

A Fresh Approach to ASTM D5769 Analysis using a Thermo Scientific ISQ 7610 Single Quadrupole GCMS

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Agenda

- Introduction to ASTM D5769
- Introduction to Thermo Scientific GC, GC-MS systems
- Thermo Scientific XLXR™ detector system
- Instruments and instrument method used in this study
- Analysis requirements of ASTM D5769
- Results and discussions of this study
- Summary and conclusion

What is ASTM D5769

- Method to determine aromatics in gasoline by GC-MS
- Benzene, Toluene and Total Aromatics are reported
- Uses Internal standard calibration (3 IS or 4 IS)

Peculiarities of this method

- % level analysis without dilution
 - High split flows (split ratios between 250:1 to 700:1)
 - Low injection volumes (0.1-0.5 µL)
 - “detune” the MS in order to avoid detector saturation



Designation: D5769 – 20

Standard Test Method for Determination of Benzene, Toluene, and Total Aromatics in Finished Gasolines by Gas Chromatography/Mass Spectrometry¹

This standard is issued under the fixed designation D5769; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method covers the determination of benzene, toluene, other specified individual aromatic compounds, and total aromatics in finished motor gasoline, including gasolines containing oxygenated blending components, by gas chromatography/mass spectrometry (GC/MS).

1.2 This test method has been tested for the following concentration ranges, in liquid volume percent, for the following aromatics: benzene, 0.1 % to 4 %; toluene, 1 % to 13 %; and total (C6 to C12) aromatics, 10 % to 42 %. The round-robin study did not test the method for *individual* hydrocarbon process streams in a refinery, such as reformates, fluid catalytic cracked naphthas, and so forth, used in the blending of gasolines.

1.3 Results are reported to the nearest 0.01 % for benzene and 0.1 % for the other aromatics by liquid volume.

1.4 This test method includes a relative bias section for EPA spark-ignition engine fuel benzene regulations reporting based on Practice D6708 accuracy assessment between Test Method D5769 and Test Method D3606 as a possible Test Method D5769 alternative to Test Method D3606. The Practice D6708 derived correlation equation is only applicable for blended fuels in the benzene concentration range from 0.0 % to 2.50 % by volume as measured by Test Method D5769. The applicable Test Method D3606 range for benzene is from 0.0 % to 2.47 % by volume as reported by Test Method D3606.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appro-*

priate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to its use.

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 ASTM Standards:²

- D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method
- D3606 Test Method for Determination of Benzene and Toluene in Spark Ignition Fuels by Gas Chromatography
- D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter
- D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
- D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards
- D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

- 3.1.1 *aromatic, n*—any hydrocarbon compound containing a benzene or naphthalene ring.
- 3.1.2 *calibrated aromatic component, n*—the individual aromatic components that have a specific calibration.
- 3.1.3 *cool on-column injector, n*—in gas chromatography, a

Thermo Scientific TRACE 1600 Series GC and ISQ 7610 MS

Efficient use of the resources

Spare backup Thermo Scientific™ iConnect™ modules instead of full GC systems

Interchangeable modules on existing TRACE GC systems (1300 and 1600 series)

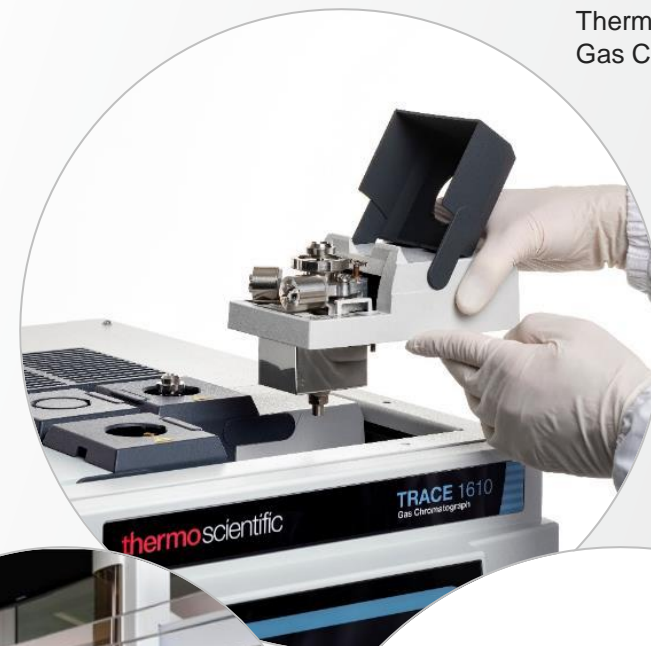
Injector and detector modules can be purchased on-line (*SSL, PTV, FID, TCD*)

Compact design (44 cm width) for a better use of the bench space

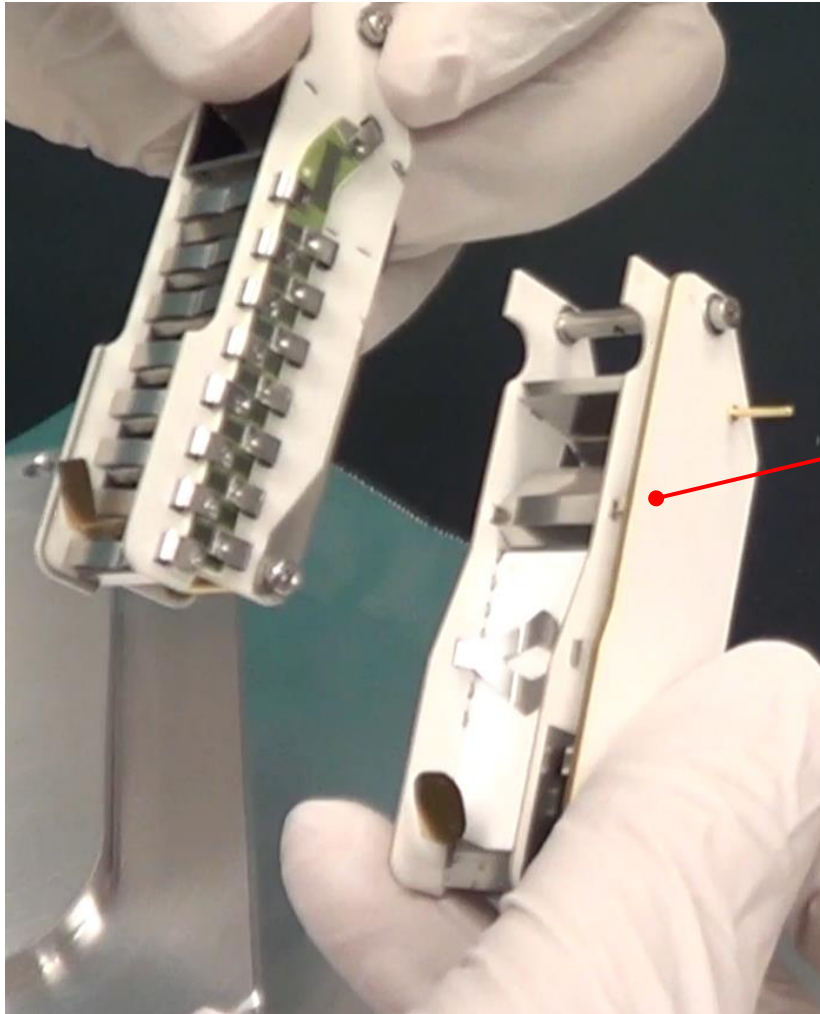
Patented carrier gas saving during operations

