GC Analysis of Gasoline Aromatics and Oxygenates for the Modern Lab: New Approaches to Using ASTM Methods D5580, D3606, and D4815

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Outline

• Overview of ASTM GC methods for gasoline analysis
  – D3606, D4815 and D5580
  – most commonly run GC methods for measuring oxygenates and aromatics

• New Large Valve Oven for the Agilent 7890B GC
  – capacity to fit 3 ASTM gasoline methods on one GC

• Automating sample preparation for gasoline samples
  – Agilent Work Bench with new weigh station balance automates gravimetric sample prep

• Reducing helium usage for GC gasoline methods
  – new 7890 Helium Conservation Module allows easy switching to nitrogen as alternative carrier gas
Analysis of Oxygenates and Aromatics in Gasoline

**ASTM D3606 – Benzene and Toluene in Gasoline**
- official EPA method for benzene (0.1 - 5.0 vol%) and toluene (2 to 20 vol%) in gasoline

**ASTM Method D4815 – Oxygenated Additives**
- 14 different ethers and alcohols from 0.1 to 15 wt%
- usually only one or two oxygenates found in a sample

**ASTM Method D5580 – Aromatics in Gasoline**
- measures benzene (0.1 to 5%), toluene (1 to 15%), C₈ aromatics (0.5 to 10%) C₉ plus aromatics (5 to 30%), and total aromatics (10 to 80%)
- requires two injections per sample for complete analysis
### 7890 Instrument Conditions for D3606

| Pre-column | 10% HP-1 on 100/120 Silcoport W, 1/8 in. x 6 ft. stainless |
| Analytical column | Polar polymer, 1/8 in x 15 ft. stainless |
| carrier gas | helium |
| Inlet | Purge Packed |
| inlet temperature | 200 Deg C |
| inlet total flow | 33 mL/min |
| septum purge flow | 3 mL/min |
| column flow | 30 mL/min |
| Aux pressure | 10 psi |
| FID temperature | 200 deg C |
| oven temperature | 145 deg C isothermal |
| Run time | 12 min |
Configuration and Operation of ASTM D3606

Valve off - Sample injection onto non-polar pre-column

Heavy hydrocarbons trapped

benzene, toluene, light HC pass to polar column

Polar packed column

TCD
Configuration and Operation of ASTM D3606
Valve On - Back flush to polar TCEP analytical column

heavy hydrocarbons back flushed to vent

Purge/Packed Inlet

P/P EPC

HP-1 packed column

vent

Aux EPC

benzene, toluene, light HC separated on polar column

Polar packed column

TCD
D3606 – Benzene and Toluene in Gasoline

![Graph showing light hydrocarbons, benzene, and toluene peaks](image)

- **light hydrocarbons**
- **2-butanol (IS)**
- **toluene**
- **benzene**

Min.

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**Agilent Technologies**
GC Configuration for D4815 and D5580

Similarities between each method

– same GC hardware requirements
  • Inlets, detectors, plumbing and valve configuration
– same separation scheme
  • 2-D separation using polar TCEP micro-packed primary column
  • 20% TCEP on 80/100 Chromosorb PAW, 22“ x 1/16“ stainless
• Only one difference in instrument requirements – non-polar capillary column
  – D4815 – 2.65 µm methyl silicone, 30m x 0.53mm
  – D5580 – 5 µm methyl silicone, 30m x 0.53mm
Valve is “off” at injection and initial separation on TCEP column.
Valve is “on” when back flushing TCEP column to HP-1 column
# 7890 Instrument Conditions for D4815 and D5580

<table>
<thead>
<tr>
<th></th>
<th>D4815 Method</th>
<th>D5580 Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>carrier gas</td>
<td>helium</td>
<td>helium</td>
</tr>
<tr>
<td>Inlet</td>
<td>Split/Splitless</td>
<td>Split/Splitless</td>
</tr>
<tr>
<td>inlet temperature</td>
<td>200 Deg C</td>
<td>200 Deg C</td>
</tr>
<tr>
<td>inlet pressure</td>
<td>9 psi (constant P)</td>
<td>25 psi (constant P)</td>
</tr>
<tr>
<td>TCEP column flow</td>
<td>5 mL/min</td>
<td>10 mL/min</td>
</tr>
<tr>
<td>split vent flow</td>
<td>70 mL/min</td>
<td>100 mL/min</td>
</tr>
<tr>
<td>split ratio</td>
<td>15:1</td>
<td>100:1</td>
</tr>
<tr>
<td>PCM pressure program</td>
<td>13 psi for 14 min</td>
<td>23 psi for 12.1 min</td>
</tr>
<tr>
<td></td>
<td>99 psi/min to 40 psi</td>
<td>99 psi/min to 40 psi</td>
</tr>
<tr>
<td>HP-1 column flow</td>
<td>3 mL/min</td>
<td>10 mL/min</td>
</tr>
<tr>
<td>FID temperature</td>
<td>250 deg C</td>
<td>250 deg C</td>
</tr>
<tr>
<td>oven temperature</td>
<td>80 deg C isothermal</td>
<td>60 C for 6 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 C/min to 115 C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>115 C for 1.5 min</td>
</tr>
<tr>
<td>Run time</td>
<td>16 min</td>
<td>35 min</td>
</tr>
</tbody>
</table>
Determining Back Flush Times for D5580

