Improvement of ASTM D-5769 by GCMS High Concentration Tuning and Automated Data Processing

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Introduction

Method ASTM D-5769 is a standard GCMS method to determine aromatics in finished motor gasoline or ethanol blends. However, the intrinsic high sensitivity of mass spectrometry usually gives rise to a limited linear range that makes it difficult to meet method requirements. GCMS-QP2010 Ultra, a new single transmission quadruple GCMS, allows for tuning the instrument in a "high concentration" mode that is suitable for ASTM D-5769 type of analysis without making any hardware compromises. In addition, newly improved Shimadzu aromatics report software is now capable of conducting automated data acquisition, processing and reporting. These new features have greatly enhanced method robustness and efficiency, providing a total solution of running ASTM D-5769.

ASTM D5769 Compounds of Interest

• Benzene:	0.1 – 4 %
• Toluene:	1 – 13 %
• C6-C12 Aromatics:	10 – 42 %

Method Challenges

- Good linearity is difficult to obtain
  - MS detector saturates easily at high concentrations due to limited fragmentation
  - Quadratic calibration is implemented for these high concentration compounds
- Automation is hard to realize
  - Data acquisition
  - Processing
  - Reporting

GCMS-QP2010 Ultra New Features

Enhanced Performance

- Maximum scan speed of 20,000 u/sec (100Hz)
- ASSP function for greater sensitivity in fast scan
- Ultra-fast data acquisition speed for comprehensive 2 dimensional gas chromatography
- Increased sensitivity

Increased Productivity

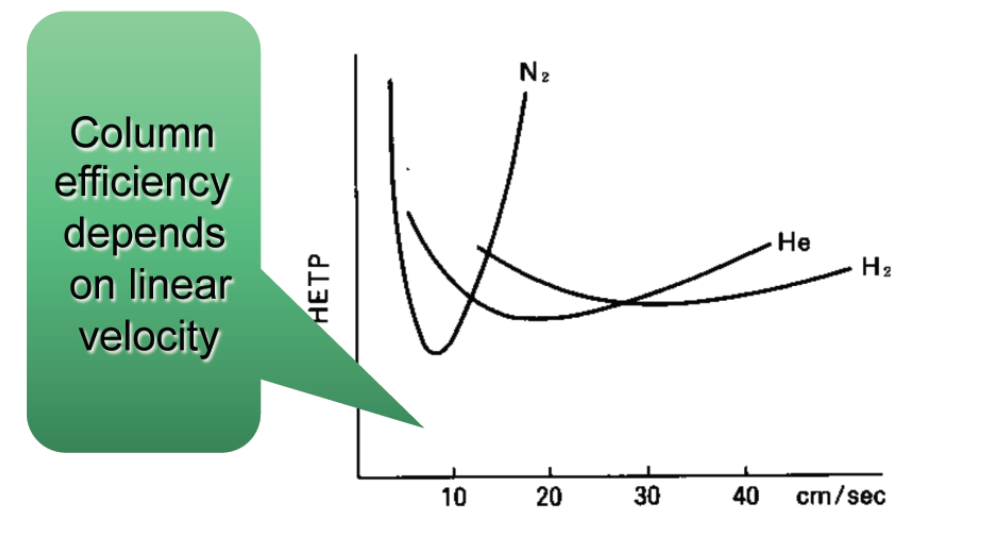
- Analysis cycle shortened significantly
- Maintenance downtime reduced

Eco-friendly

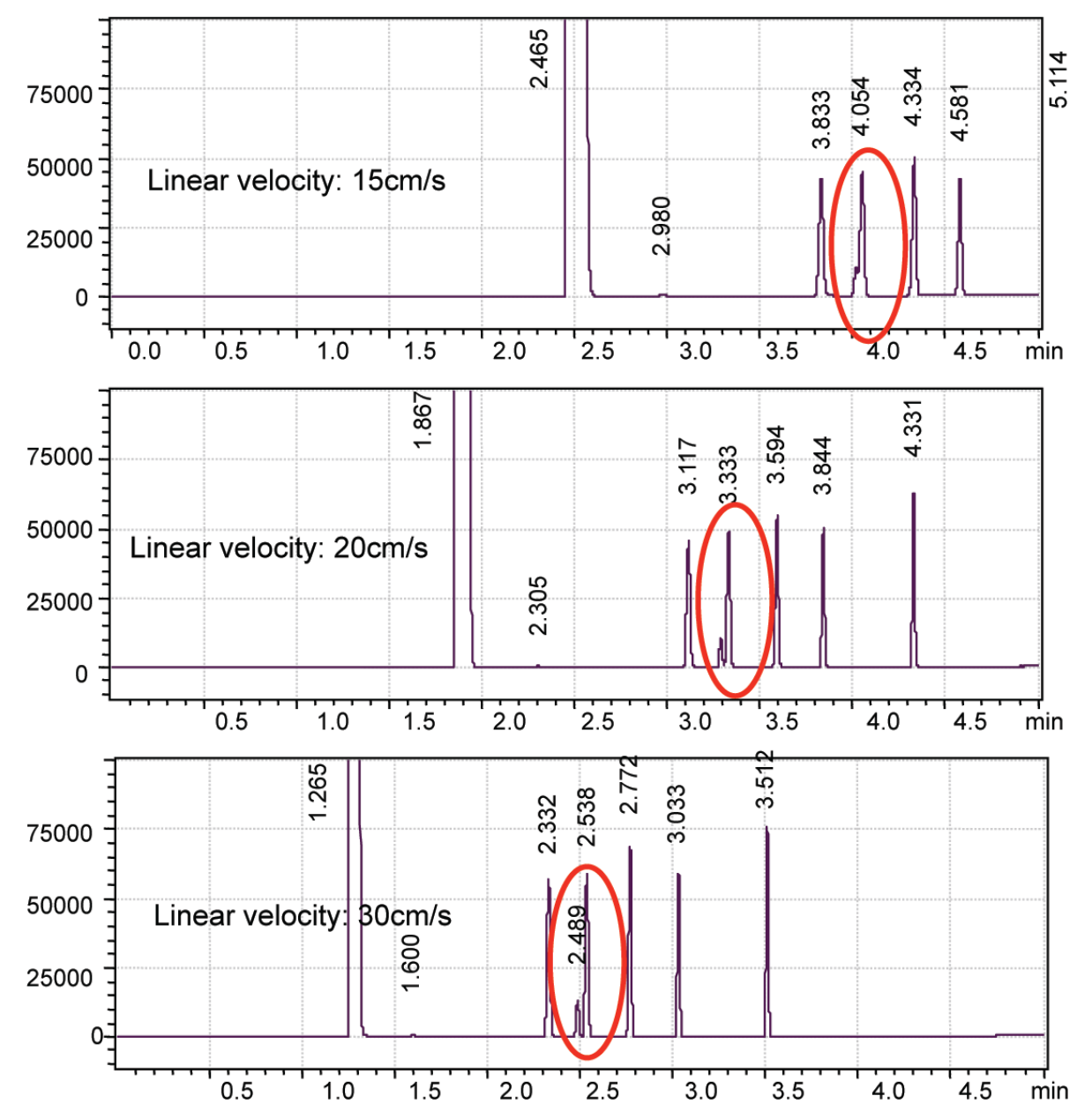
- 36% reduction of power consumption in analysis standby mode
- 30% reduction of CO_2 factory emission