Ability to remove the source and change column without venting the MS

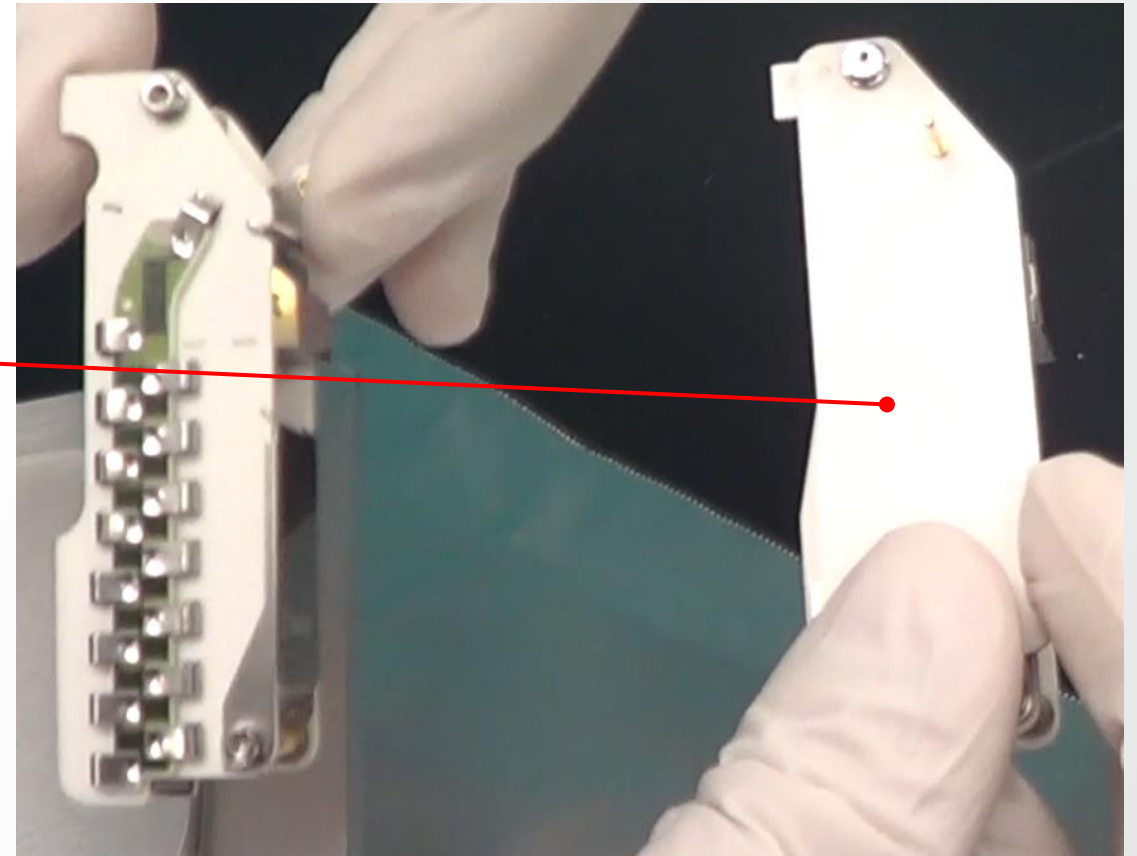
Thermo Scientific™ TRACE™ 1610
Gas Chromatograph (GC)



Next Generation Detector (XLXR™ detector system)



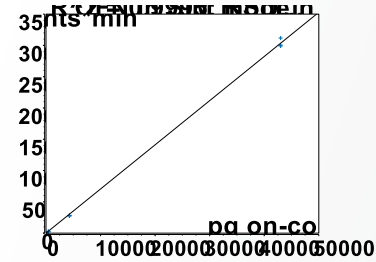
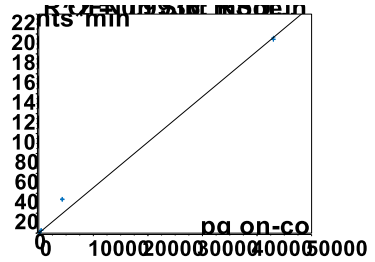
XLXR
detector



New Detector system includes new EM and change in the electrometer design

Longer lifetime due to new EM and larger dynamic range (2-3 times) because of both EM and electrometer

OFN – 4.3fg to 43ng on-column



Old (EM + electrometer)

New (EM + electrometer)

7 orders of magnitude

Instruments used for this study

- AI/AS 1610 Autosampler
- TRACE 1610 GC,
- ISQ 7610 MS, **ExtractaBrite source with default ion volume**
- Software- Chromeleon 7.3.1



Instrument method used

Autosampler Conditions

Inject Options | **Sampler Wash Program**

Sampling Parameters

- Draw speed: Slow
- Fill strokes: 3 [0...15]
- Air volume: 0.00 [0.00...1.50 µl]
- Sample depth: Bottom

Injection Parameters

- Cold needle injection
- GC type: TRACE_1300_1310
- Pre injection delay time: 0.0 [0.0...63.0 s]
- Post injection delay time: 3.0 [0.0...63.0 s]

Pre Injection Washing Parameters

- Pre injection washing cycles: 2 [0...15]
- Pre injection washing vial(s): A

Sample Washing Parameters

- Sample wash cycles: 1 [0...15]

Post Injection Washing Parameters

- Post injection washing cycles: 3 [0...15]
- Post injection washing vial(s): A

Syringe used- 0.5 µL syringe (P/N- 36504045)

Injection Volume- 0.2 µL

Wash solvent used- Isooctane

GC Column used- RTX-1 20 m, 0.18 mm ID, 0.4 µm

Inlet Liner used- Straight liner with GW (453A2265)

Inlet Conditions

FrontInlet Options | **FrontInlet Flow/Pressure Options**

- Use this inlet

Temperature Settings

- Enable temperature control
- Temperature: 300 [0...400 °C]

Inlet Parameters

- Operating mode: Split
- Split flow control
- Split flow: 250.0 [5.0...1250.0 ml/min]
- Split ratio: 500
- Splitless time: [0.00...999.99 min]
- Purge flow control
- Purge flow: 5.000 [0.500...50.000 ml/min]
- Constant septum purge
- Stop purge for: [0.00...999.99 min]
- Surge pressure: [5.00...1000.00 kPa]
- Surge duration: [0.00...999.99 min]
- Vacuum compensation
- Enable gas saver mode
- Gas Saver Flow: 10.0 [5.0...500.0 ml/min]
- Gas saver time: 2.00 [0.00...999.99 min]

Mode: Constant flow at: 0.500 [0.001...100.000 ml/min]

Instrument method used

GC Oven Settings

GC Oven Settings

Prep Run Timeout: 10.00 [0.00...999.99 min] Set default values

Oven equilibration time: 0.10 [0.00...999.99 min]

Ready delay: 0.10 [0.00...99.99 min]

Send parameters only (don't run the GC)

Mode: Ramped temperature

No	Retention time [min]	Rate [°C/min]	Target value [°C]	Hold time [min]
1	0.000	Run		
2	1.000	0.00	35.0	1.00
3	9.000	25.00	210.0	1.00
4		New Row		
5	9.000	StopRun		

