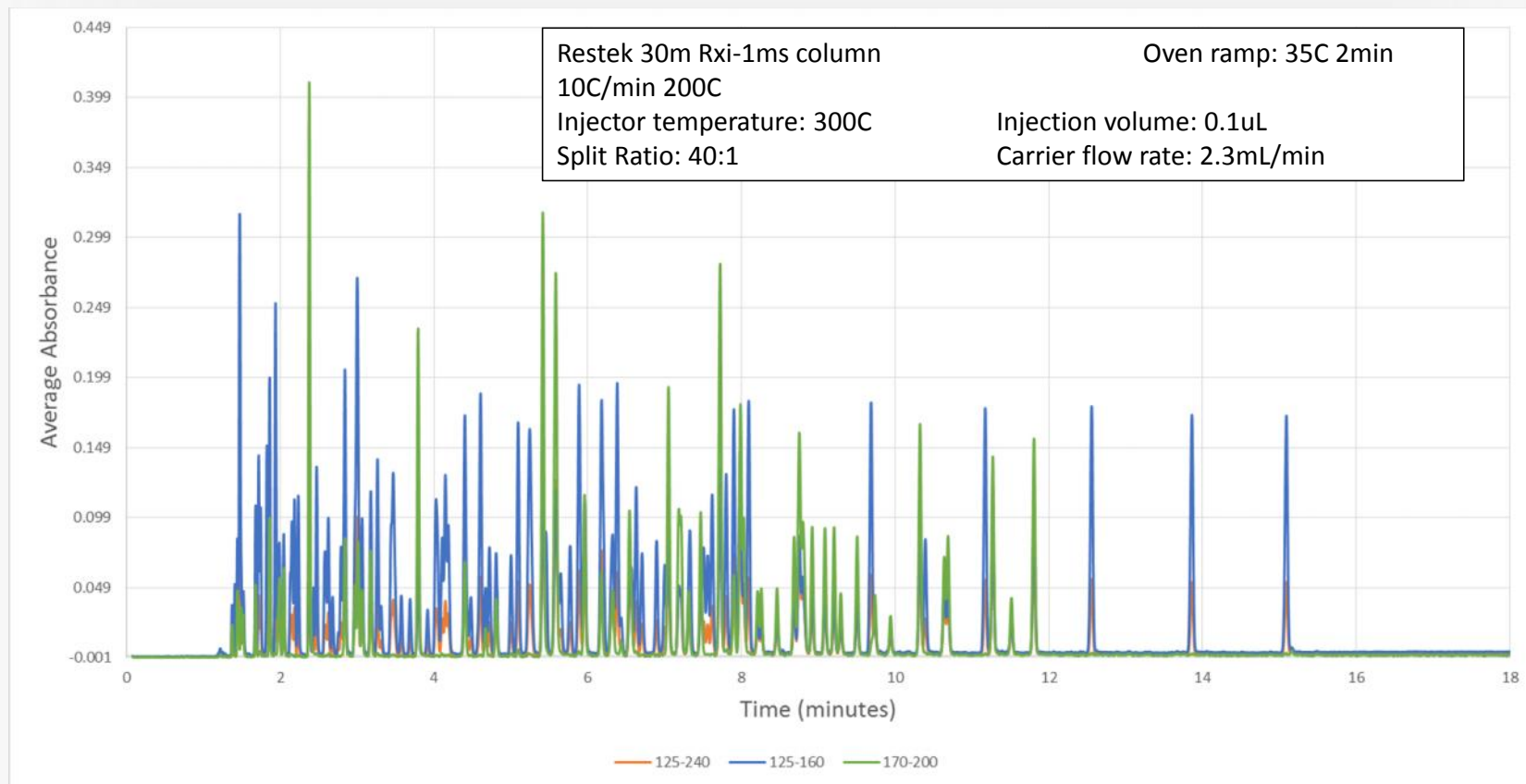
Proposed Analysis Steps



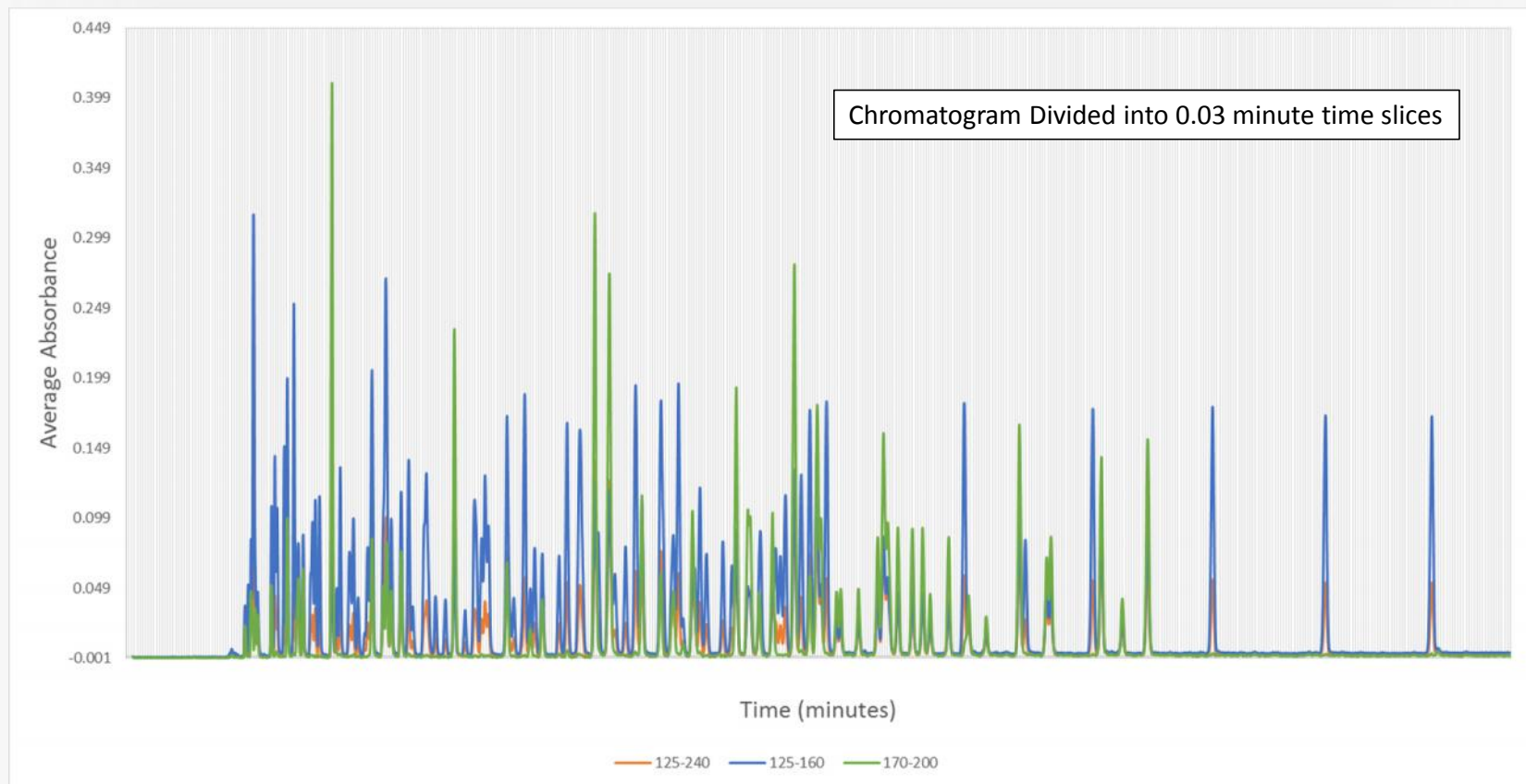
Analysis of full PIONA chromatogram:

- Divide chromatogram into 0.03 minute intervals.
- If the absorbance changes by more than a predefined threshold within the time window, generate a total absorbance spectrum and analyze it.
- If the absorbance changes by less than a second predefined threshold, generate and update the background spectrum.
- If flagged for analysis, perform tiered library search. Use an RI window (+/- 40) to reduce the set of analytes to be searched. Result is a set of most likely candidates for analyte species as well as fit parameters, which are the contributions from each analyte to the total response within the time slice.
- For each of the identified species that belongs to one of the PIONA classes, bin the contribution to each class as appropriate.
- After all time slices have been analyzed, generate mass percent for each analyte class.