Constant Linear Velocity

Optimum separation in one mouse click
Transfer methods between GC's easily even if the column id's are different with constant linear velocity



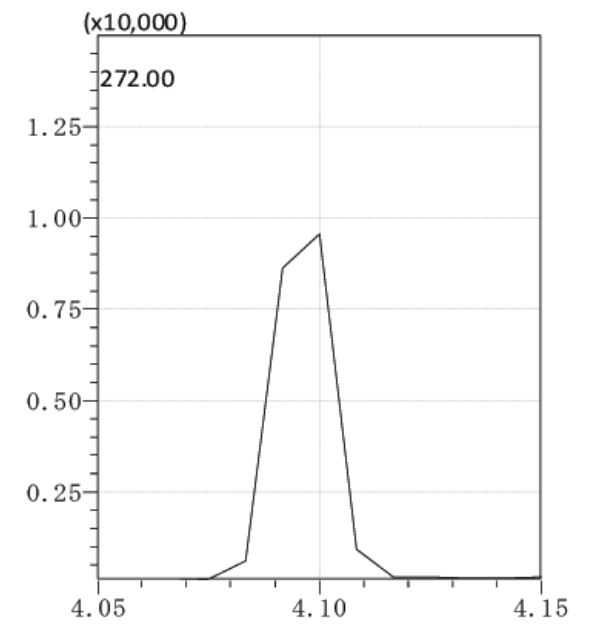
Carrier gas linear velocity



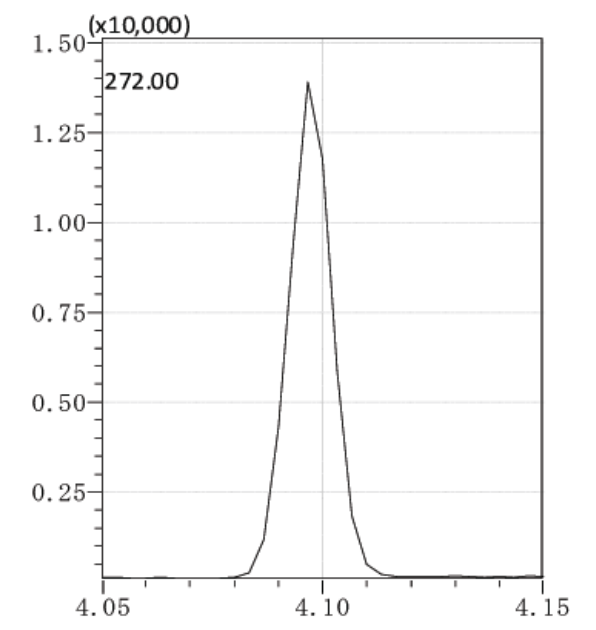
Very Fast Scan / Data Acquisition

Why is fast cycle time necessary?

Sufficient data sampling points per peak is important to acquire chromatographic data accurately, especially for quantitation.

