OLEFIN CONTENT IN FUELS BY ASTM D8071

115th meeting of the Gulf Coast Conference

October 2018

MCDERMOTT TECHNOLOGY

LUMMUS TECHNOLOGY

Jean-Francois Borny

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McDermott cautions that statements in this presentation which are forward-looking, and provide other than historical information, involve risks, contingencies and uncertainties that may impact actual results of operations. These forward-looking statements include, among other things, statements about anticipated cost and revenue synergies, accretion, best-in-class operations, opportunities to capture additional value from market trends, maintenance of a consistent customer approach to pricing, safety and transition issues, free cash flow, plans to de-lever and accretion. Although we believe that the expectations reflected in those forward-looking statements are reasonable, we can give no assurance that those expectations will prove to have been correct. Those statements are made by using various underlying assumptions and are subject to numerous risks, contingencies and uncertainties, including, among others: the possibility that the expected synergies from the recently completed combination will not be realized, or will not be realized within the expected time period; difficulties related to the integration of the two companies; disruption from the combination making it more difficult to maintain relationships with customers, employees, regulators or suppliers; the diversion of management time and attention related to integration matters; adverse changes in the markets in which the company operates; the inability to execute on contracts in backlog successfully; changes in project design or schedules; the availability of qualified personnel; changes in the terms; scope or timing of contracts; contract cancellations; change orders and other modifications and actions by customers and other business counterparties; changes in industry norms; and adverse outcomes in legal or other dispute resolution proceedings. If one or more of these risks materialize, or if underlying assumptions prove incorrect, actual results may vary materially from those expected. You should not place undue reliance on forward-looking statements. For a more complete discussion of these and other risk factors, please see the company's most recent filings with the Securities and Exchange Commission, including its annual report on Form 10-K for the year ended December 31, 2017 and subsequent quarterly reports on Form 10-Q. This presentation reflects the views of the company's management as of the date hereof. Except to the extent required by applicable law, the company undertakes no obligation to update or revise any forward-looking statement.

LUMMUS TECHNOLOGY

HISTORICAL BACKGROUND

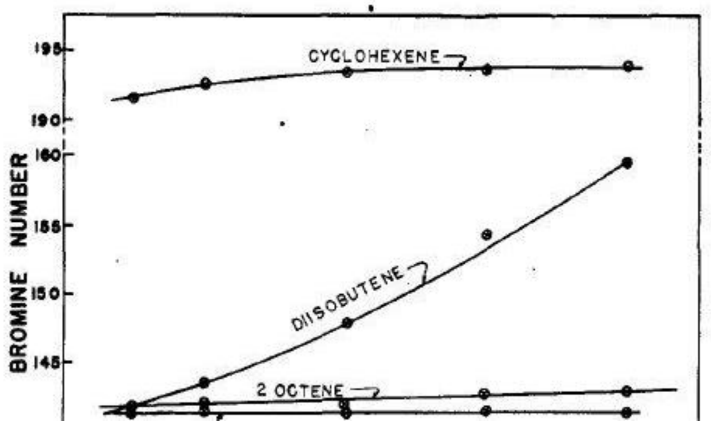
IT ALL STARTED IN 1941

Procedure for Determination of the Bromine Number of Olefinic Hydrocarbons

HERBERT L. JOHNSON AND RICHARD A. CLARK, *Sun Oil Company Experimental Division, Norwood, Pa.*

The procedure described in this paper for the determination of olefinic unsaturation was developed in 1941 but publication was held up because of wartime conditions.

tion was held up because of wartime conditions. In 1942 it was submitted to the American Society for Testing Materials and formed the basis of the bromine number procedure incorporated in Method ES-45, Method ES-45a, and finally a tentative A.S.-T.M. standard (D-875-46T) for olefins and aromatics in petroleum distillates. The method as originally developed is applicable to olefin samples with high or low bromine absorptions. Data justifying the scope of this procedure are included in this paper.



theoretical value for all molecules containing olefinic unsaturation. It is desirable that minor changes in temperature, excess of reagent, or nature of the solvent should not appreciably affect the bromine number obtained.

The difficulty in developing a satisfactory halogen titration procedure is increased by the fact that the rate of reaction of halogen with the various types of olefins differs widely. The tendency for halogen substitution to occur with saturated and aromatic hydrocarbons, as well as with olefins, is pronounced under certain conditions. The development of a satisfactory halogen titration procedure is in fact an attempt to find a procedure which will give satisfactory conditions for the reaction of halogen with all types of olefins and will in general avoid substitution or other side reactions.

Many procedures have appeared in the literature for the determination of olefinic unsaturation by means of halogen titration.

The methods of Hubl (*7*), Hanus (*6*), and Wijs (*15*), which were among those first used, gave good results on some compounds while on others they gave high values because substitution occurs as well as addition. To correct this deficiency McIlhiney (*11*) developed a method whereby both addition and substitution could be measured. Johansen (*8*) compared the Hanus and McIlhiney methods and concluded that the latter after some minor modifications, gave satisfactory results. However, since negative numbers for the bromine addition were sometimes ob-

PODREBARAC & JUDZIS - *ENERGY & FUELS* 2007 ARTICLE

2964 *Energy & Fuels* **2007,** *21,* 2964–2968

Improved Designs of FCC Gasoline Hydrodesulfurization Units by Properly Measuring the Olefin Content of the Gasoline Feed

Gary G. Podrebarac* and Arvids Judzis, Jr.

CDTECH, 10100 Bay Area Boulevard, Pasadena, Texas 77507

Received November 21, 2006. Revised Manuscript Received July 9, 2007

Hydrodesulfurization of cracked gasoline is now a vital step for the production of clean fuels. Along with sulfur removal, however, olefin saturation occurs. Knowing the olefin content of the gasoline is key to achieving a proper design, as olefin saturation largely sets the heat release and hydrogen consumption that will be experienced. More specifically, the molar concentration of the olefins must be known, and determining this in cracked gasoline is not as straightforward as it seems. There are a number of seemingly appropriate analytical methods for olefin measurement. This study examines several of the more common methods used in the refining industry and compares their performance on a sample of full-range FCC gasoline. A case is made that the bromine number is the most appropriate measurement to use as the basis for a reactor design.

Introduction

The removal of sulfur from gasoline has become a vital refining step as governments have enacted laws requiring cleaner burning fuels. Of particular importance is the desulfurization

resolution GC, ASTM-D6733;[2] (3) PIANO: detailed hydrocarbon analysis, ASTM-D5134;[3] and (4) MD-GC Reformulizer method, ASTM-D6839.[4]

Each of these methods is a reproducible technique. However, we observed that comparisons of these various methods tend

Table 4. Example of Treating a 160−450 °F FCC Gasoline Feedstock for HDS

	Br #	PONA	PIANO
feed total S (ppmw)	940	940	940
feed density (g/mL)	0.79	0.79	0.79
feed Br # (g/100 g)	52.5	33.6[a]	23.7[a]
H_2 consumption (scf/bbl)	141.7	90.7	63.9
heat release (Btu/bbl)	18804	12028	8477

[a] Calculated Br # starting from either PONA or PIANO method.

Summary:

The designer still needs some measure of aliphatic unsaturation that will aid in calculating the hydrogen uptake and heat release in the reactor when dealing with heavy gasoline. It should be clear that the Br # characterizes all of the **reactive olefins** in the cracked gasoline and helps prevent design errors.

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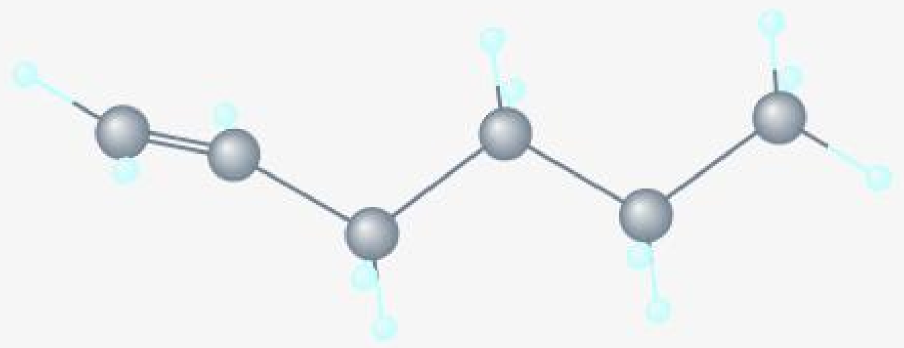
HYDROGEN CONSUMPTION & HEAT BALANCE

AND

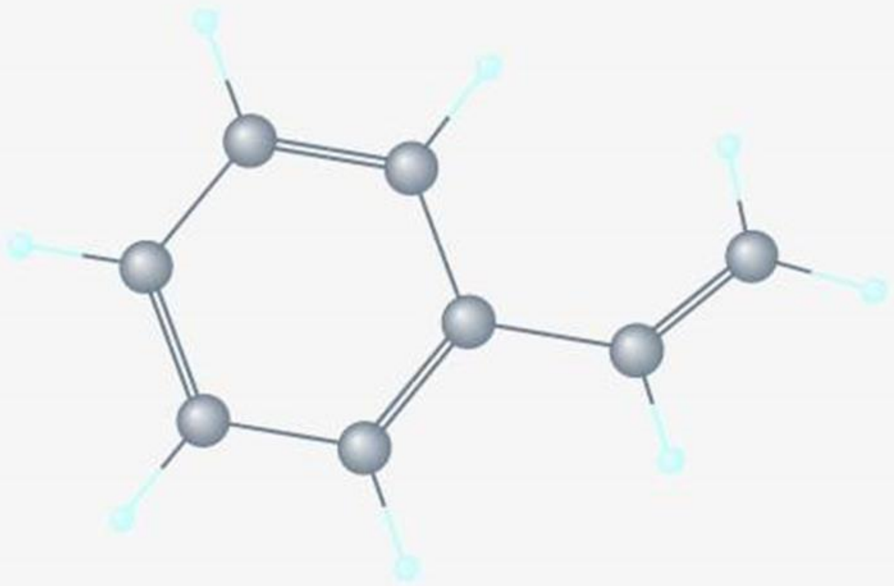
OLEFIN CONTENT

WHAT’S THE DIFFERENCE?