MS settings

ISQ-Mass Detector

Use this detector

MS transfer line temperature: 280 °C

Ion source temperature: 300 °C

Acquisition threshold: 1,000

Method type: General Mode Copy Timed Scans

Run completion: GC run time Stop after: 9.00 min

Scans					Groups				
	Time (min)	Scan Name	Mass list or range (amu)	Dwell or Scan Times (sec)	Tune File Name	Time (min)	Total Scan Time (sec)	Emission current:	Detector gain
▶	2.00	FULL	45-300	0.1	(Last Saved)	2.00	0.1041	10	1.00E+005
*									

Emission current is 10 μ A

Detector gain is 1e5

Analysis requirements

- Sensitivity test criteria-
 - Solution of 0.01% of 1,4-Diethylbenzene should give signal to noise ratio of at least 5 for m/z 134
- Resolution test criteria-
 - Resolution (R) between 3% of 1,3,5-trimethylbenzene and 1-Methyl-2-ethylbenzene must be equal to or greater than 2.
- Ion check test criteria-
 - Solution of 3% of 1,2,3-Trimethylbenzene will have a fragmentation pattern that meets the below criteria-

Ion, m/z	Relative intensity, %
120	30-60
105	100
91	7-15

- Calibration criteria-
 - r^2 value for the calibration fit should be greater than 0.99
 - A quadratic fit can be used if the deviation of the response factors between the highest standard and the lowest standard is less than 10%
- Quality control reference material check-
 - The values obtained for the quality control standard should be within $\pm 5\%$ of the actual value for all aromatics (except 1,2,4,5-Tetramethylbenzene and naphthalene where it should be within $\pm 10\%$)

Standards and sample used

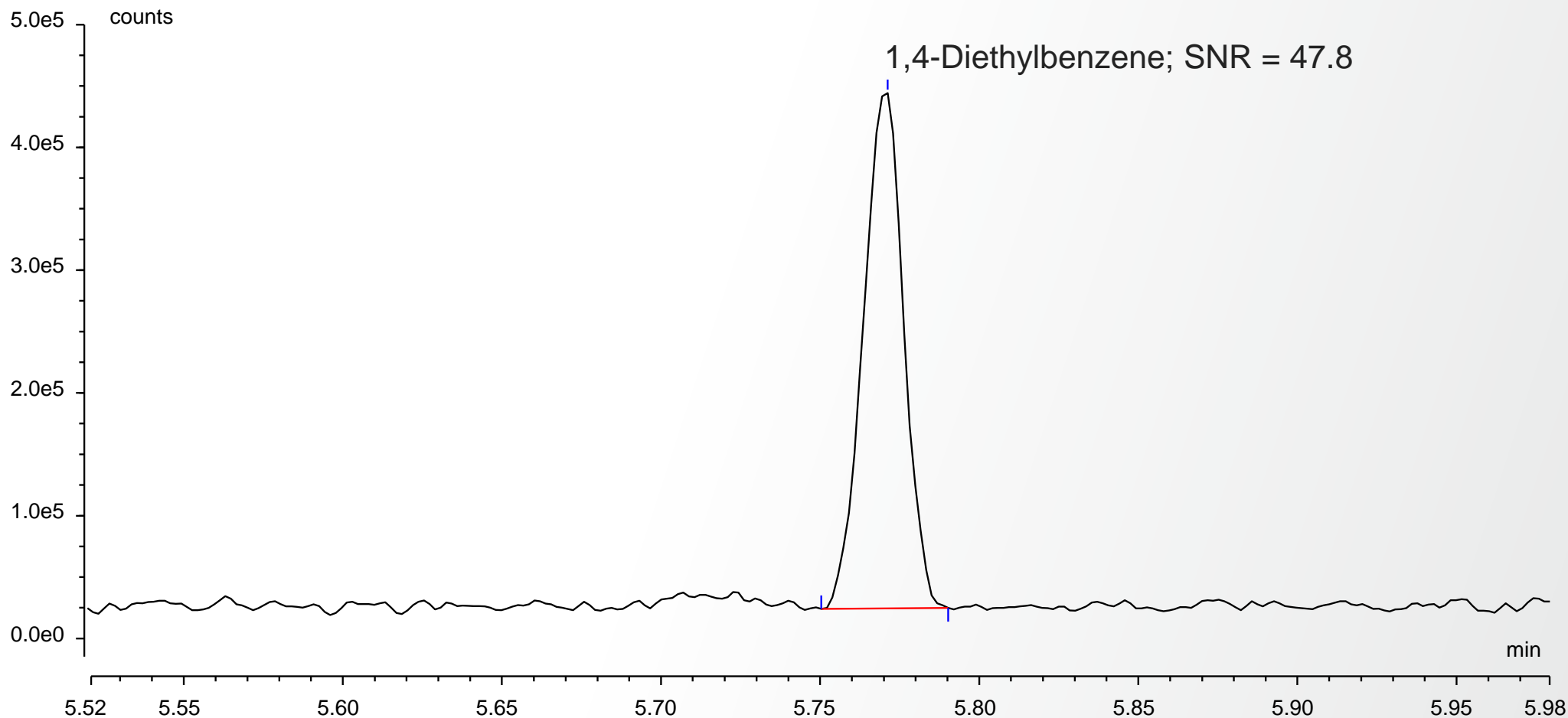
- Accustandard catalog # D-5769-ADD-IS-R (6 Level ASTM/EPA Gasoline Refinery Standards)
- Accustandard catalog # M-GRA-Res (Resolution standard)
- Accustandard catalog # M-GRA-FP (Fragmentation pattern standard)
- Accustandard catalog # M-GRA-ST (Sensitivity criteria standard)
- Accustandard catalog # M-5769-QC-IS-5ML (Daily quality control standard)
- Accustandard catalog # M-GRA-IS-R (Deuterated Internal standard mix)
- Gasoline proficiency sample RFG-2101