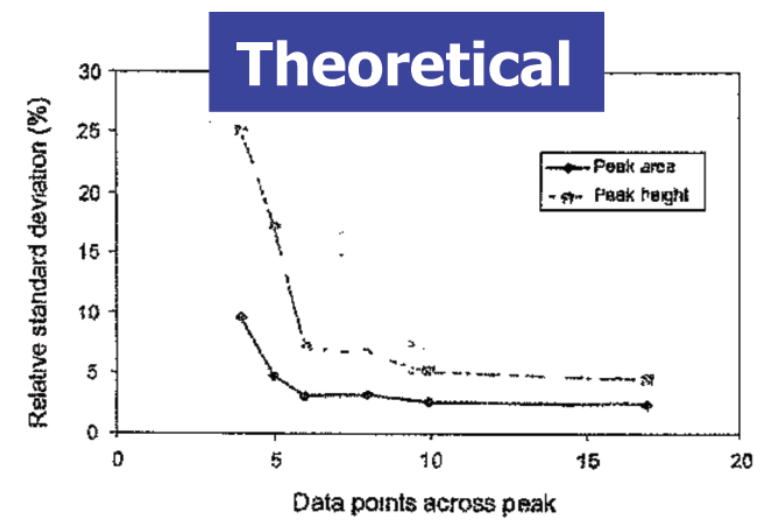


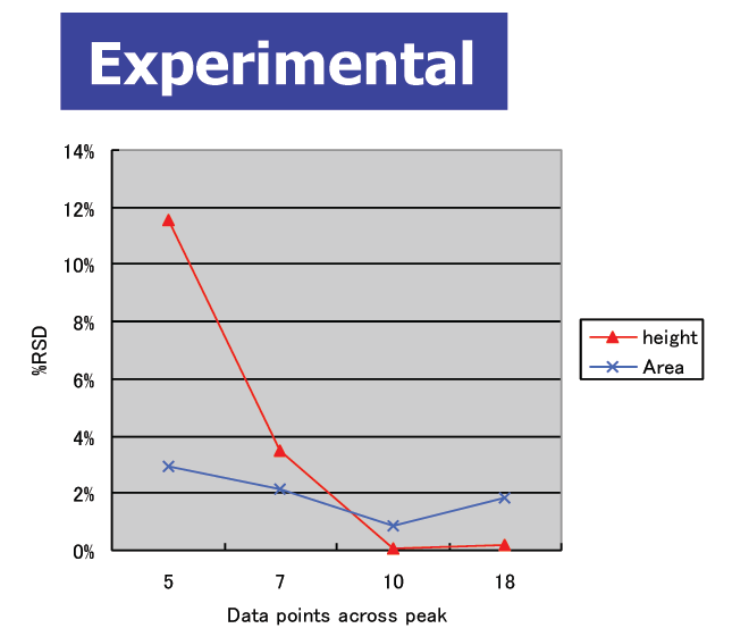
4-5 points



10-12 points

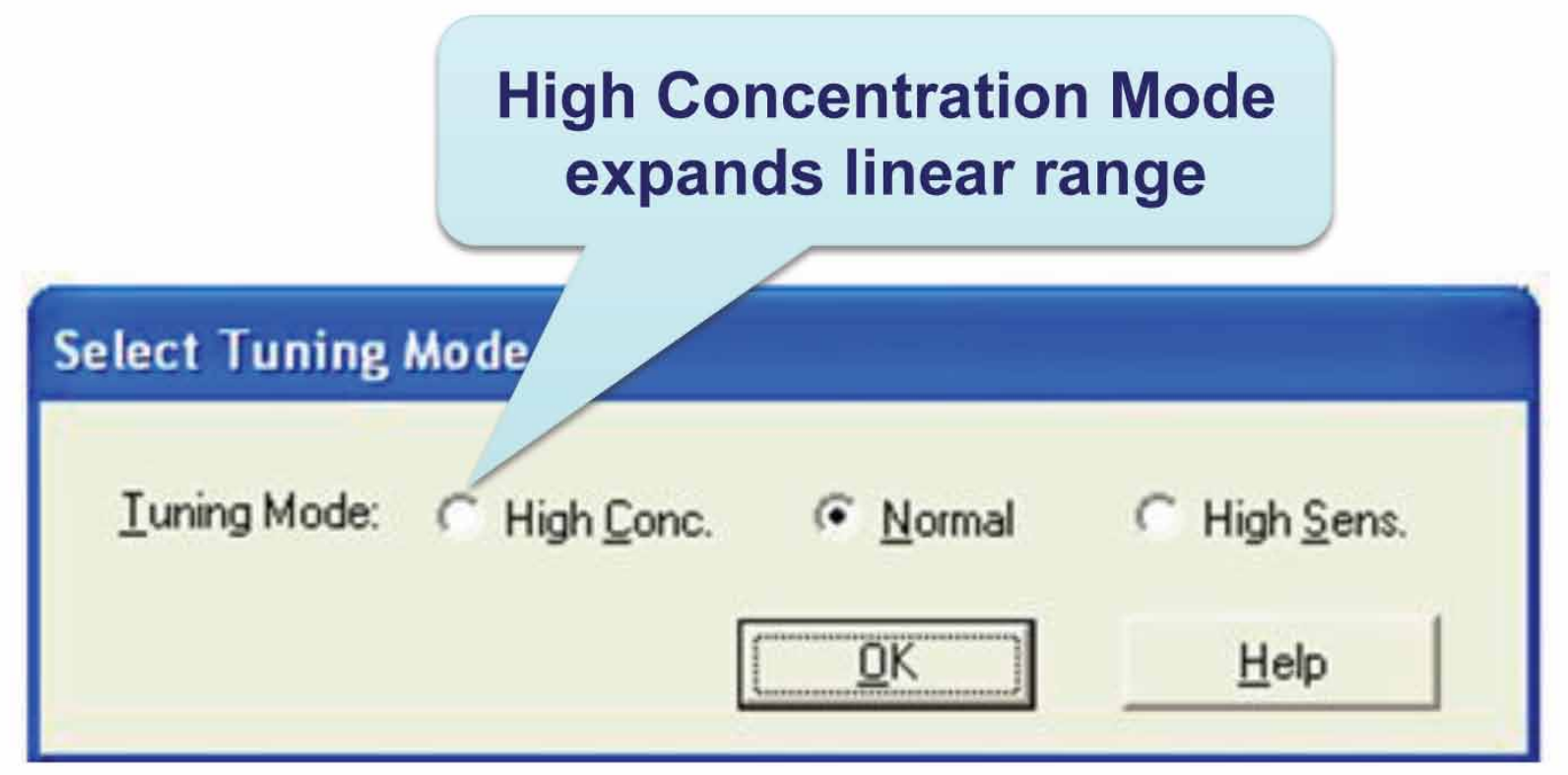
Precision / accuracy is poor with only 4-5 scans across a GC peak.