1-hexene



styrene



ASTM D1159 BROMINE NUMBER

ADVANTAGES & PROBLEMS

Advantages

- Measures all olefinic aspect of compounds
- Titration method is simple and inexpensive
- 5-minute analysis

Problems

- Reproducibility (R) is quite large
- May also react with sulfur, nitrogen and other non-olefinic compounds
- Not a direct measure of olefin content

A2. CALCULATION OF OLEFIN CONTENT

A2.1 Scope

A2.1.1 This procedure covers the calculation of the volume percentage of olefins from the bromine number in straight-run, reformed, cracked gasolines and commercial gasolines that have a 90 % boiling point below 200 °C (392 °F); and turbine fuel and kerosine etc., boiling below 315 °C (600 °F) and having a bromine number of less than 20.

A2.1.2 The procedure is not intended for synthetic olefinic blends of pure or nearly pure compounds having a boiling range of less than 14 °C (25 °F).

A2.1.3 Sulfur, nitrogen, or oxygen compounds, if present in concentrations of 1 % by volume or greater will reduce the accuracy (see Note A2.1).

A2.2 Procedure

A2.2.1 Determine the bromine number in accordance with this test method.

NOTE A2.1—For information on types of compounds that may yield anomalous data in the bromine number test, see Annex A1. In the case of special samples that contain high concentrations of certain hydrocarbon types, caution in the interpretation of the bromine number is needed.

A2.2.2 Calculate the concentration of olefins from the bromine number as follows:

$$\text{olefins, mass \%} = \int BM/160 \qquad (A2.1)$$

where:

$\int$ = boiling range correction (see Fig. A2.1 and Table A2.1),
B = bromine number expressed as grams of bromine/100 g of sample, and
M = molecular weight (relative molecular mass) of olefins (see Table A2.2).

NOTE A2.2—The boiling range correction is needed for cracked naphthas since it is an empirical fact that the percentage by volume of olefins is higher in the lower boiling fractions and that these olefins are also of lower relative molecular mass (molecular weight).

A2.2.3 Using the 50 % boiling point (see Test Method D86), estimate the average density of the olefins using Fig. A2.2. Multiply the mass percentage of olefins (as calculated in

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D1159 – 07 (2017)

A2.2.2) by the ratio of the density of the original sample to the density of the olefins to obtain percentage by volume as follows:

$$\text{olefins, volume \%} = (A/B) \times C \quad (A2.2)$$

where:

A = density of the sample,
B = average density of the olefins, and
C = mass percentage of olefins.

A2.3 Precision[9]

A2.3.1 The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

A2.3.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Straight-Run Fuels (less than 1 volume % olefins)	Cracked Gasolines (1 to 25 volume % olefins)
0.2	0.6

A2.3.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators, working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Straight-Run Fuels (less than 1 volume % olefins)	Cracked Gasolines (1 to 25 volume % olefins)
0.4	3

A2.3.2 *Bias*—The procedure for calculating olefin content has no bias because the value obtained can be defined only in terms of a procedure.

NOTE A2.3—The precision for this test method was not obtained in accordance with RR:D02-1007.

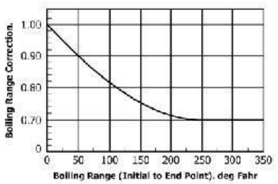

FIG. A2.1 Boiling Range Correction

TABLE A2.1 Boiling Range Corrections for Olefins

Boiling Range Correction, f	Boiling Range, °C (°F) Initial to End, (see Test Method D86)
1.00	0 (0)
0.975	7 (13)
0.950	14 (25)
0.925	21 (38)
0.900	28 (50)
0.875	38 (68)
0.850	43 (78)
0.825	53 (95)
0.800	62 (112)
0.775	72 (130)
0.750	95 (152)
0.725	99 (178)
0.700	125 or greater (225)

TABLE A2.2 Relation of Average Relative Molecular Mass (Molecular Weight) to 50 % Boiling Point by Test Method D86

50 % Boiling Point, °C (°F)	Average Molecular Weight of Olefins
38 (100)	72
66 (150)	83
93 (200)	96
121 (250)	110
149 (300)	127
177 (350)	145
204 (400)	164
232 (450)	186

BROMINE NUMBER ANALYSES FROM FOUR LABORATORIES

Sample	Lummus Technology	Laboratory 1	Commercial Lab 1	Commercial Lab 2
Sample # 1	59	48	43	55
Sample # 2	49	35	36	43
Standard # 1 83 g/100g	82	77	n/a	76
Standard # 2 20 g/100g	18	n/a	20	17

Standards are single olefin solution (cyclohexene)

Samples are light cat naphtha

The definition of R is *the difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the following values only in one case in twenty*.

Sample	R
Sample # 1	11
Sample # 2	10
Standard # 1 - 83 g/100g	16
Standard # 2 - 20 g/100g	6

For sample with 90% distillation point under than 205°C, $R = 0.72 \cdot X^{0.70}$

Sample	Lummus	Laboratory 1	Commercial Lab 1	Commercial Lab 2
Sample # 1	59 → 48 – 70	48 → 37 – 59	43 → 32 – 54	55 → 44 – 66
Sample # 2	49 → 39 – 59	35 → 25 – 45	36 → 26 – 46	43 → 33 – 53
Standard # 1 – 83 g/100g	82 → 66 – 98	77 → 61 - 93	N/A	76 → 60 – 92
Standard # 2 – 20 g/100g	18 → 12 – 24	N/A	20 → 14 – 26	17 → 11 – 23