Compound list

Compound	CAS No.	Formula	Mol.Wt.	Quant Ion	Confirming Ion 1	Confirming Ion 2	Associated ISTD
Benzene-d6 (ISTD)	1076-43-3	C ₆ D ₆	84.08	84.0, 83.0	82	56	-
Benzene	71-43-2	C ₆ H ₆	78.05	78	77	79	Benzene-d6 (ISTD)
Toluene-d8 (ISTD)	2037-26-5	C ₇ D ₈	100.11	100.0, 99.0	98	70	-
Toluene	108-88-3	C ₇ H ₈	92.06	92	91	89	Toluene-d8 (ISTD)
Ethylbenzene-d10 (ISTD)	25837-05-2	C ₈ D ₁₀	116.14	116.0, 115.0	98	70	-
Ethylbenzene	100-41-4	C ₈ H ₁₀	106.08	106	91	105	Ethylbenzene-d10 (ISTD)
m-Xylene	108-38-3	C ₈ H ₁₀	106.08	106	91	105	Ethylbenzene-d10 (ISTD)
p-Xylene	106-42-3	C ₈ H ₁₀	106.08	106	91	105	Ethylbenzene-d10 (ISTD)
o-Xylene	95-47-6	C ₈ H ₁₀	106.08	106	91	105	Ethylbenzene-d10 (ISTD)
Isopropylbenzene	98-82-8	C ₉ H ₁₂	120.09	120	105	77	Ethylbenzene-d10 (ISTD)
n-Propylbenzene	103-65-1	C ₉ H ₁₂	120.09	120	91	92	Ethylbenzene-d10 (ISTD)
3-Ethyltoluene	620-14-4	C ₉ H ₁₂	120.09	120	105	91	Ethylbenzene-d10 (ISTD)
4-Ethyltoluene	622-96-8	C ₉ H ₁₂	120.09	120	105	91	Ethylbenzene-d10 (ISTD)
1,3,5-Trimethylbenzene	108-67-8	C ₉ H ₁₂	120.09	120	105	119	Ethylbenzene-d10 (ISTD)
2-Ethyltoluene	611-14-3	C ₉ H ₁₂	120.09	120	105	91	Ethylbenzene-d10 (ISTD)
1,2,4-Trimethylbenzene	95-63-6	C ₉ H ₁₂	120.09	120	105	119	Ethylbenzene-d10 (ISTD)
1,2,3-Trimethylbenzene	526-73-8	C ₉ H ₁₂	120.09	120	105	119	Ethylbenzene-d10 (ISTD)
Indan	496-11-7	C ₉ H ₁₀	118.08	117	118	115	Naphthalene-d8 (ISTD)
1,4-Diethylbenzene	105-05-5	C ₁₀ H ₁₄	134.11	134	105	91	Naphthalene-d8 (ISTD)
n-Butylbenzene	104-51-8	C ₁₀ H ₁₄	134.11	134	105	91	Naphthalene-d8 (ISTD)
1,2-Diethylbenzene	135-01-3	C ₁₀ H ₁₄	134.11	134	105	91	Naphthalene-d8 (ISTD)
1,2,4,5-Tetramethylbenzene	95-93-2	C ₁₀ H ₁₄	134.11	134	120	91	Naphthalene-d8 (ISTD)
1,2,3,5-Tetramethylbenzene	527-53-7	C ₁₀ H ₁₄	134.11	134	120	91	Naphthalene-d8 (ISTD)
Naphthalene-d8 (ISTD)	1146-65-2	C ₁₀ D ₈	136.11	136.0, 135.0	137	108	-
Naphthalene	91-20-3	C ₁₀ H ₈	128.06	128	127	102	Naphthalene-d8 (ISTD)
Naphthalene, 2-methyl-	91-57-6	C ₁₁ H ₁₀	142.08	142	141	115	Naphthalene-d8 (ISTD)
Naphthalene, 1-methyl-	90-12-0	C ₁₁ H ₁₀	142.08	142	141	115	Naphthalene-d8 (ISTD)

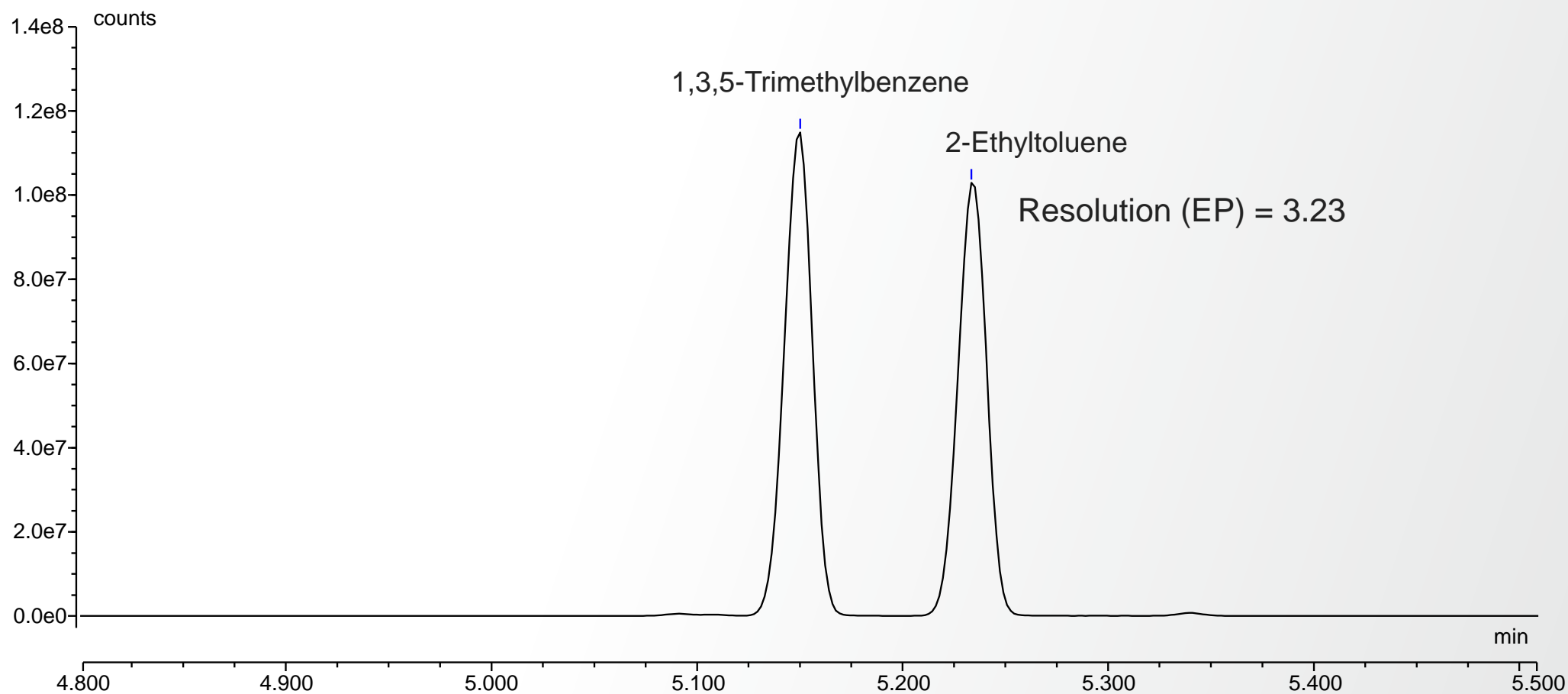
Sensitivity criteria check-

0.01% of 1,4-Diethylbenzene should give signal to noise ratio of at least 5 for m/z 134



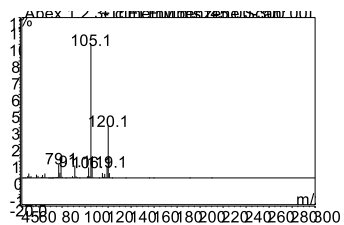
Resolution criteria check-

Resolution (R) between 3% of 1,3,5-trimethylbenzene and 1-Methyl-2-ethylbenzene must be equal to or greater than 2.