Flexible Tuning Modes

Three tuning modes to select from



Select Tuning Mode

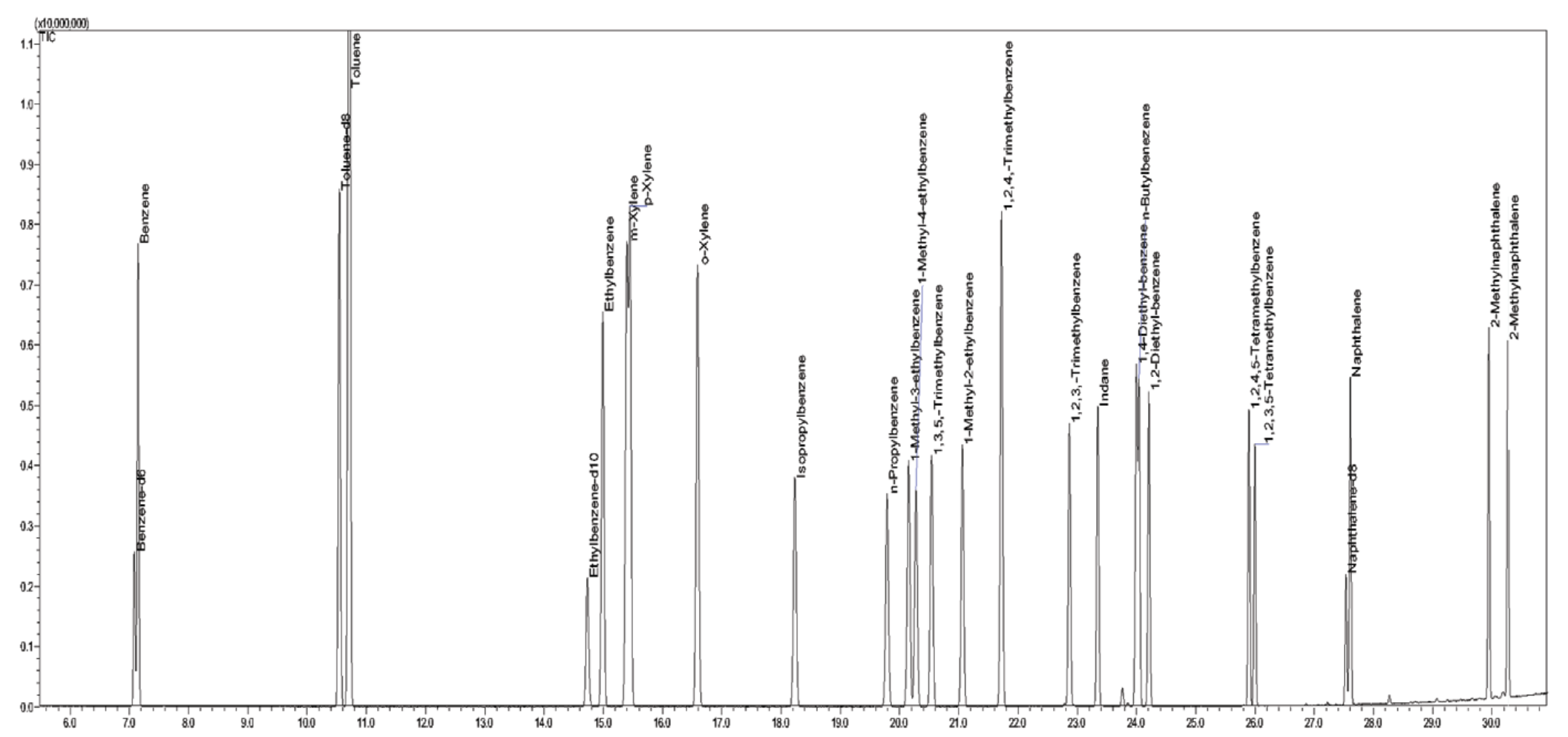
Tuning Mode: ○ High Conc. ● Normal ○ High Sens.