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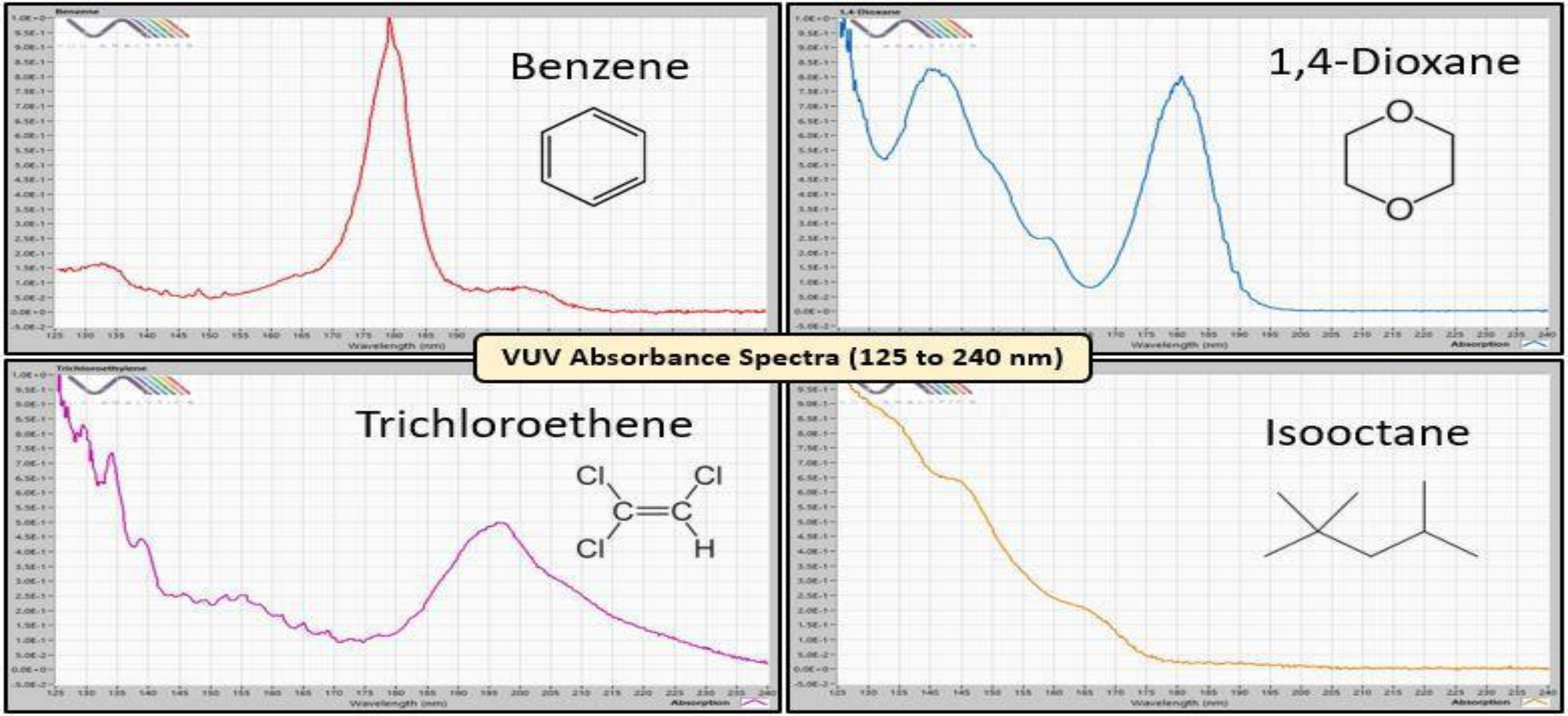
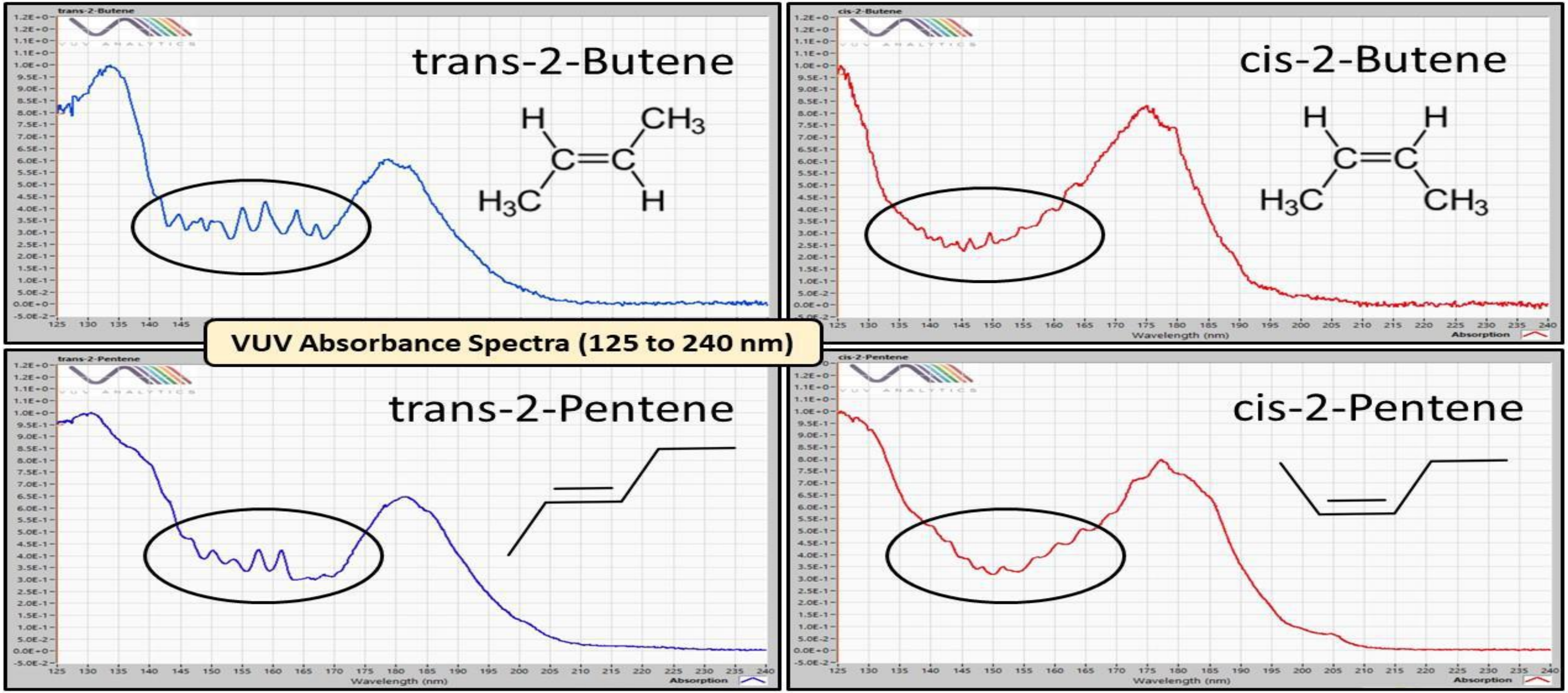
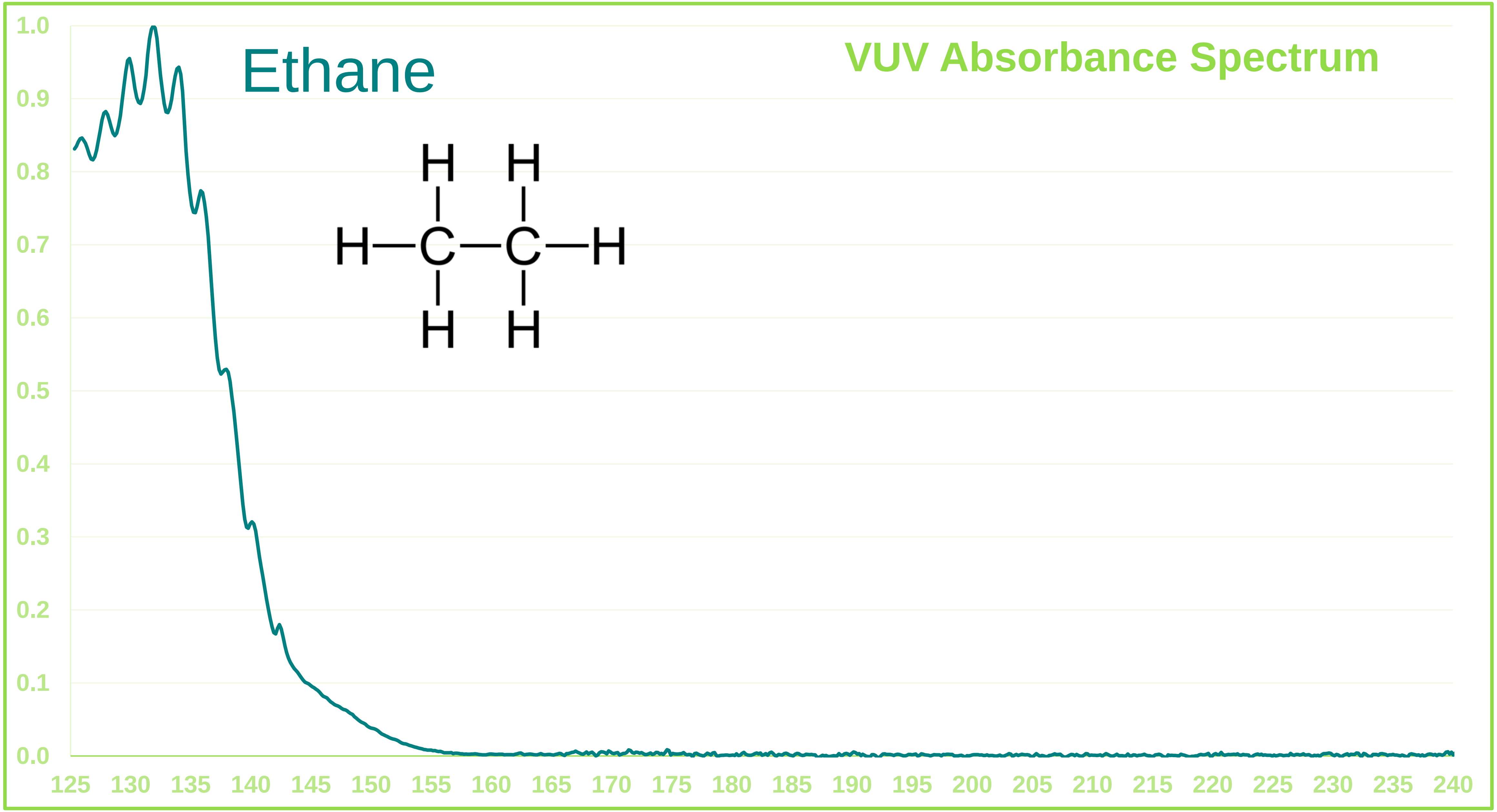
WHY GC-VUV?