Inject test mix onto TCEP column – do not back flush (valve always off)

Examine TCEP chromatogram to determine two different back flush times:

– T1 is used for the analysis of benzene and toluene
– T2 is used for C_8 and C_9 plus aromatics

Save as two different methods for complete aromatics analysis per sample
Typical D5580 Results for Aromatics Analysis in Gasoline

Back Flush T1 = 0.58 min

Back Flush T2 = 1.67 min
Determining Back Flush Time for D4815

MtBE  DIPE  EtBE  methyl-cyclopentane

BF = 0.20 min
BF = 0.22 min
BF = 0.24 min
BF = 0.26 min
BF = 0.28 min
BF = 0.30 min

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Gulf Coast Conference - Agilent Workshop
Determining Back Flush Time for D4815

- Choose a time after MCP elution
- Shorter time necessary for DIPE
- Choose longer time if DIPE not analyzed
D4815 – Oxygenates (ethanol) in Gasoline

- Ethanol
- DME (IS)
- Heavy hydrocarbons

pA

2 4 6 8 10 12 14 16 18 min
3-in-1 Gasoline Solution using the New 7890B GC with Large Valve Oven (LVO)

- Greater capacity for valves, packed columns and micro-packed columns
- Greater flexibility for method using complex valve/column configurations
- Enables multiple methods to reside on a single GC
  - reduce instrument costs
  - run more samples in less lab space
- Agilent 7890B 3-in-1 Gasoline Solution
  - D3606
  - D4815
  - D5580
LVO Specifications

- Temperature Limit: 330°C (high temperature valve dependent)
- Valves: 6 heated valve positions, 4 needle valve positions
- Temperature control: Independent control of Large Valve Oven and GC oven
- Valve configurations: 4/6/10/14 port valves including Hastelloy valves
- Large column mandrels (each uses 1 valve position) accept up to 15 feet of 1/8inch OD metal column
- Small column mandrel (one allowed, does not use a valve position) accepts up to 7 feet of 1/8inch OD metal column
3-in-1 Gasoline Solution – LVO Configuration

Cover Off - Front View

- Valves
- Variable Restrictor
- TCEP Pre-column
- Heated Column Mandrel

Cover Off - Rear View

- Pneumatic Valve Actuators
- Variable Restrictor Control
3-in-1 Gasoline Solution – Detailed LVO Configuration
3-in-1 Gasoline Solution – Main Column Oven

- D3606 Packed Columns
- D4815 and D5580 Capillary Columns

- HP-1 packed pre-column
- Polar packed analytical column

- D4815 HP-1 (30 m x 0.53 mm x 2.65 µm)
- D5580 HP-1 (30 m x 0.53 mm x 5.0 µm)
Laboratory Workflow Review

Sample Log-in (LIMS) → Sample Worklist generated (LIMS) → Sample Extraction
- Automated
- Quechers
- Filtration

Sample Preparation
- Calibration Curves
- Dilutions
- Weights for correction
- Internal Standard Additions
- Derivatization

Data Review
- OpenLab CDS

Analysis
- GC, GC-MS
- LC, LC-MS
- Other instrumentation

Link data to lab customer (LIMS) → Provide complete reports to Lab customer (LIMS)
New Weigh Station – Weight Based Sample Prep

High Resolution

• Mettler Toledo high resolution balance
• 5 decimal place readability (0.00001g)
• Build-in deionizer to address static influence on accurate weighing

Compact Design

• Integrated into 7696A Sample Prep WorkBench
• Small footprint system to fit into a fume hood

Automation

• Build-in reference weight for Automatic Internal Calibration
• Automated vial taring and weighing of dispensable liquids
• EZ Sample Prep software records sample and ISTD weight for transfer to OpenLab CDS

- Maintain high quality lab work with Ensured Accuracy
- Reduce lab worker’s exposure to hazardous chemicals – Safe Working Environment
- Improve Efficiency by free up lab resources from manual weighing
- Ensure Consistent Precision and eliminate analyst-to-analyst variability
7696A Sample Prep Workbench Features Overview

Single Vial Heating

Spin-vortex Mixing

Bar Code Reading

Sample Tray Heating (50 vials)