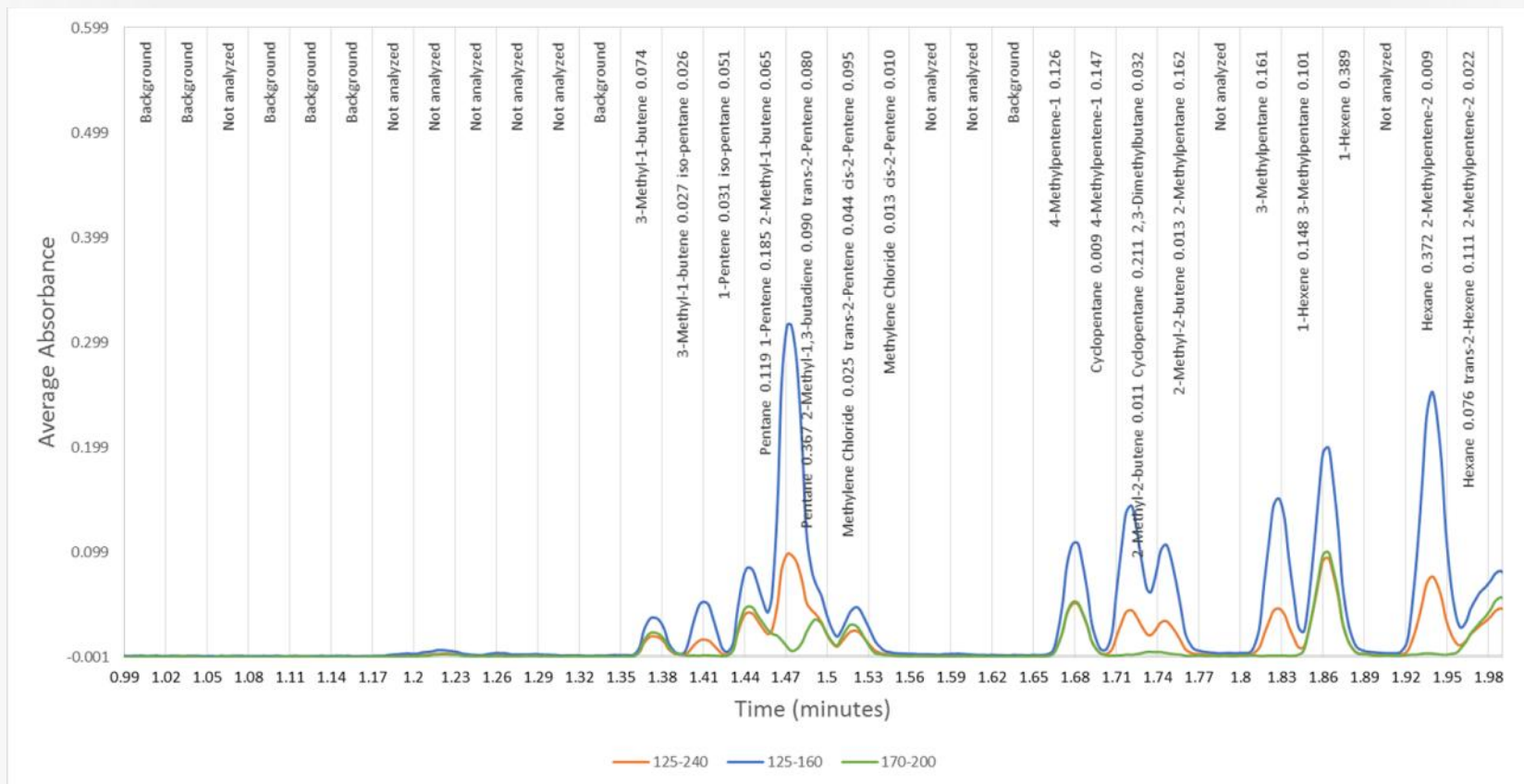
PIONA Sample 30m Column



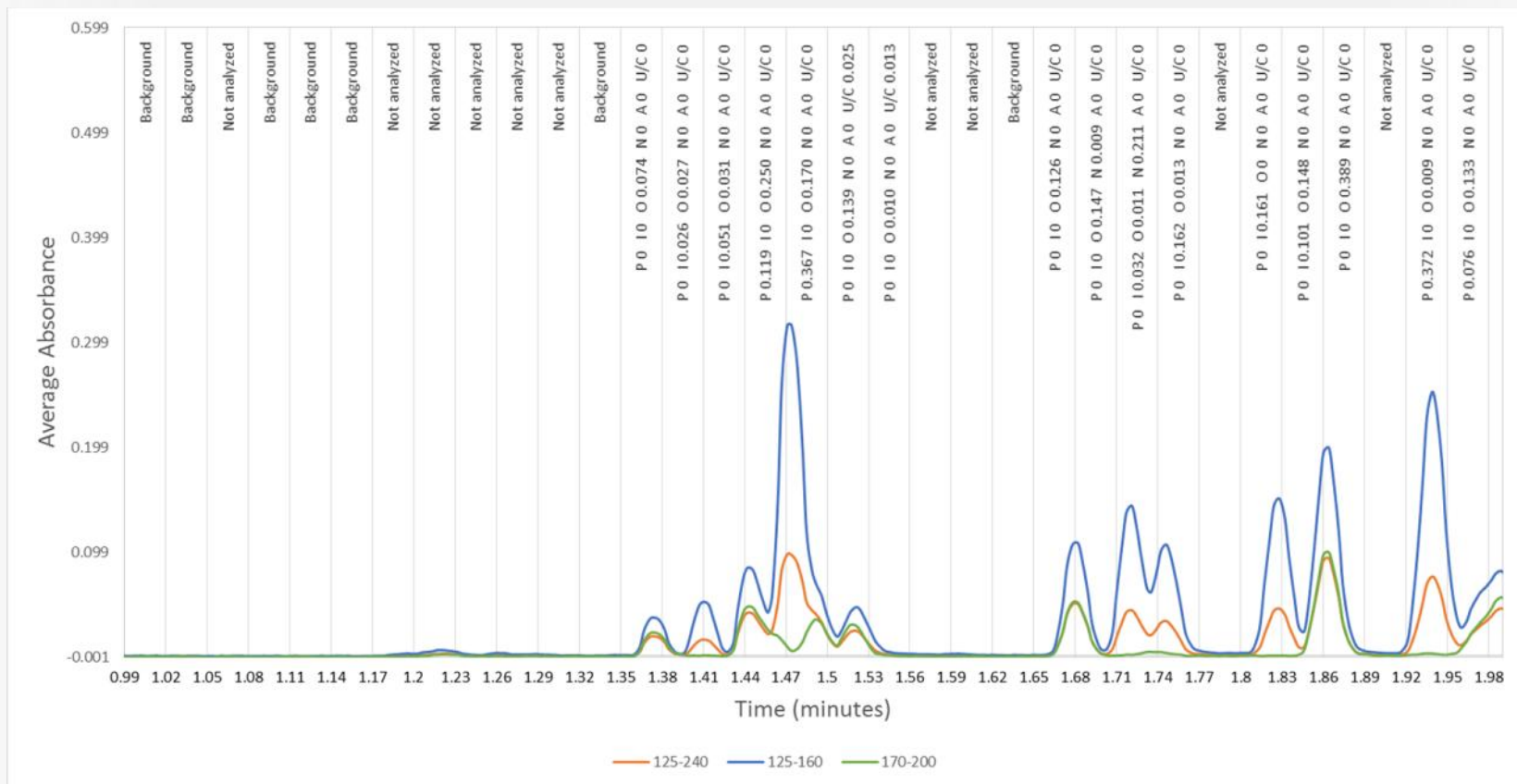
PIONA Sample 30m Column



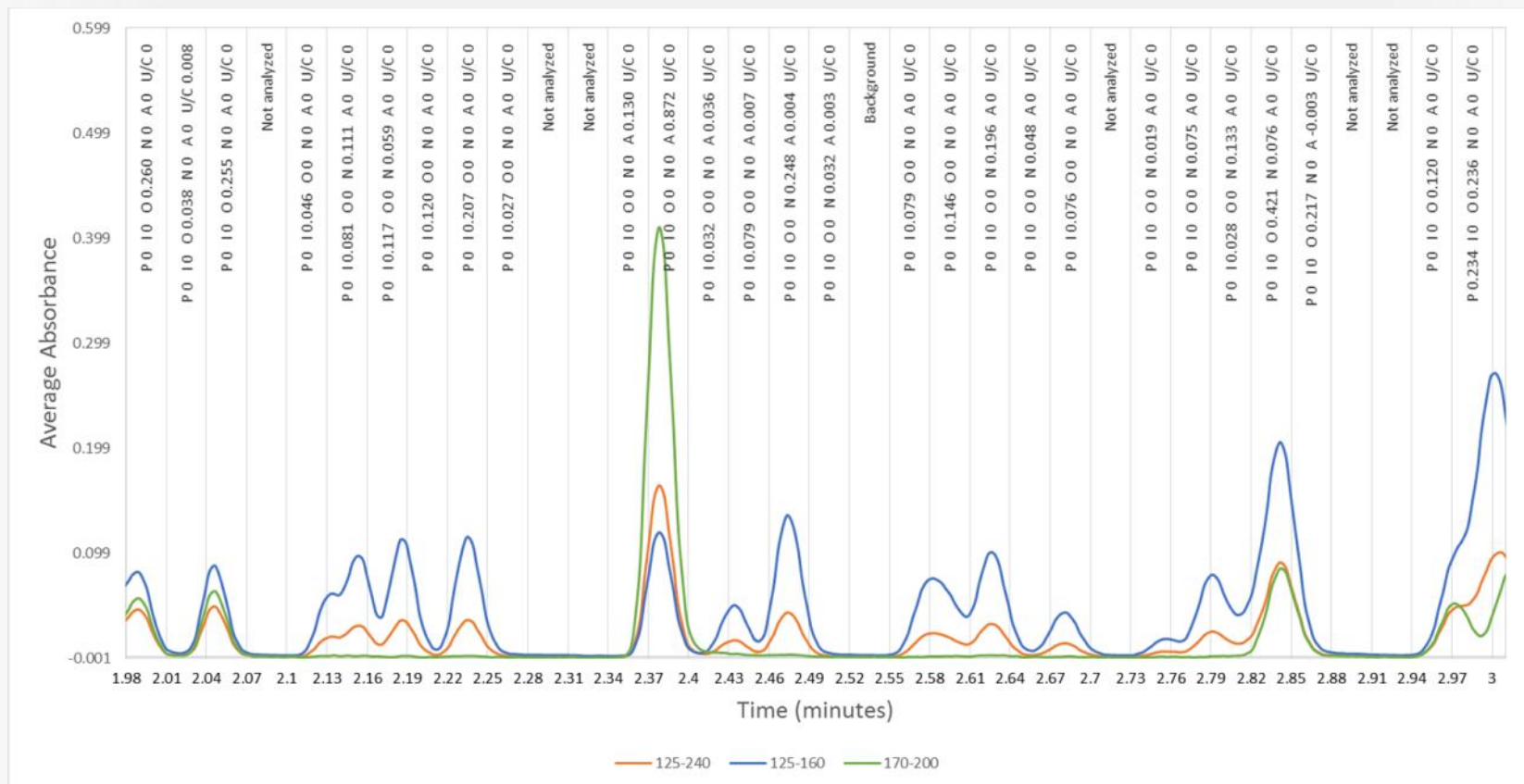
PIONA Chromatogram 1-2 Minutes



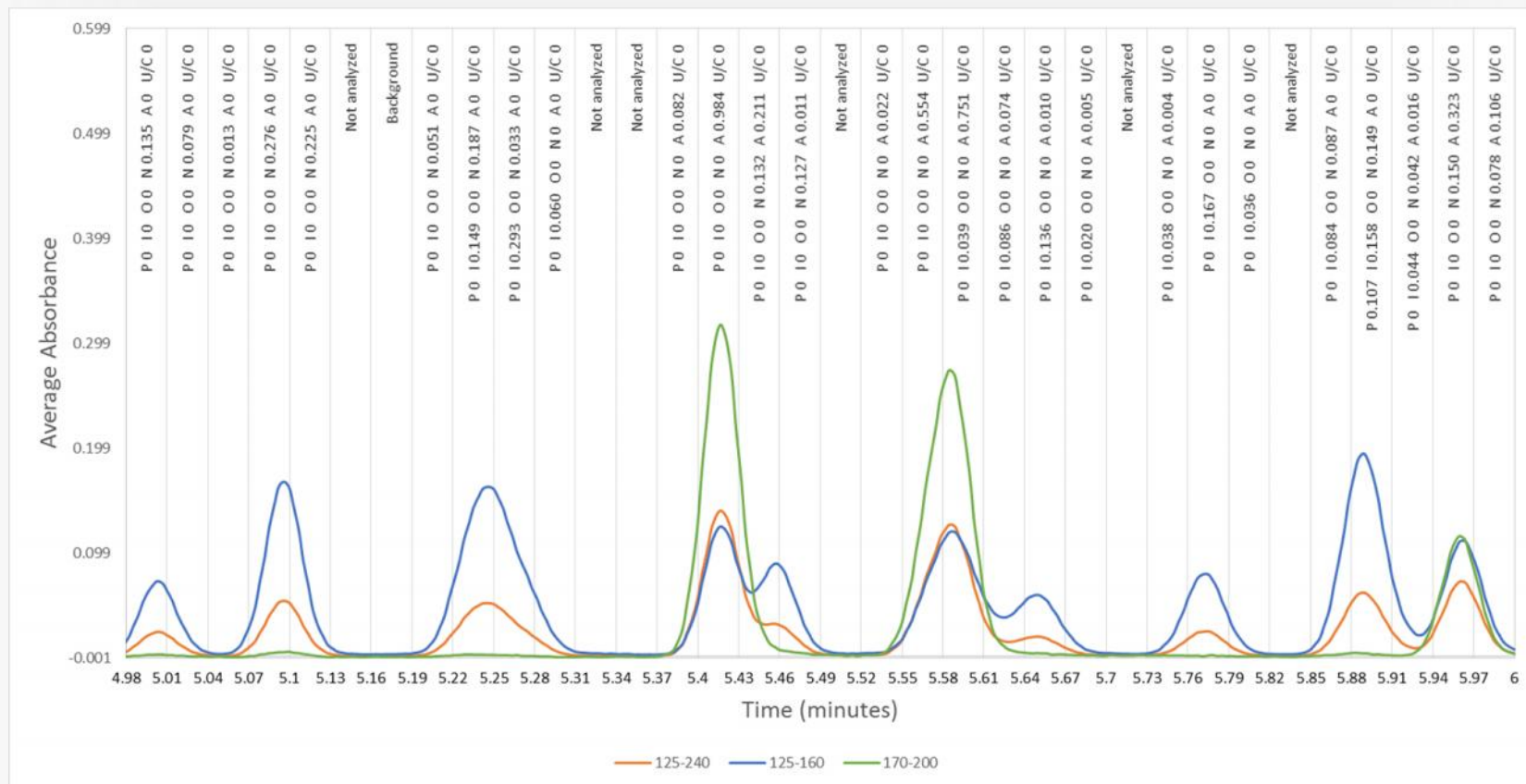
PIONA Chromatogram 1-2 Minutes



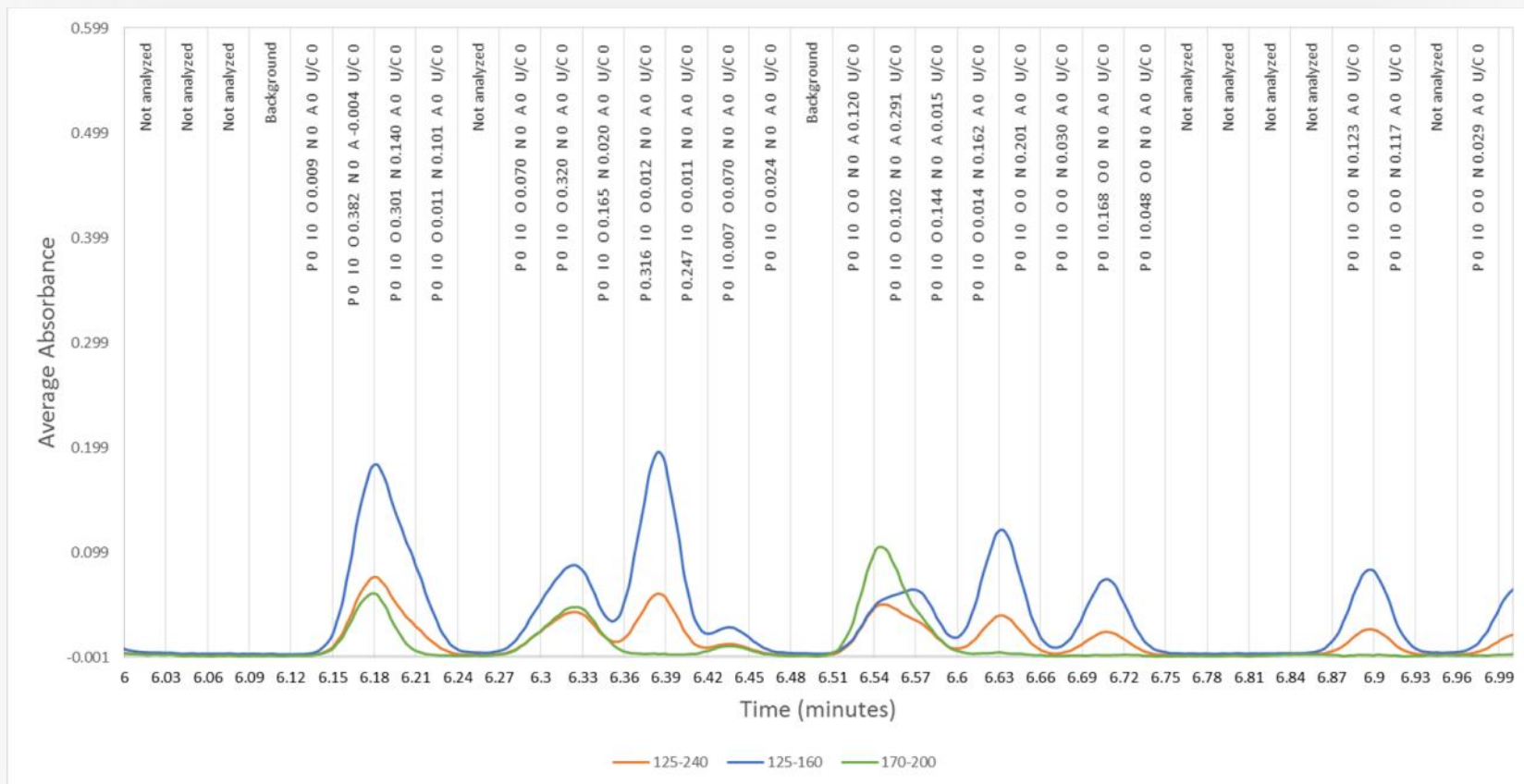
PIONA Chromatogram 2-3 Minutes



PIONA Chromatogram 5-6 Minutes



PIONA Chromatogram 6-7 Minutes



PIONA Chromatogram Repeated Runs