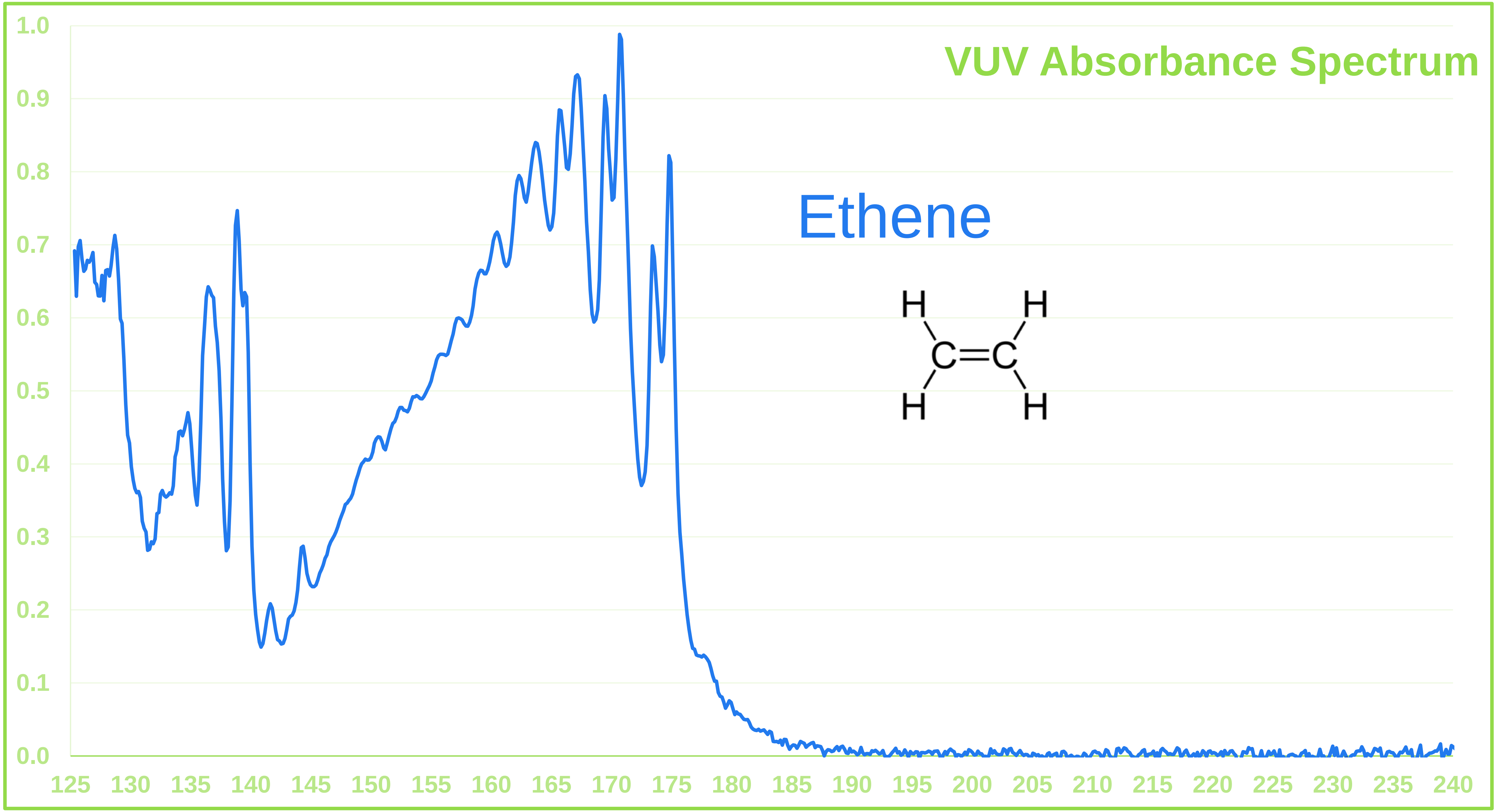
MORE THAN DETAILED HYDROCARBON ANALYSIS


Benzene
1,4-Dioxane
Trichloroethene
Isooctane
VUV Absorbance Spectra (125 to 240 nm)
Wavelength (nm)
Absorption
Cl
C=C
H

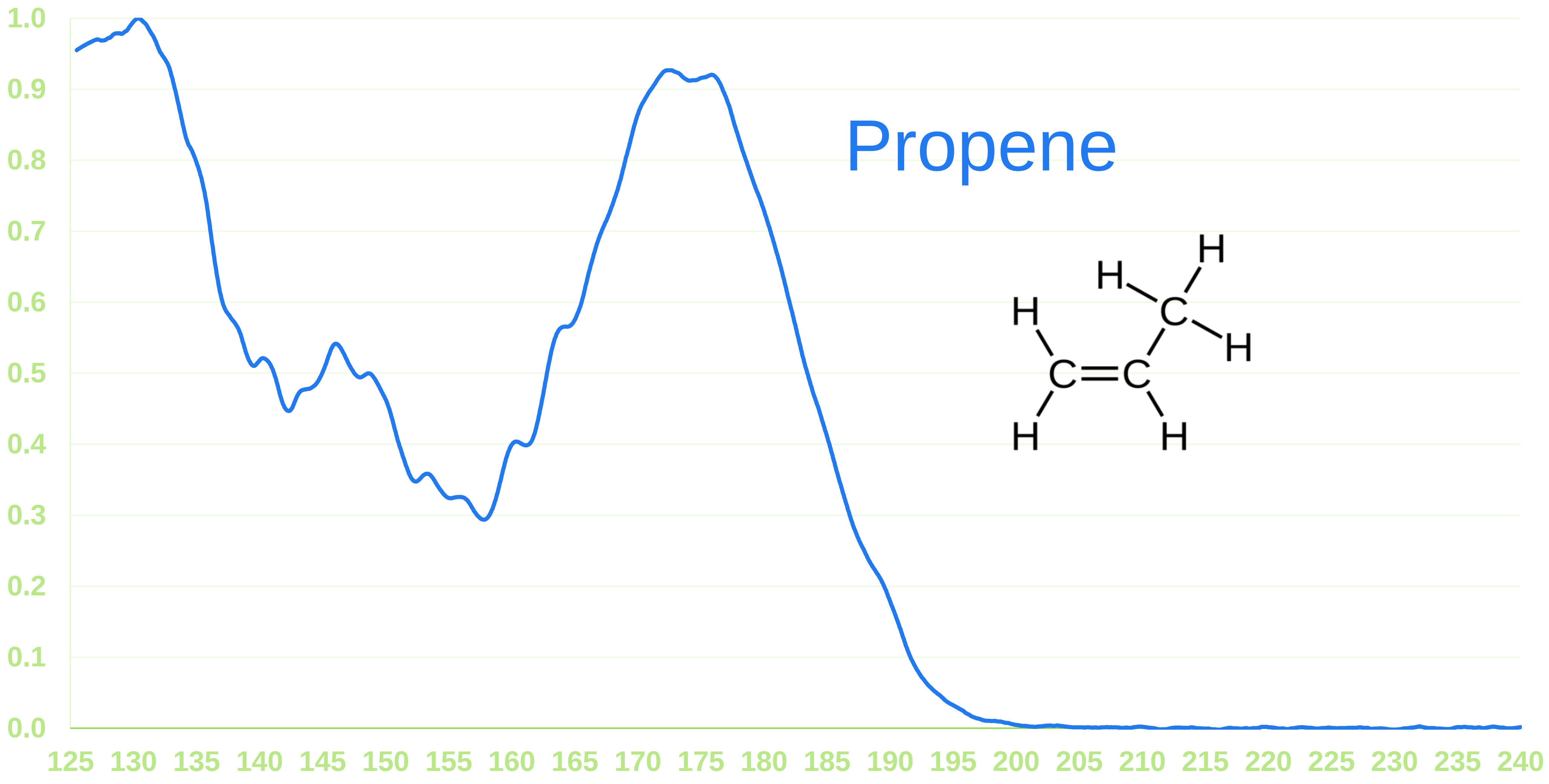
VUV Absorbance Spectra (125 to 240 nm)