LC Vial Rack

Dilution, Aliquoting and Reconstitution

Reagent and Standard Addition

Liquid/Liquid Extraction

Automatic Weighing

Sample Tray Peltier Cooling (50 Vials)

Economic & Green
Low cost of ownership
Reduce cost per sample and reduce waste

Precise & Accurate
Decrease variability and reduce precision errors in manual sample handling

Safe
Reduce lab worker’s chemical exposure

Efficient
Automated sample prep steps without manual intervention
D5580 – Comparison of Manual and WorkBench Sample Prep

Manual Sample Prep

- Add 1 mL 2-hexanone (IS) to 10 mL volumetric flask
- Record 2-hexanone weight to 0.1 mg
- Add 9 mL sample to 10 mL volumetric flask
- Record sample weight to 0.1 mg

WorkBench Sample Prep

- Add 0.1 mL 2-hexanone (IS) to 2 mL vial
- Record 2-hexanone weight to 0.01 mg
- Add 0.9 mL sample to 2 mL vial
- Record sample weight to 0.01 mg

<table>
<thead>
<tr>
<th>Component (wt%)</th>
<th>Gasoline Sample 1</th>
<th>Gasoline Sample 2</th>
<th>Gasoline Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>0.98</td>
<td>0.96</td>
<td>1.09</td>
</tr>
<tr>
<td>toluene</td>
<td>9.00</td>
<td>8.92</td>
<td>9.48</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>2.98</td>
<td>2.97</td>
<td>2.63</td>
</tr>
<tr>
<td>m,p-xylene</td>
<td>3.02</td>
<td>3.00</td>
<td>6.49</td>
</tr>
<tr>
<td>o-xylene</td>
<td>3.02</td>
<td>3.00</td>
<td>2.31</td>
</tr>
<tr>
<td>C9 plus</td>
<td>6.14</td>
<td>6.11</td>
<td>13.10</td>
</tr>
<tr>
<td>Total</td>
<td>25.14</td>
<td>24.96</td>
<td>35.10</td>
</tr>
</tbody>
</table>
D5580 – Work Bench Prepared Gasoline Sample
Overlay of 5 replicates
D5580 - Precision for WorkBench Samples
Meets ASTM Repeatability (r) Specifications

<table>
<thead>
<tr>
<th></th>
<th>wt% Found in Gasoline Sample 1</th>
<th>wt% Found in Gasoline Sample 2</th>
<th>wt% Found in Gasoline Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>benzene toluene</td>
<td>ethylbenzene</td>
<td>m,p-xylene to o-xylene</td>
</tr>
<tr>
<td>Run 1</td>
<td>0.96 8.93</td>
<td>2.97 3.00</td>
<td>6.12</td>
</tr>
<tr>
<td>Run 2</td>
<td>0.96 8.91</td>
<td>2.96 3.00</td>
<td>6.11</td>
</tr>
<tr>
<td>r (calc)</td>
<td>0.00 0.02</td>
<td>0.01 0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>r (ASTM spec)</td>
<td>0.03 0.09</td>
<td>0.03 0.07</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run 1</td>
<td>1.08 9.56</td>
<td>2.67 6.57</td>
<td>13.39</td>
</tr>
<tr>
<td>Run 2</td>
<td>1.08 9.49</td>
<td>2.66 6.55</td>
<td>13.30</td>
</tr>
<tr>
<td>r (calc)</td>
<td>0.01 0.07</td>
<td>0.02 0.02</td>
<td>0.09</td>
</tr>
<tr>
<td>r (ASTM spec)</td>
<td>0.03 0.09</td>
<td>0.03 0.07</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run 1</td>
<td>0.43 5.99</td>
<td>1.27 4.71</td>
<td>13.79</td>
</tr>
<tr>
<td>Run 2</td>
<td>0.43 6.00</td>
<td>1.27 4.71</td>
<td>13.81</td>
</tr>
<tr>
<td>r (calc)</td>
<td>0.00 0.01</td>
<td>0.00 0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>r (ASTM spec)</td>
<td>0.02 0.07</td>
<td>0.03 0.07</td>
<td>0.27</td>
</tr>
</tbody>
</table>
## D5580 – Accuracy Check for Work Bench Prepared Sample

<table>
<thead>
<tr>
<th>Compound</th>
<th>known</th>
<th>measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>1.00</td>
<td>0.96</td>
</tr>
<tr>
<td>toluene</td>
<td>8.96</td>
<td>8.92</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>2.99</td>
<td>2.97</td>
</tr>
<tr>
<td>m,p-xylene</td>
<td>2.99</td>
<td>3.00</td>
</tr>
<tr>
<td>o-xylene</td>
<td>2.99</td>
<td>3.00</td>
</tr>
<tr>
<td>C9 plus</td>
<td>6.12</td>
<td>6.12</td>
</tr>
<tr>
<td>Total</td>
<td>25.05</td>
<td>24.97</td>
</tr>
</tbody>
</table>
D4815 – Comparison of Manual and WorkBench Sample Prep