Total peak areas for 3 successive runs (Absorbance Units)

Analyte Class	Run 1	Run 2	Run 3	Std. Dev.	Rel. Std. Dev. (%)
Paraffins	6.148	6.071	6.219	0.074	1.2
Isoparaffins	5.978	6.087	5.951	0.072	1.2
Olefins	8.106	8.242	8.268	0.087	1.1
Naphthenes	6.458	6.591	6.684	0.113	1.7
Aromatics	19.033	19.379	19.625	0.297	1.5

PIONA Chromatogram Repeated Runs



Same data as prior slide with relative response calibrated to mass % information provided with PIONA standard (mass %)

Analyte Class	Run 1	Run 2	Run 3	Std. Dev. (%)	Rel. Std. Dev. (%)
Paraffins	19.37	18.89	19.22	0.246	1.3
Isoparaffins	19.12	19.22	18.67	0.294	1.5
Olefins	17.96	18.04	17.97	0.042	0.23
Naphthenes	20.45	20.62	20.77	0.157	0.76
Aromatics	23.11	23.24	23.37	0.134	0.58

PIONA Chromatogram Repeated Runs



Mass % for 10 successive runs

Analyte Class	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Average	Std. Dev.	Rel. Std. Dev. (%)
Paraffins	20.32	20.03	20.67	20.41	20.49	20.50	20.39	20.39	20.73	20.93	20.49	0.25	1.2