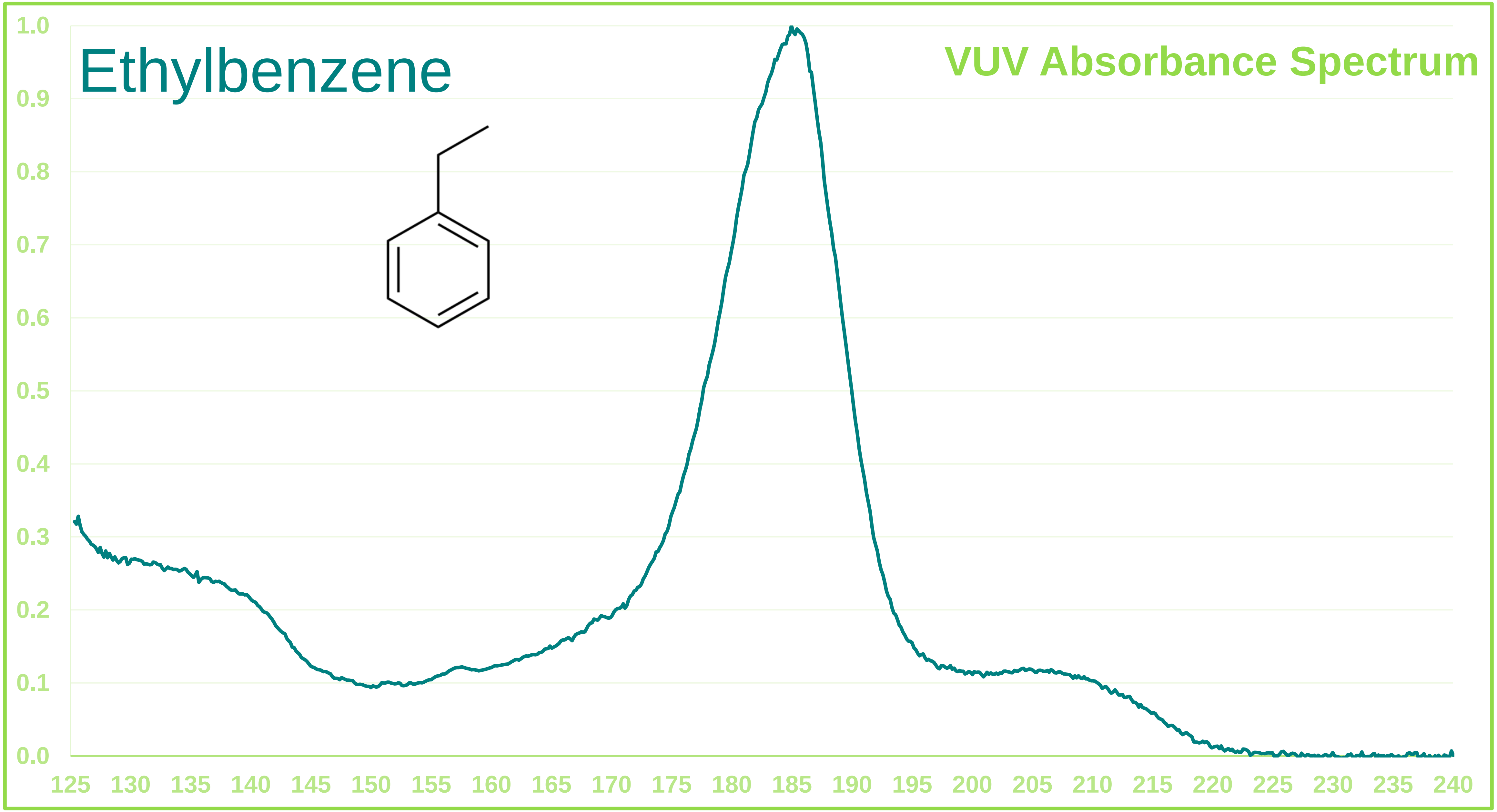


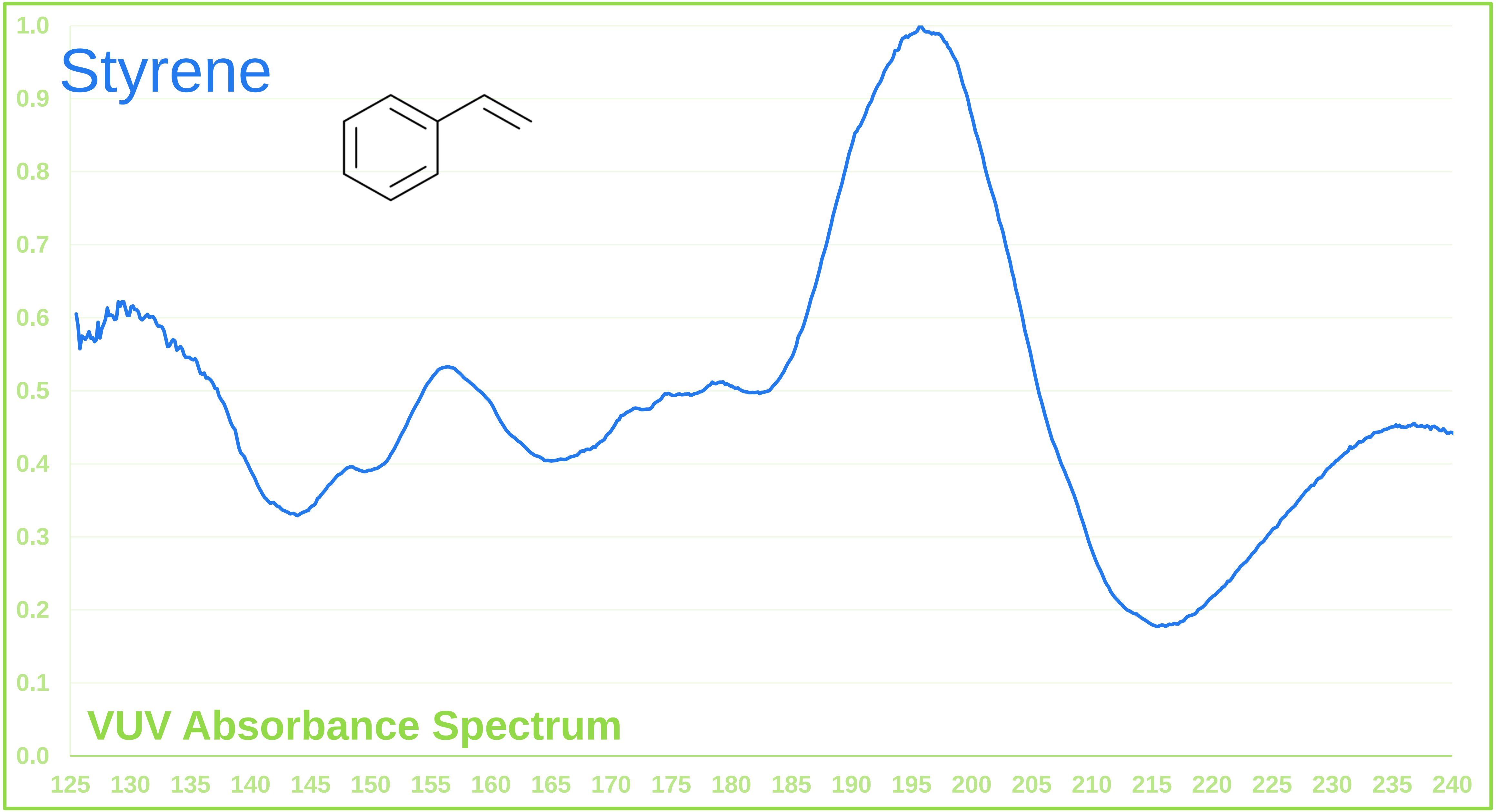

Ethane
VUV Absorbance Spectrum
H H
H—C—C—H
H H
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240

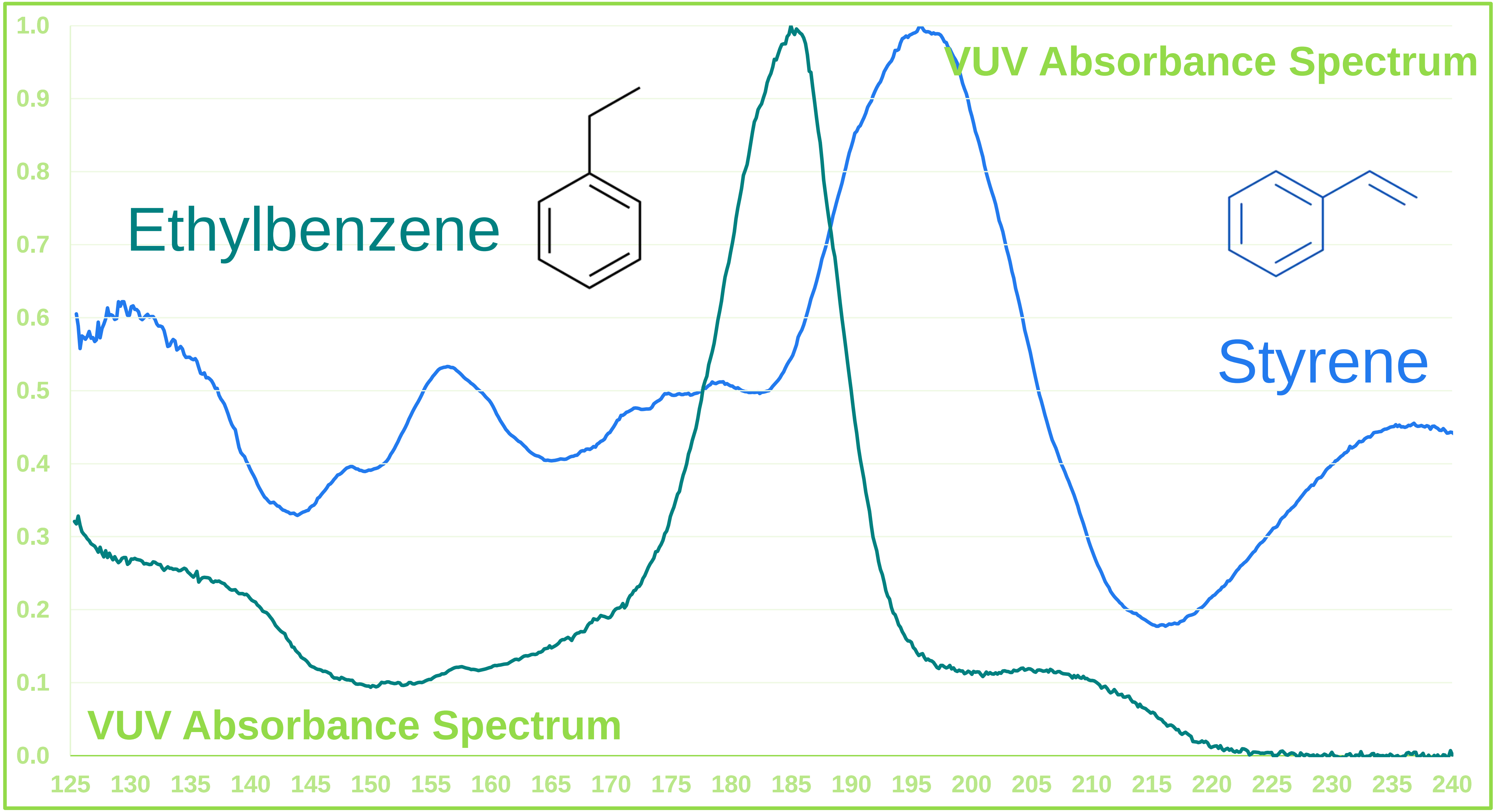

VUV Absorbance Spectrum
Ethene
H
H
C=C
H
H
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240