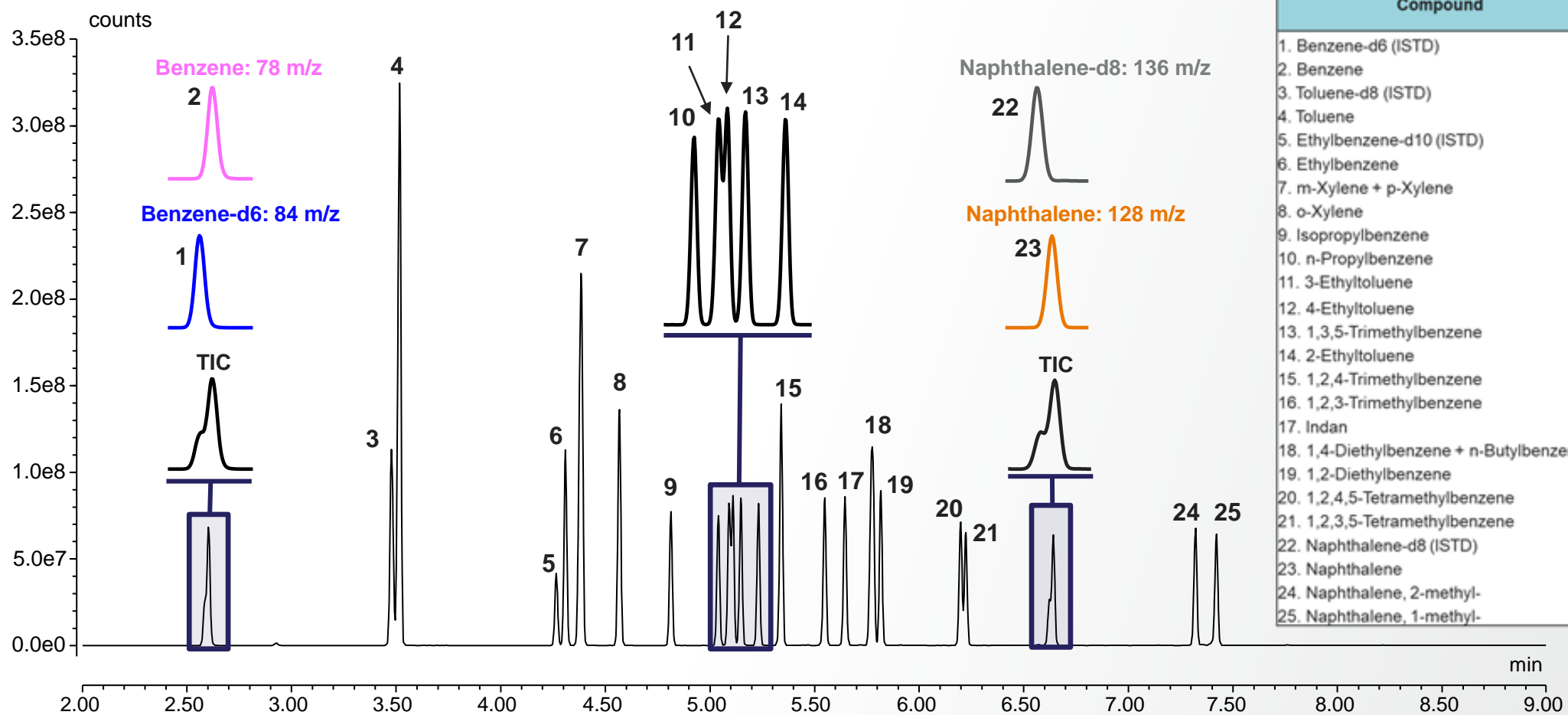
Ion check criteria

Solution of 3% of 1,2,3-Trimethylbenzene will have a fragmentation pattern that meets the required criteria-



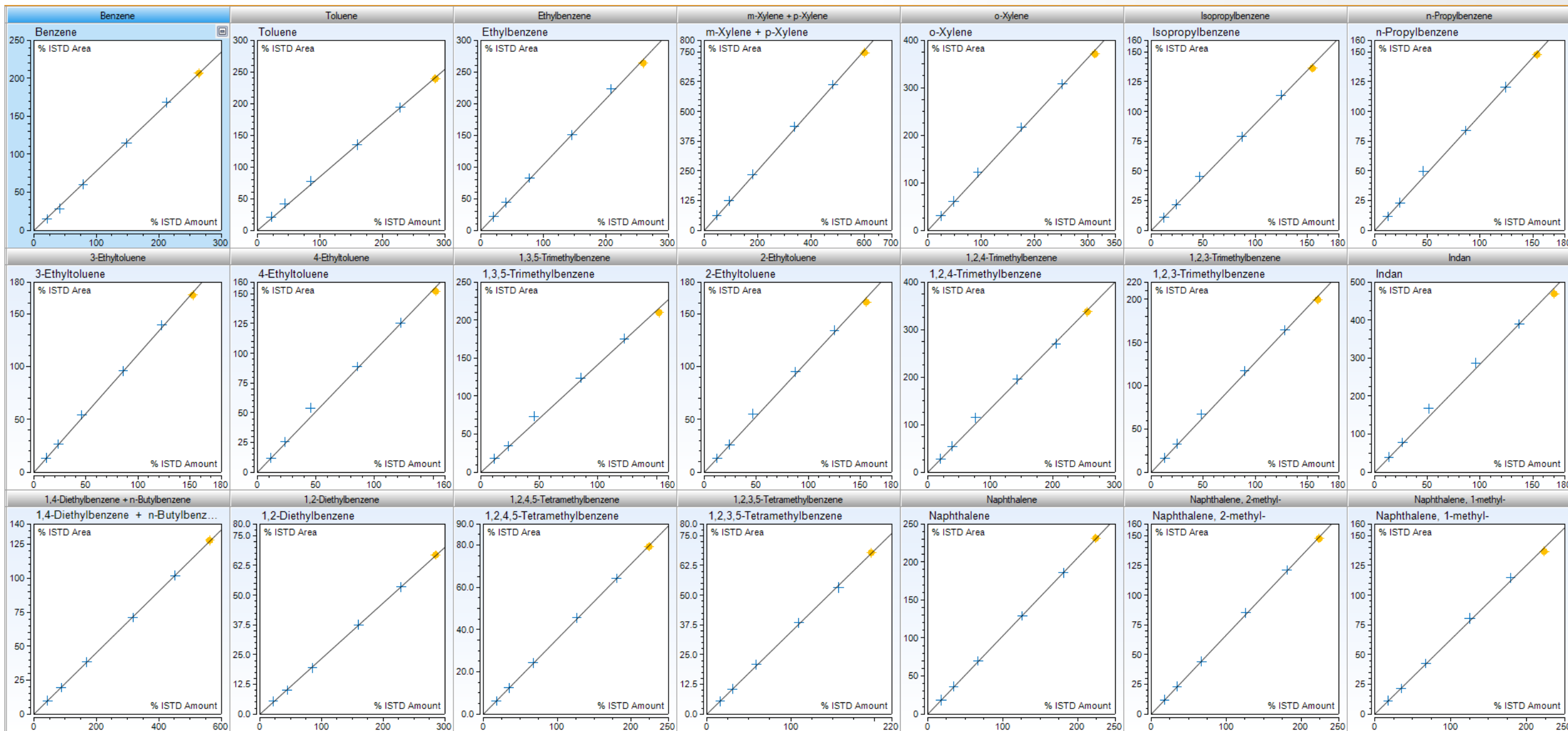
Ion, m/z	Relative intensity criteria, %	Actual Relative Intensity, %	Result
120	30-60	39	Pass
105	100	100	Pass
91	7-15	9	Pass