Experimental – GCMS-QP2010 *Ultra* with AOC20i/s Autosampler

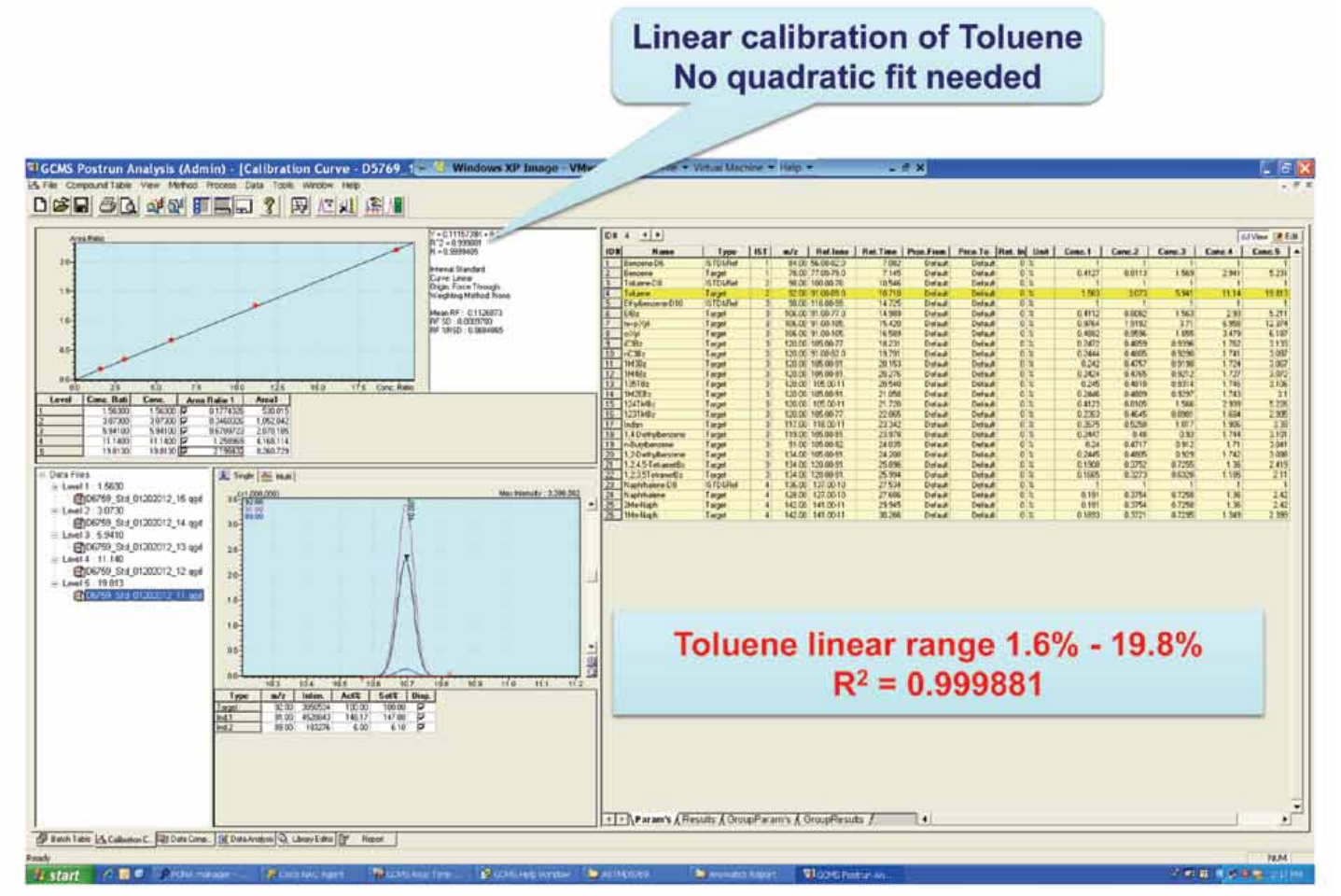
- GC
  - INJ: 250.00°C
  - Linear velocity mode: 35.0 cm/sec
  - Split ratio: 250
  - Gas saver: On (split ratio 250 to 5 after 1min)
  - Column: ZB-1 60 m x 0.25 mm x 1 µm
  - Column: 60.0°C, 3.0°C/min to 120.0°C, 10.0°C/min to 250.0°C
  - Injection Volume: 0.1 µL
- MS
  - Ion Source Temp: 200.00°C
  - Interface Temp: 280.00°C