VUV Absorbance Spectrum

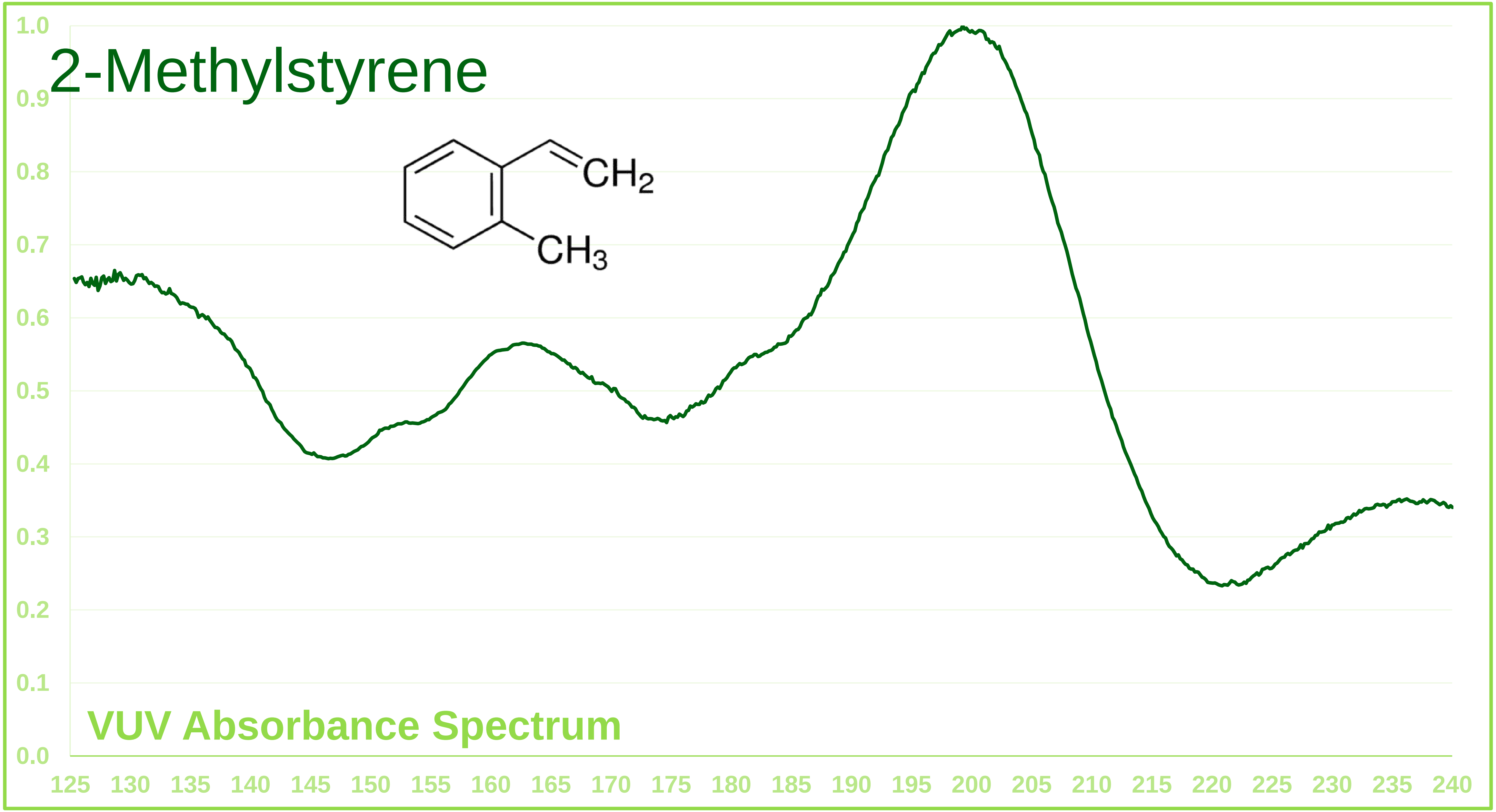


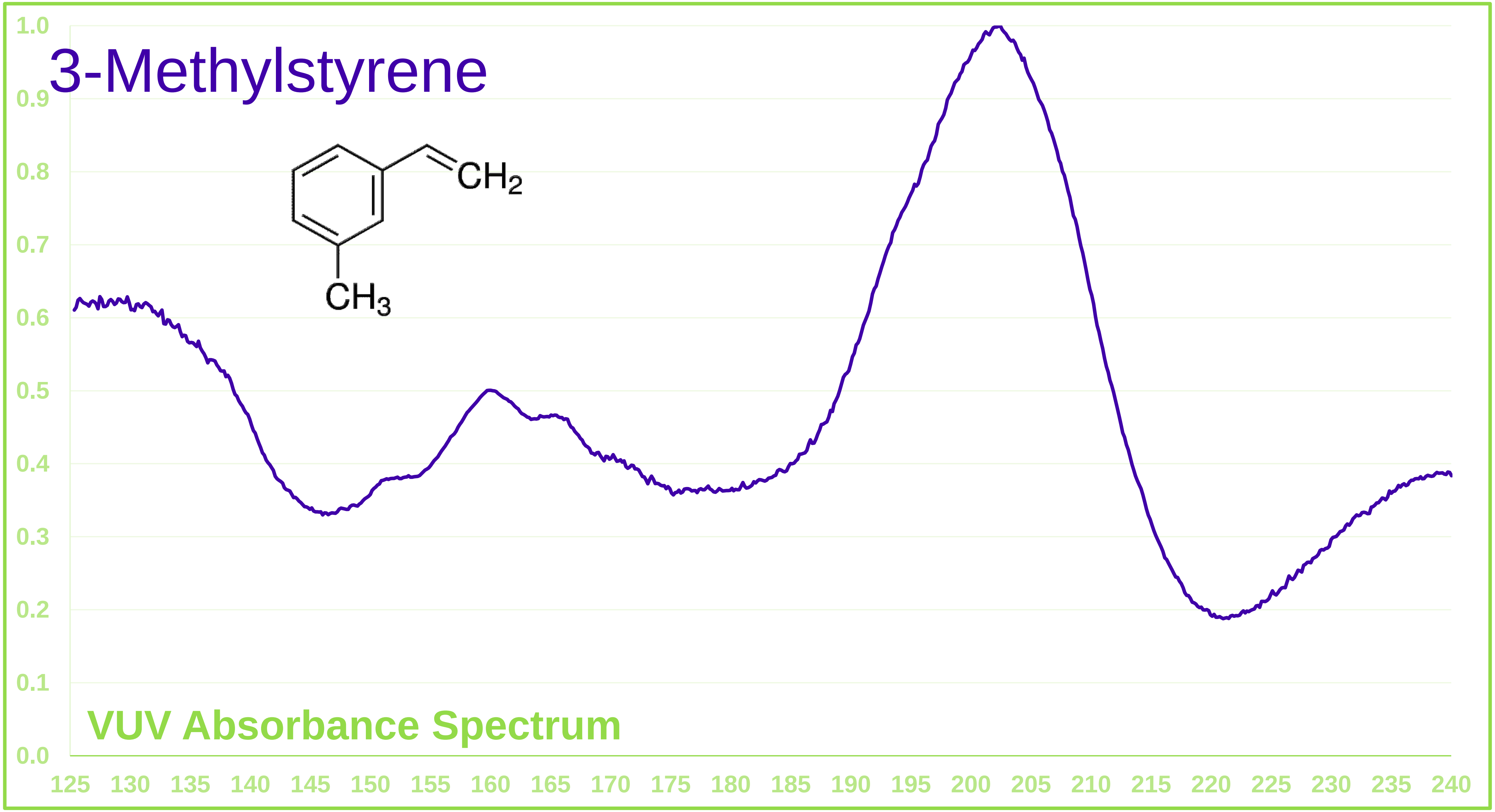

Ethylbenzene
VUV Absorbance Spectrum
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240


Styrene
VUV Absorbance Spectrum
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240