Chromatogram of a calibration solution



Compound	Retention time (min)
1. Benzene-d6 (ISTD)	2.58
2. Benzene	2.60
3. Toluene-d8 (ISTD)	3.48
4. Toluene	3.52
5. Ethylbenzene-d10 (ISTD)	4.27
6. Ethylbenzene	4.31
7. m-Xylene + p-Xylene	4.38
8. o-Xylene	4.57
9. Isopropylbenzene	4.81
10. n-Propylbenzene	5.04
11. 3-Ethyltoluene	5.09
12. 4-Ethyltoluene	5.11
13. 1,3,5-Trimethylbenzene	5.15
14. 2-Ethyltoluene	5.23
15. 1,2,4-Trimethylbenzene	5.34
16. 1,2,3-Trimethylbenzene	5.55
17. Indan	5.65
18. 1,4-Diethylbenzene + n-Butylbenzene	5.77
19. 1,2-Diethylbenzene	5.82
20. 1,2,4,5-Tetramethylbenzene	6.20
21. 1,2,3,5-Tetramethylbenzene	6.22
22. Naphthalene-d8 (ISTD)	6.62
23. Naphthalene	6.64
24. Naphthalene, 2-methyl-	7.32
25. Naphthalene, 1-methyl-	7.42

Calibration Curves

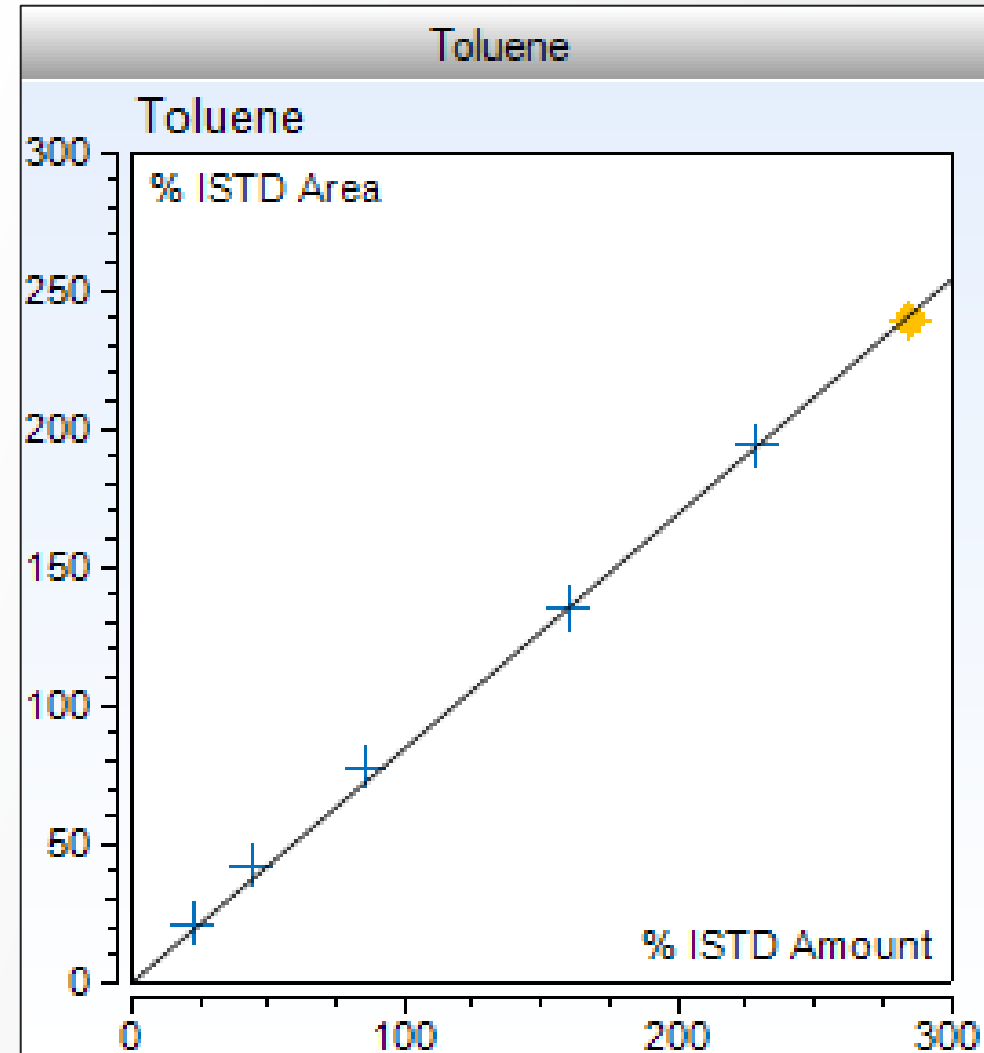
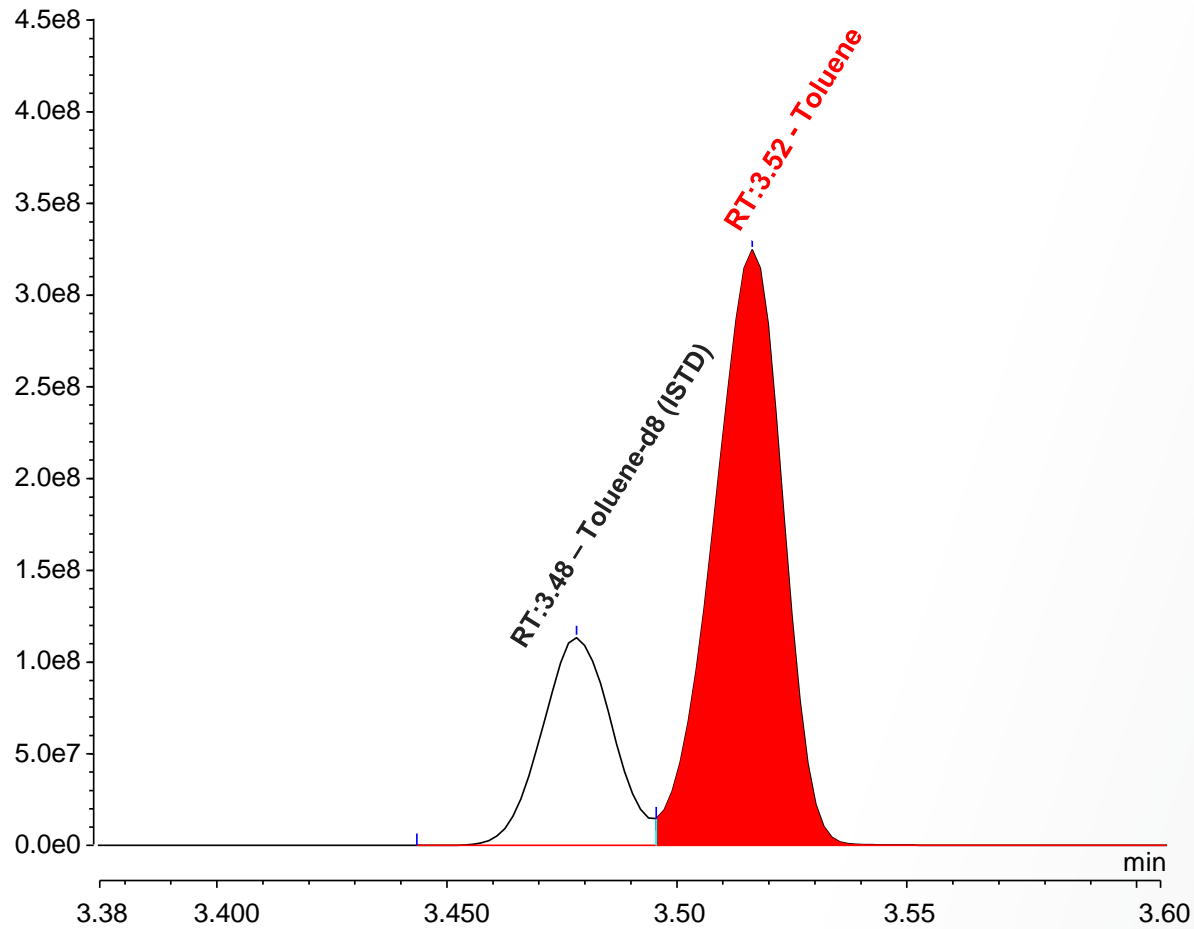