  - Detector Voltage: -0.1KV relative to tune (0.98kV)
  - Scan range: 45.00 – 300.00
  - Scan interval: 0.10sec
  - Scan rate: 10 spectra/sec
- Software
  - GCMSsolution Ver. 2.71
  - Shimadzu Aromatics Report Software Ver. 2.0

TIC Chromatogram

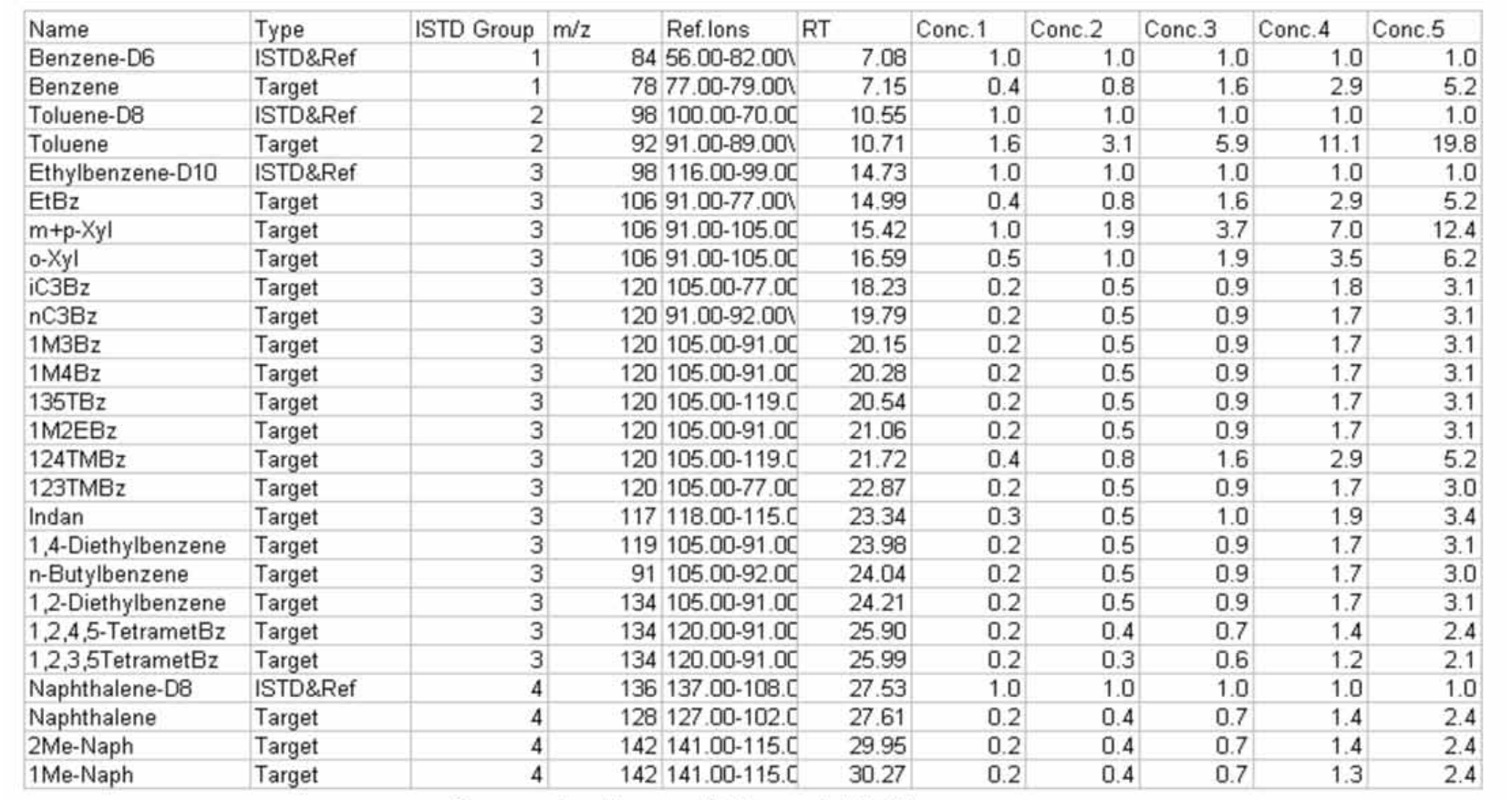
0.1 µL injection of AccuStandard® Gasoline Refinery Aromatics Calibration Set Std-01 (Highest Concentration Set)