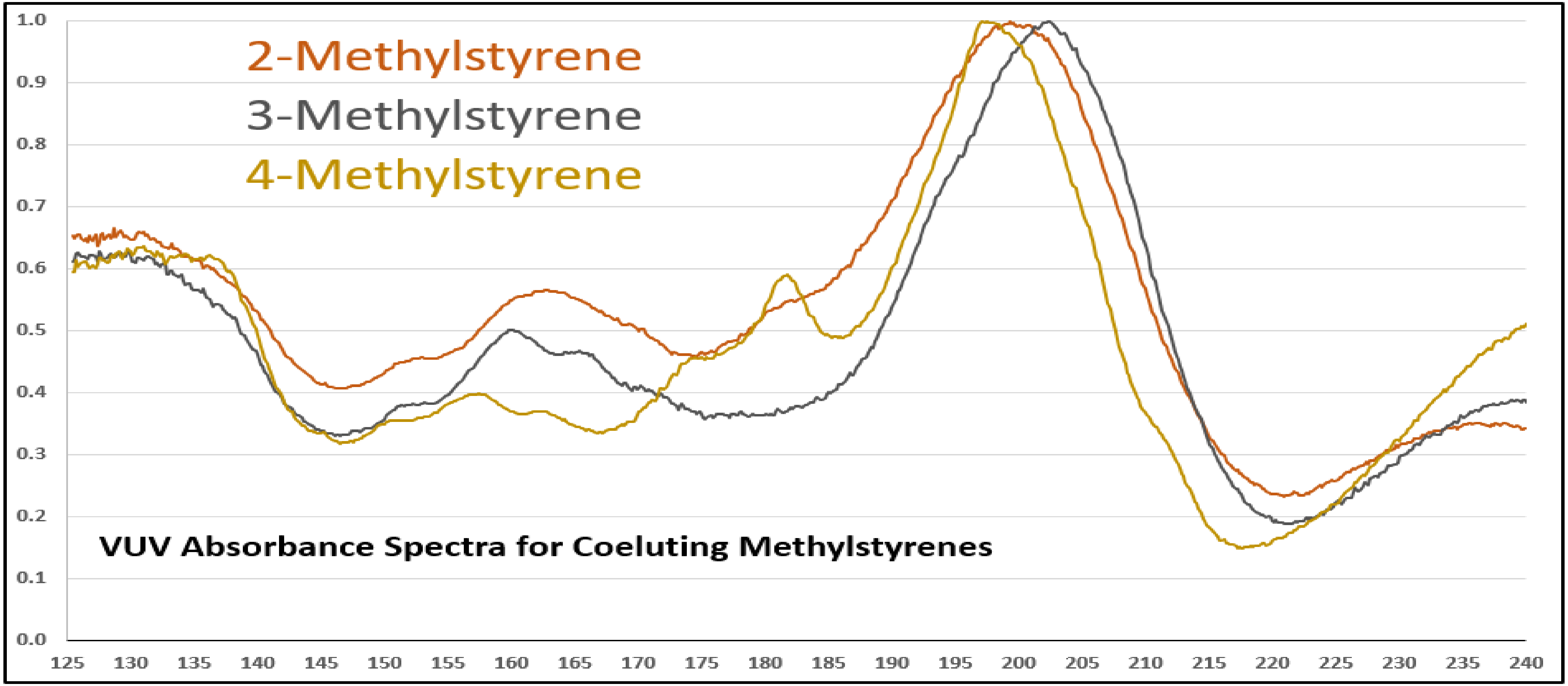


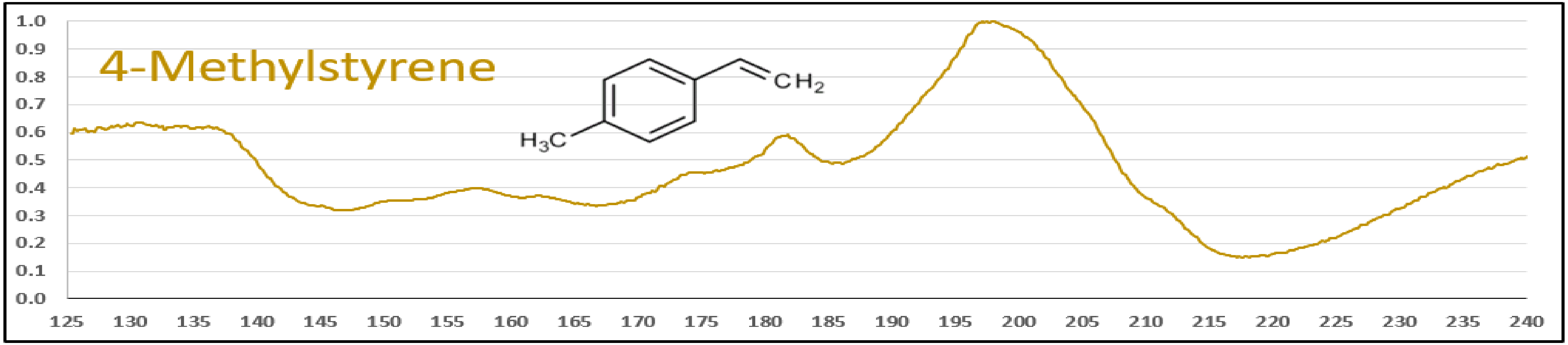
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240
Ethylbenzene
Styrene
VUV Absorbance Spectrum
VUV Absorbance Spectrum

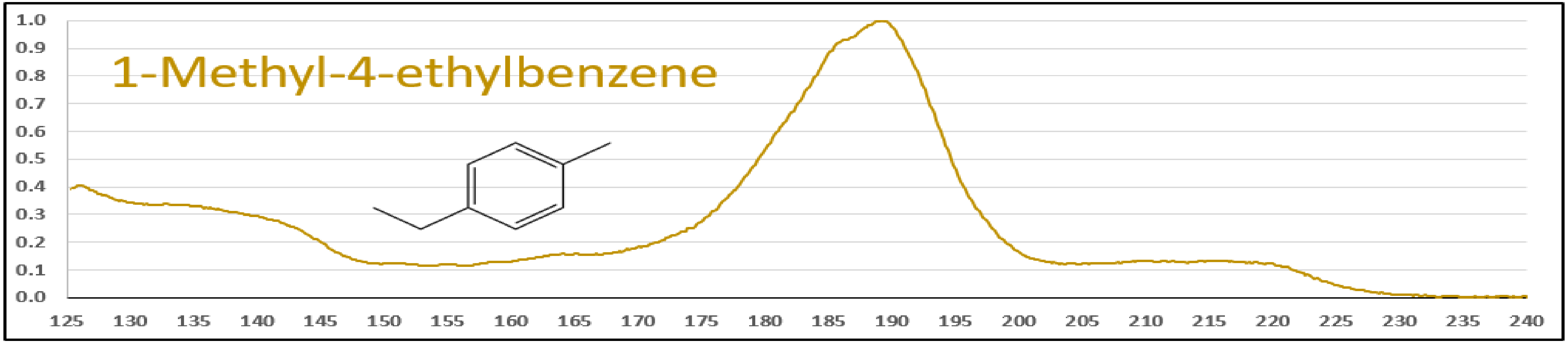

2-Methylstyrene
CH2
CH3
VUV Absorbance Spectrum
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240



3-Methylstyrene
CH2
CH3
VUV Absorbance Spectrum
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240


2-Methylstyrene
3-Methylstyrene
4-Methylstyrene
VUV Absorbance Spectra for Coeluting Methylstyrenes
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240


4-Methylstyrene
CH_2
H_3C
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240


1-Methyl-4-ethylbenzene
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240

ASTM D8071 – IS THAT THE ANSWER?

NOT YET, BUT THERE IS DEFINITELY HOPE

				Olefins	
Sample Point	Cut	Boiling Range	Bromine #	VUV	DHA
Sample # 1	Cut 1	101 - 192	51	23.6143	18.9116
Sample # 1	Cut 2	142 - 233	45	25.3726	19.8069
Sample # 1	Cut 3	151 - 264	41	18.3403	13.8049
Sample # 1	Cut 4	199 - 308	27	8.8164	2.9915
Sample # 1	Cut 5	232 - 377	9	2.7974	1.0596
Sample # 1	Cut 6	341 - 480	2	0.3545	1.301
Sample # 1	Original	108 - 455	28	12.077	
Sample # 1	Recombined	112 - 455	27	9.6774	10.6438

				Olefins	
Sample Point	Cut	Boiling Range	Bromine #	VUV	DHA
Sample # 2	Cut 1	40 - 167	96	43.51	44.7069
Sample # 2	Cut 2	89 - 196	84	42.1557	37.8668
Sample # 2	Cut 3	95 - 249	74	37.8176	26.75414
Sample # 2	Cut 4	145 - 300	54	20.8984	8.23033
Sample # 2	Cut 5	279 - 456	21	5.4642	1.4851
Sample # 2	Full	21 - 449	59.9	29.5737	23.8147

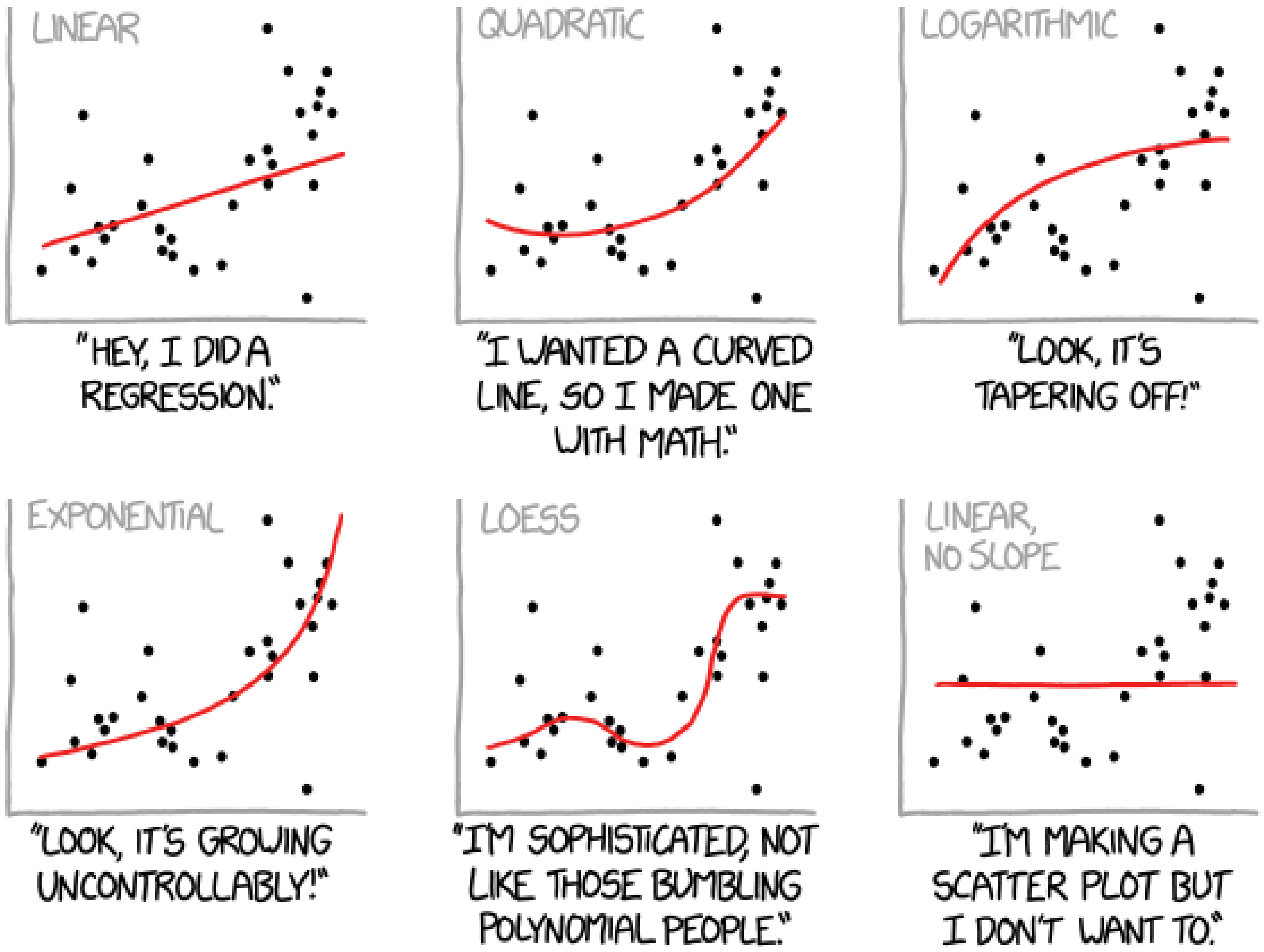
				Olefins	
Sample Point	Cut	Boiling Range	Bromine #	VUV	DHA
Sample # 3	Cut 1	102 - 190	39	20.4989	17.00684
Sample # 3	Cut 2	142 - 233	46	23.5567	18.11526
Sample # 3	Cut 3	162 - 265	39	16.7215	8.14864
Sample # 3	Cut 4	195 - 309	27	8.3037	3.06839
Sample # 3	Cut 5	235 - 375	9	2.1719	1.09797
Sample # 3	Cut 6	341 - 475	2	0.4109	
Sample # 3	Original	124 - 455	25	10.5548	
Sample # 3	Recombined	138 - 452	26	8.1839	30.4887