Calibration results table

r^2 value for the calibration fit should be greater than 0.99

Compound	Retention time, min	Calibration type	Number of points	%RSD	correlation coefficient, r^2
Benzene	2.6	Lin	6	2.20	0.99921
Toluene	3.52	Lin	6	2.85	0.99849
Ethylbenzene	4.31	Lin	6	3.09	0.99831
m-Xylene + p-Xylene	4.39	Lin	6	2.32	0.99902
o-Xylene	4.57	Lin	6	3.07	0.99829
Isopropylbenzene	4.81	Lin	6	3.09	0.99829
n-Propylbenzene	5.04	Lin	6	3.26	0.99808
3-Ethyltoluene	5.09	Lin	6	2.50	0.99889
4-Ethyltoluene	5.11	Lin	6	4.94	0.99542
1,3,5-Trimethylbenzene	5.15	Lin	6	4.79	0.9957
2-Ethyltoluene	5.23	Lin	6	4.08	0.99693
1,2,4-Trimethylbenzene	5.34	Lin	6	3.99	0.99705
1,2,3-Trimethylbenzene	5.55	Lin	6	3.52	0.99772
Indan	5.65	Lin	6	5.84	0.99344
1,4-Diethylbenzene + n-Butylbenzene	5.77	Lin	6	0.65	0.99993
1,2-Diethylbenzene	5.82	Lin	6	0.98	0.99984
1,2,4,5-Tetramethylbenzene	6.2	Lin	6	1.036	0.99981
1,2,3,5-Tetramethylbenzene	6.22	Lin	6	1.72	0.99948
Naphthalene	6.64	Lin	6	0.50	0.99996
Naphthalene, 2-methyl-	7.32	Lin	6	1.31	0.9997
Naphthalene, 1-methyl-	7.42	Lin	6	2.85	0.99856
			Max	5.84	0.99996
			Min	0.50	0.99344

Cal6 Toluene peak at 17.7%



How can one figure out if the detector is saturating?

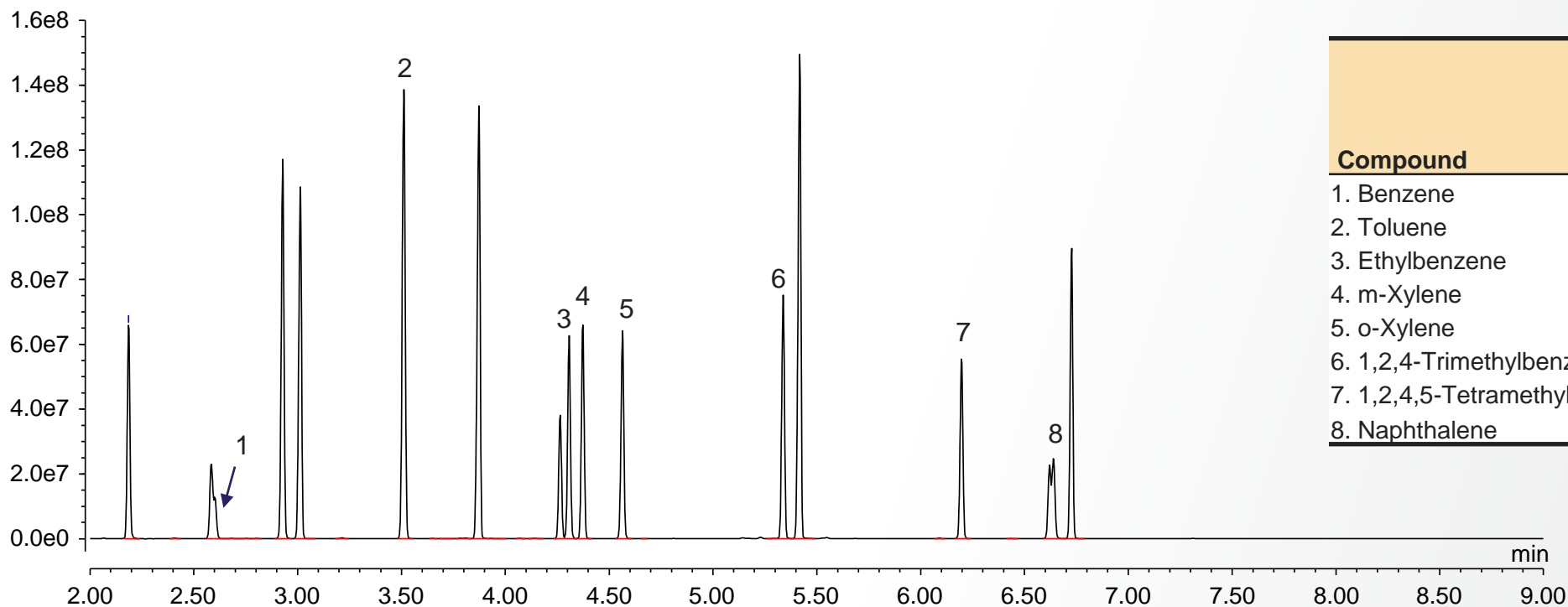
There is a variable for that!

Chromeleon variable for saturation flag is- `ms.spectrum("By Interactive").saturated`

	A	B	C
1	Peak Name	Ret. Time	Saturated
2		min	
4	Benzene	6.79	FALSE
5	Benzene-d6 (ISTD)	6.85	FALSE
6	Pentane, 2,2,4-trimethyl- (IsoOcta	7.88	FALSE
7	Toluene-d8 (ISTD)	10.07	FALSE
8	Toluene	10.24	TRUE
9	Ethylbenzene-d10 (ISTD)	14.06	FALSE
10	Ethylbenzene	14.31	FALSE
11	m-Xylene	14.71	FALSE
12	p-Xylene	14.77	FALSE
13	o-Xylene	15.85	FALSE
14	Isopropylbenzene	17.43	FALSE
15	n-Propylbenzene	18.94	FALSE
16	3-Ethyltoluene	19.29	FALSE
17	4-Ethyltoluene	19.42	FALSE
18	1,3,5-Trimethylbenzene	19.69	FALSE
19	2-Ethyltoluene	20.24	FALSE
20	1,2,4-Trimethylbenzene	20.96	FALSE
21	n-Decane	21.62	FALSE
22	1,2,3-Trimethylbenzene	22.07	FALSE
23	Indan	22.65	FALSE
24	1,4-Diethylbenzene	23.19	FALSE
25	n-Butylbenzene	23.35	FALSE
26	1,2-Diethylbenzene	23.56	FALSE