Isoparaffins	19.23	19.36	18.82	19.06	18.98	19.04	19.01	18.92	18.67	18.80	18.99	0.20	1.1
Olefins	14.84	14.72	14.37	14.60	14.50	14.38	14.37	14.31	14.38	14.22	14.47	0.19	1.3
Naphthenes	19.90	20.09	20.39	19.95	20.01	19.81	20.00	20.27	20.14	19.99	20.05	0.17	0.87
Aromatics	25.71	25.80	25.76	25.99	26.03	26.26	26.24	26.12	26.08	26.05	26.00	0.19	0.74

PIONA Chromatogram Repeated Runs



Mass % for 10 successive runs

Analyte Class	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Average	Std. Dev.	Rel. Std. Dev. (%)
Paraffins	20.32	20.03	20.67	20.41	20.49	20.50	20.39	20.39	20.73	20.93	20.49	0.25	1.2
Isoparaffins	19.23	19.36	18.82	19.06	18.98	19.04	19.01	18.92	18.67	18.80	18.99	0.20	1.1
Olefins	14.84	14.72	14.37	14.60	14.50	14.38	14.37	14.31	14.38	14.22	14.47	0.19	1.3
Naphthenes	19.90	20.09	20.39	19.95	20.01	19.81	20.00	20.27	20.14	19.99	20.05	0.17	0.87
Aromatics	25.71	25.80	25.76	25.99	26.03	26.26	26.24	26.12	26.08	26.05	26.00	0.19	0.74