				Olefins	
Sample Point	Cut	Boiling Range	Bromine #	VUV	DHA
Sample # 4	Cut 1	90 - 191	55	26.0178	24.9848
Sample # 4	Cut 2	113 - 195	49	25.7061	22.7942
Sample # 4	Cut 3	143 - 213	59	31.0208	25.6188
Sample # 4	Cut 4	145 - 237	43	21.3002	14.902
Sample # 4	Cut 5	164 - 255	43	20.5848	13.7579
Sample # 4	Cut 6	196 - 280	39	16.428	7.2791
Sample # 4	Cut 7	206 - 300	34	11.6672	5.5003
Sample # 4	Cut 8	234 - 330	18	5.7524	2.6686
Sample # 4	Cut 9	255 - 360	13	3.0771	1.3232
Sample # 4	Cut 10	334 - 475	6	0.8121	0.6187
Sample # 4	Original	95 - 454	32	14.0856	10.2625
Sample # 4	Recombined	102 - 446	34	15.1862	10.6729

				Olefins	
Sample Point	Cut	Boiling Range	Bromine #	VUV	DHA
Sample # 3	Full	99 - 450	35.9	16.5151	14.0709
Sample # 4	Full	108 - 462	46.5	21.346	15.265
Sample # 4	Full	107 - 461	46.4	23.2229	15.3367
Sample # 5	Full	117 - 462	34.5	16.2702	11.436
Sample # 5	Full	115 - 460	35.4	15.9458	11.6975
Sample # 6	Full	276- 627	50.1	23.6636	17.8109
Sample # 7	Full	21 - 185	80.5	44.1892	39.102
Sample # 8	Full	99 - 450	9.4	0.9277	1.2675

THE ALL IMPORTANT GRAPH

CURVE-METHODS and THE MESSAGE THEY SEND



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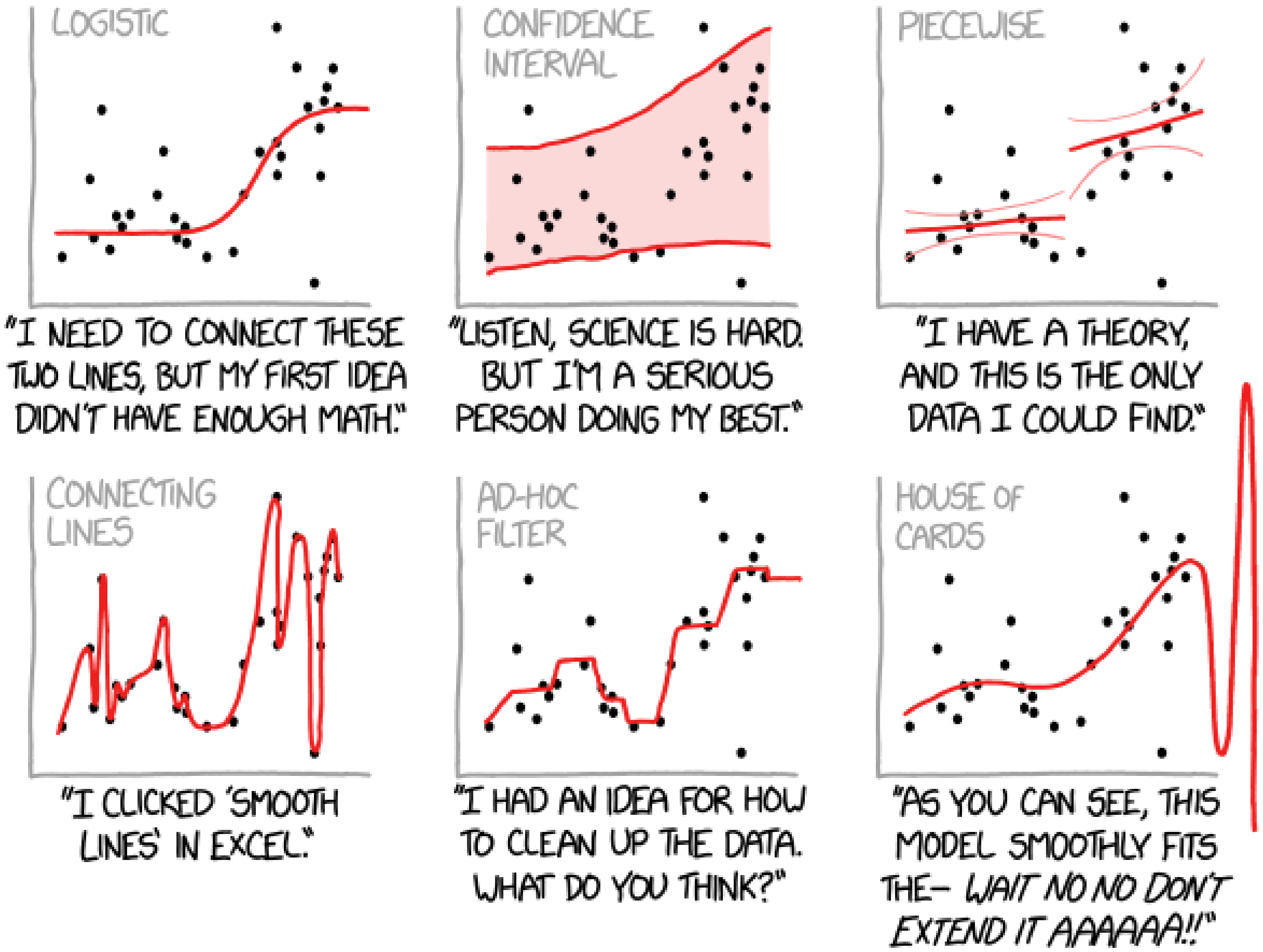
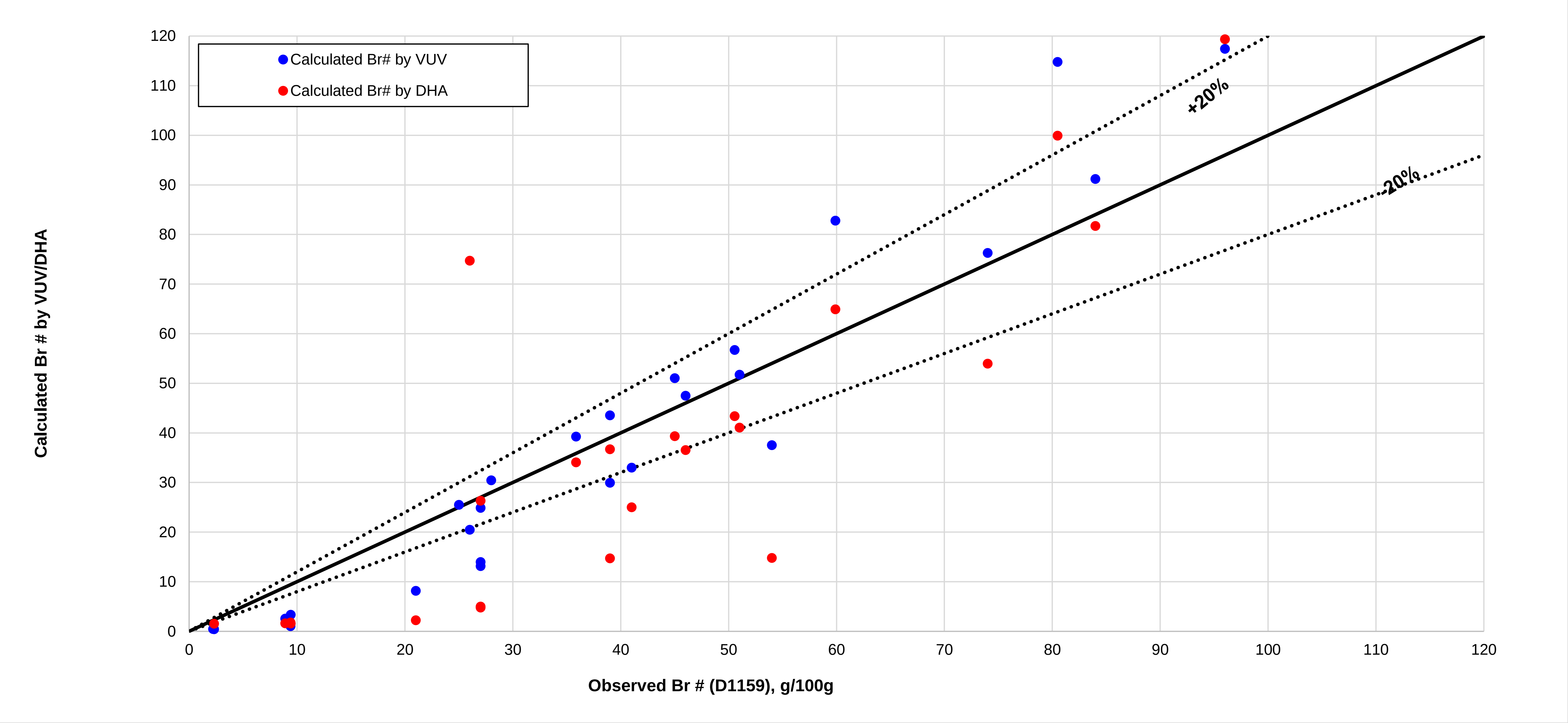
CURVE-METHODS and THE MESSAGE THEY SEND



www.xkcd.com

VUV vs DHA vs Bromine Number



LUMMUS TECHNOLOGY

GC-VUV – WHAT’S NEXT?

BIGGER, BETTER, FASTER

I HOPE SO!

Advantages

- Determine classes vs compounds
- Determine olefinic aromatic
- Determine diolefins
- Determine many others
- Fast method

What I’d like to see

- Even more accurate olefin determination
- Automate the determination of class in addition to compounds
- Calculate bromine number & octane
- Cross-check samples with other laboratories

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