Calibration Curve



Compound Table

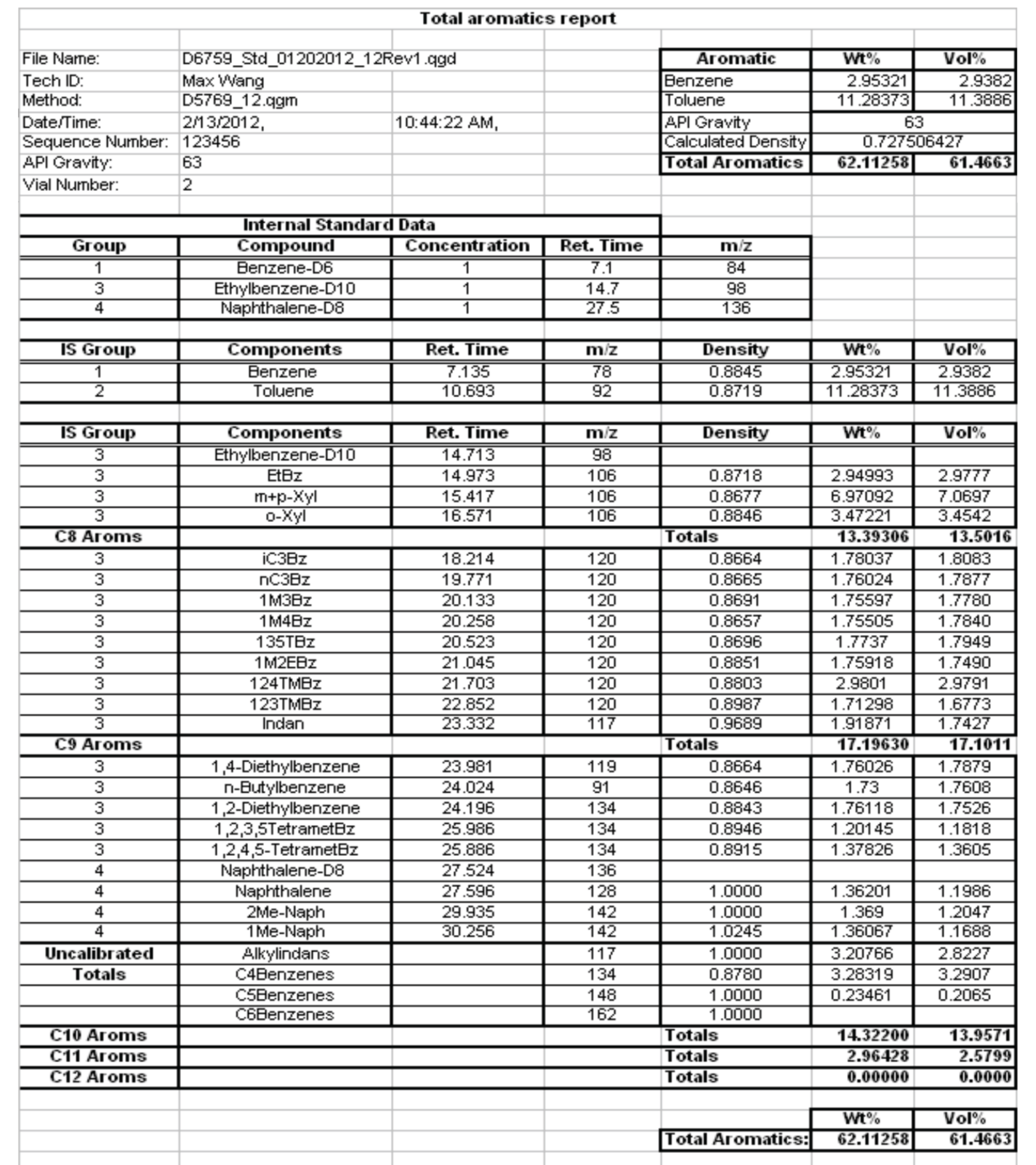


Name	Type	ISTD Group	m/z	Ref.Ions	RT	Conc.1	Conc.2	Conc.3	Conc.4	Conc.5
Benzene-D6	ISTD&Ref	1	84	56.00-82.00\	7.08	1.0	1.0	1.0	1.0	1.0
Benzene	Target	1	78	77.00-79.00\	7.15	0.4	0.8	1.6	2.9	5.2
Toluene-D8	ISTD&Ref	2	98	100.00-70.0C	10.55	1.0	1.0	1.0	1.0	1.0
Toluene	Target	2	92	91.00-89.00\	10.71	1.6	3.1	5.9	11.1	19.8
Ethylbenzene-D10	ISTD&Ref	3	98	116.00-99.0C	14.73	1.0	1.0	1.0	1.0	1.0
EtBz	Target	3	106	91.00-77.00\	14.99	0.4	0.8	1.6	2.9	5.2
m+p-Xyl	Target	3	106	91.00-105.0C	15.42	1.0	1.9	3.7	7.0	12.4
o-Xyl	Target	3	106	91.00-105.0C	16.59	0.5	1.0	1.9	3.5	6.2
iC3Bz	Target	3	120	105.00-77.0C	18.23	0.2	0.5	0.9	1.8	3.1
nC3Bz	Target	3	120	91.00-92.00\	19.79	0.2	0.5	0.9	1.7	3.1
1M3Bz	Target	3	120	105.00-91.0C	20.15	0.2	0.5	0.9	1.7	3.1
1M4Bz	Target	3	120	105.00-91.0C	20.28	0.2	0.5	0.9	1.7	3.1
135TBz	Target	3	120	105.00-119.C	20.54	0.2	0.5	0.9	1.7	3.1
1M2EBz	Target	3	120	105.00-91.0C	21.06	0.2	0.5	0.9	1.7	3.1
124TMBz	Target	3	120	105.00-119.C	21.72	0.4	0.8	1.6	2.9	5.2
123TMBz	Target	3	120	105.00-77.0C	22.87	0.2	0.5	0.9	1.7	3.0
Indan	Target	3	117	118.00-115.C	23.34	0.3	0.5	1.0	1.9	3.4
1,4-Diethylbenzene	Target	3	119	105.00-91.0C	23.98	0.2	0.5	0.9	1.7	3.1
n-Butylbenzene	Target	3	91	105.00-92.0C	24.04	0.2	0.5	0.9	1.7	3.0
1,2-Diethylbenzene	Target	3	134	105.00-91.0C	24.21	0.2	0.5	0.9	1.7	3.1
1,2,4,5-TetrametBz	Target	3	134	120.00-91.0C	25.90	0.2	0.4	0.7	1.4	2.4
1,2,3,5TetrametBz	Target	3	134	120.00-91.0C	25.99	0.2	0.3	0.6	1.2	2.1
Naphthalene-D8	ISTD&Ref	4	136	137.00-108.C	27.53	1.0	1.0	1.0	1.0	1.0
Naphthalene	Target	4	128	127.00-102.C	27.61	0.2	0.4	0.7	1.4	2.4
2Me-Naph	Target	4	142	141.00-115.C	29.95	0.2	0.4	0.7	1.4	2.4
1Me-Naph	Target	4	142	141.00-115.C	30.27	0.2	0.4	0.7	1.3	2.4

Concentration unit in weight %

Aromatics Report

Reports are generated automatically when running GCMSsolution batch processing



Total aromatics report

File Name:	D6759_Std_01202012_12Rev1.qgd			**Aromatic**	**Wt%**	**Vol%**
Tech ID:	Max Wang			Benzene	2.95321	2.9382
Method:	D5769_12.qgm			Toluene	11.28373	11.3886
Date/Time:	2/13/2012,	10:44:22 AM,		API Gravity	63	
Sequence Number:	123456			Calculated Density	0.727506427	
API Gravity:	63			**Total Aromatics**	**62.11258**	**61.4663**
Vial Number:	2					