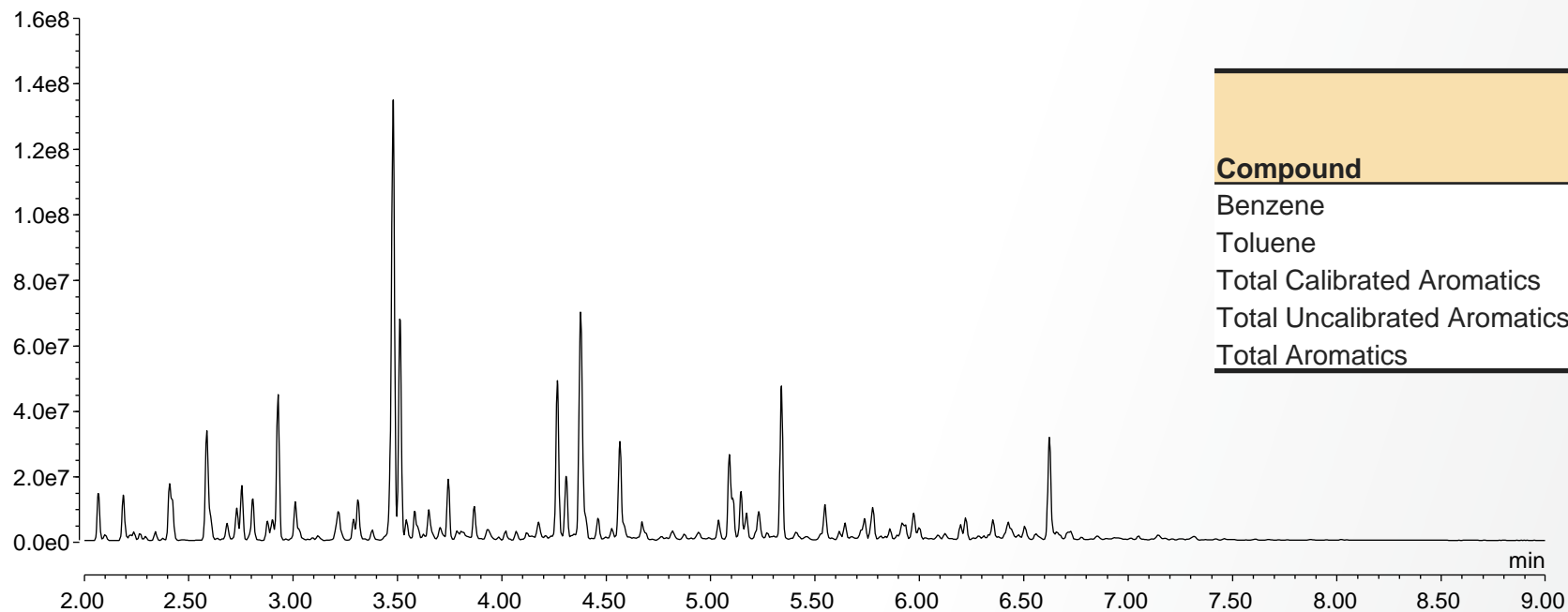
Quality Control Reference material

The values obtained for the quality control standard should be within $\pm 5\%$ of the actual value for all aromatics (except 1,2,4,5-Tetramethylbenzene and naphthalene where it should be within $\pm 10\%$)



Compound	Relative difference (%) between certified and obtained value
1. Benzene	4.70%
2. Toluene	3.50%
3. Ethylbenzene	3.96%
4. m-Xylene	3.46%
5. o-Xylene	4.28%
6. 1,2,4-Trimethylbenzene	1.65%
7. 1,2,4,5-Tetramethylbenzene	0.02%
8. Naphthalene	1.52%

Interlaboratory study (ILS) sample RFG 2101



Compound	Concentration obtained (Vol %)	Z-Score
Benzene	0.48	0.01
Toluene	3.1	0.12
Total Calibrated Aromatics	13.7	n/a
Total Uncalibrated Aromatics	2.6	n/a
Total Aromatics	16.3	0.91

Obtained value is within 1 standard deviation of the mean value

Summary and Conclusion

- Separation of targeted aromatics achieved in under 8 minutes while meeting resolution (R_s) requirements between 1,3,5-trimethylbenzene and 2-ethyltoluene ($R_s > 2$).
- Linear response observed at %vol concentrations without of detector saturation due to the new XLXR™ detector system.
- Sensitivity obtained by the ISQ 7610 GC-MS system was a factor of 9 times greater than criteria outlined by ASTM Method D5769.
- Ion ratios for 1,2,3-trimethylbenzene passed the method criteria ranges for relative intensity.
- Accurate quantitation was achieved with both a quality control reference standard and interlaboratory gasoline sample, with deviation from reference values well within accepted criteria.



Analysis of aromatics in gasoline by ASTM D5769 using gas chromatography–single quadrupole mass spectrometry

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Keywords

Benzene, toluene, total aromatics,
GC-MS, full scan

Goal

The goal of this application note is to demonstrate the capability of the Thermo Scientific[®] ISQ[™] 7610 single quadrupole GC-MS to deliver accurate quantitation of aromatics in gasoline in accordance with ASTM Method D5769.

Introduction

Monocyclic aromatics, unsaturated hydrocarbons containing a benzene ring, are inherent components of gasoline refined from crude oil. Refineries manipulate the content of aromatics in gasoline to increase the octane rating and overall performance. However, there is considerable concern over the current allowable content of aromatics in gasoline, with growing evidence of their detrimental effects on human and environmental health. The content of benzene, a known carcinogen, in gasoline is restricted to 1.0%^{1,2} with total content of aromatics not to exceed 42%.³ Thus, gasoline producers must be able to accurately assess fuel purity to ensure compliance with regulatory standards.

The ASTM Method D5769 is a standardized method for the determination of aromatics in gasoline by gas chromatography-mass spectrometry (GC-MS).³ A major challenge of performing this analysis is the high content (fvol) of individual aromatics present, which can cause instrument detector saturation. This can result in a non-linear response in the concentration range of gasoline samples, yielding inaccurate quantitation.

thermo scientific

Application Note



Extended linear dynamic range with the XLXR detector system on the Thermo Scientific ISQ 7610 single quadrupole GC-MS

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Keywords

Detector linear dynamic range,
spectral fidelity, method consolidation

Introduction

Analytical laboratories that are analyzing food, environmental, pharma, petrochemical, or clinical samples utilize GC-MS or GC-MS/MS for both targeted and known unknowns analysis and employ commercially available libraries such as NIST or Wiley. These laboratories often face challenges when analyzing compounds at both high and low concentrations in a single run. When analytes of interest are present in widely varying concentrations, it can be difficult to accurately quantify the compounds due to the limits of the dynamic range of the mass spectrometer detector system. This leads to the analysis being split into class- or compound-specific methods, which impedes the sample throughput in a laboratory. Even single methods are subject to issues when a very high concentration sample is analyzed on the system, as it cannot be quantified accurately and a repeat analysis must be performed with a diluted sample to bring the concentration of the analyte within the calibration range. This adds further time to the sample analysis and can delay important results getting to clients.

The issues with limited detector dynamic range are not isolated to quantification. When performing sample screening, for example in drugs of abuse analysis, if a compound saturates the detection system due to high concentration, the mass spectral fidelity is affected. This poor spectral quality can lead to poor library matches and potential misidentification of the compound of interest or even a false negative. If the saturation of the detector is identified, the samples can be diluted and re-run; however, this adds to sample processing time and can potentially cause low-level contaminants to be diluted below detection limits and not reported.

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Technical Note

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