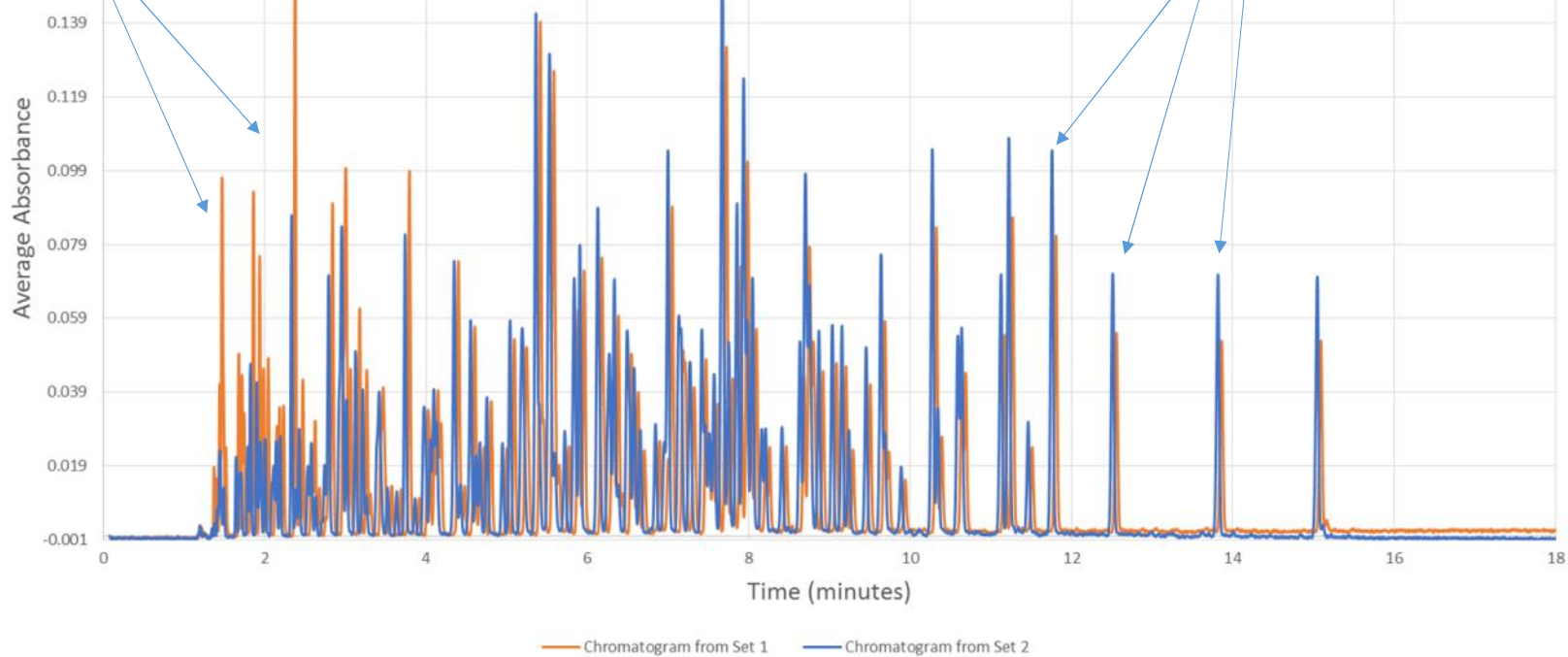
- The loss in olefin percentage was real, resulting from poor sample handling
- The olefins accounted for a disproportionate amount of lower weight (i.e. more volatile) compounds

Comparison of Chromatograms From Two Sets



Significant loss of more volatile compounds

Slightly larger overall injection volume



Further Steps: Analysis of Gasoline



Obtain samples with different weights of the five PIONA classes.

Finalize relative response factors for analyte classes.

Characterize more aromatics, olefins, diolefins for gasoline applications.

First step in analysis of real gasoline samples: Quantification of Aromatics, Olefins, PAHs, and saturated compounds?

Currently only allow three simultaneous classes during fit – extend to 5+?

Conclusions



Developed a methodology for automated analysis of PIONA-type samples.

Applied methodology to a PIONA standard run on a 30m column.

Promising results for all five analyte classes (would have been happy to have separated Aromatics, Olefins, and saturates as a first step).

Next steps will push methodology toward analysis of real gasoline samples

Thank You!