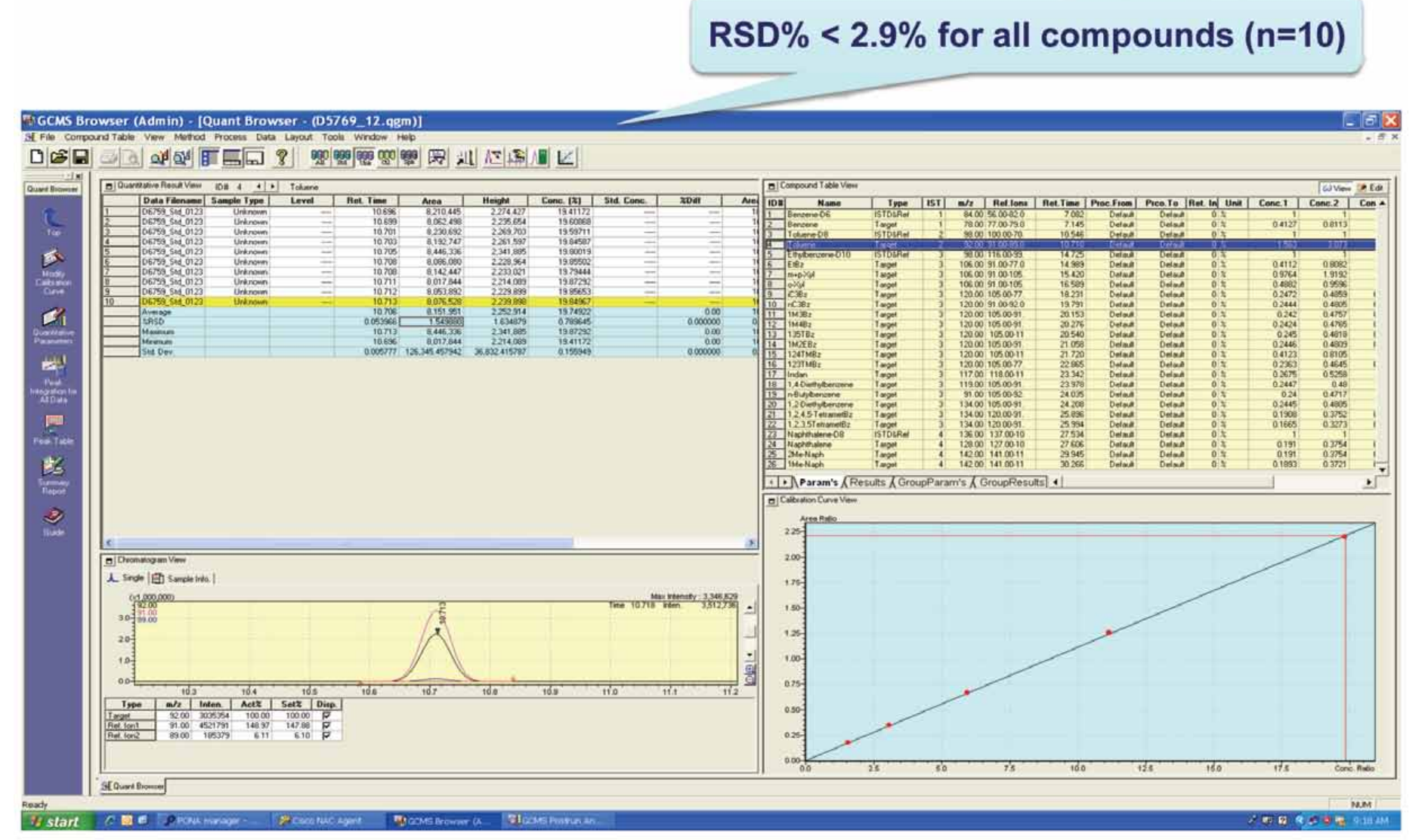
Internal Standard Data

Group	Compound	Concentration	Ret. Time	m/z
1	Benzene-D6	1	7.1	84
3	Ethylbenzene-D10	1	14.7	98
4	Naphthalene-D8	1	27.5	136

IS Group	Components	Ret. Time	m/z	Density	Wt%	Vol%
1	Benzene	7.135	78	0.8845	2.95321	2.9382
2	Toluene	10.693	92	0.8719	11.28373	11.3886

IS Group	Components	Ret. Time	m/z	Density	Wt%	Vol%
3	Ethylbenzene-D10	14.713	98			
3	EtBz	14.973	106	0.8718	2.94993	2.9777
3	m+p-Xyl	15.417	106	0.8677	6.97092	7.0697
3	o-Xyl	16.571	106	0.8846	3.47221	3.4542
C8 Aroms				**Totals**	**13.39306**	**13.5016**
3	iC3Bz	18.214	120	0.8664	1.78037	1.8083
3	nC3Bz	19.771	120	0.8665	1.76024	1.7877
3	1M3Bz	20.133	120	0.8691	1.75597	1.7780
3	1M4Bz	20.258	120	0.8657	1.75505	1.7840
3	135TBz	20.523	120	0.8696	1.7737	1.7949
3	1M2EBz	21.045	120	0.8851	1.75918	1.7490
3	124TMBz	21.703	120	0.8803	2.9801	2.9791
3	123TMBz	22.852	120	0.8987	1.71298	1.6773
3	Indan	23.332	117	0.9689	1.91871	1.7427
C9 Aroms				**Totals**	**17.19630**	**17.1011**
3	1,4-Diethylbenzene	23.981	119	0.8664	1.76026	1.7879
3	n-Butylbenzene	24.024	91	0.8646	1.73	1.7608
3	1,2-Diethylbenzene	24.196	134	0.8843	1.76118	1.7526
3	1,2,3,5TetrametBz	25.986	134	0.8946	1.20145	1.1818
3	1,2,4,5-TetrametBz	25.886	134	0.8915	1.37826	1.3605
4	Naphthalene-D8	27.524	136			
4	Naphthalene	27.596	128	1.0000	1.36201	1.1986
4	2Me-Naph	29.935	142	1.0000	1.369	1.2047
4	1Me-Naph	30.256	142	1.0245	1.36067	1.1688
Uncalibrated	Alkylindans		117	1.0000	3.20766	2.8227
Totals	C4Benzenes		134	0.8780	3.28319	3.2907
	C5Benzenes		148	1.0000	0.23461	0.2065
	C6Benzenes		162	1.0000		
C10 Aroms				**Totals**	**14.32200**	**13.9571**
C11 Aroms				**Totals**	**2.96428**	**2.5799**
C12 Aroms				**Totals**	**0.00000**	**0.0000**
					Wt%	**Vol%**
				Total Aromatics:	**62.11258**	**61.4663**

Repeatability



0.1 µL injection of AccuStandard® Gasoline Refinery Aromatics Calibration Set Std-01 (Highest Concentration Set)

Conclusions

- High concentration tuning mode expands calibration linearity. Good linearity has been achieved across all concentrations of all compounds; no saturated integration was observed, therefore, no quadratic fit was needed.
- Implementation of Shimadzu Aromatics report software has enabled automation of data acquisition, processing, and reporting.
- Linear velocity mode simplifies parameter settings and provides optimized separation.
- Fast scan rate (10 spectra/sec vs. 3 spectra/sec) improves both accuracy and precision.

Acknowledgements

- Mr. Mohamed Salem and Mr. Patrick Armstrong (Shimadzu R&D group) developed Aromatics Report software.
- Mrs. Karen Colclazier (CITGO group) gave valuable application feedback.
- Phenomenex provided a ZB-1 capillary column.