**Manual Sample Prep**
- Add 0.5 mL DME to 10 mL volumetric flask
- Record DME weight to 0.1 mg
- Add sample to 10 mL mark
- Record sample weight to 0.1 mg

**WorkBench Sample Prep**
- Add 0.05 mL DME to 2 mL vial
- Record DME weight to 0.01 mg
- Add 0.95 mL sample to 2 mL vial
- Record sample weight to 0.01 mg

<table>
<thead>
<tr>
<th></th>
<th>Gas1 wt% MTBE</th>
<th>Gas2 wt% Ethanol</th>
<th>Gas3 wt% Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>run1</td>
<td>13.15</td>
<td>13.18</td>
<td>6.01</td>
</tr>
<tr>
<td>run2</td>
<td>13.13</td>
<td>13.12</td>
<td>5.98</td>
</tr>
<tr>
<td>Avg</td>
<td>13.14</td>
<td>13.15</td>
<td>6.00</td>
</tr>
<tr>
<td>r (calc)</td>
<td>0.02</td>
<td>0.07</td>
<td>0.02</td>
</tr>
<tr>
<td>r (spec)</td>
<td>0.21</td>
<td>0.21</td>
<td>0.18</td>
</tr>
</tbody>
</table>
D4815 – Work Bench Prepared Gasoline Samples

- MTBE
- DME (IS)
- Heavy hydrocarbons
- Ethanol
- DME (IS)
- Ethanol
- DME (IS)
D3606 – Comparison of Manual and WorkBench Sample Prep

Manual Sample Prep

- Add 1.0 mL 2-butanol to 25 mL volumetric flask
- Add sample to 25 mL mark

Work Bench Sample Prep

- Add 0.04 mL 2-butanol to 2 mL vial
- Add 0.96 mL sample to 2 mL vial

Overlay of 9 Work Bench prepared gasoline samples
D3606 – Precision and Accuracy for Work Bench Prepared Samples

**Commercial Gasoline Sample**

<table>
<thead>
<tr>
<th>Run</th>
<th>Benzene</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.55</td>
<td>6.46</td>
</tr>
<tr>
<td>2</td>
<td>1.55</td>
<td>6.45</td>
</tr>
<tr>
<td>3</td>
<td>1.56</td>
<td>6.51</td>
</tr>
<tr>
<td>4</td>
<td>1.55</td>
<td>6.46</td>
</tr>
<tr>
<td>5</td>
<td>1.56</td>
<td>6.51</td>
</tr>
<tr>
<td>6</td>
<td>1.52</td>
<td>6.37</td>
</tr>
<tr>
<td>7</td>
<td>1.54</td>
<td>6.42</td>
</tr>
<tr>
<td>8</td>
<td>1.55</td>
<td>6.50</td>
</tr>
<tr>
<td>9</td>
<td>1.53</td>
<td>6.40</td>
</tr>
<tr>
<td>r (calc)</td>
<td>0.04</td>
<td>0.15</td>
</tr>
<tr>
<td>r (ASTM spec)</td>
<td>0.06</td>
<td>0.21</td>
</tr>
</tbody>
</table>

**D3606 Check Sample**

<table>
<thead>
<tr>
<th>Run</th>
<th>Benzene</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.98</td>
<td>5.00</td>
</tr>
<tr>
<td>2</td>
<td>0.98</td>
<td>4.98</td>
</tr>
<tr>
<td>3</td>
<td>0.97</td>
<td>4.98</td>
</tr>
<tr>
<td>4</td>
<td>0.98</td>
<td>5.00</td>
</tr>
</tbody>
</table>

*benzene = 1.00 vol% (+/- 0.02)
*toluene = 5.00 vol% (+/- 0.08)

Analysis results match known quantities in sample

Meets ASTM repeatability specifications
Helium Conservation Module
Seamlessly integrated onto 7890B GC hardware and software

- Built on 5th generation EPC
- Fully controlled by Agilent data systems
- Purge channel prevents cross contamination of gases
- Precise pressure control between tank and GC
- Switch between gases within 15-30min for most detectors
Helium Conservation Module

Helium Operation Mode

AUX EPC 1
Nitrogen
0 psig

AUX EPC 3
Purge
10 psig

AUX EPC 2
Helium
80 psig

Bridge Block

< 0.2 mL/min $\text{N}_2$

1 mL/min (out)

To GC Inlet
EPC

Helium ON at 80 psig, Nitrogen OFF
Helium Conservation Modules

Nitrogen Operation Mode

AUX EPC 1
Nitrogen
80 psig

AUX EPC 3
Purge Vent
10 psig

AUX EPC 2
Helium
0 psig

Bridge Block

1.0 mL/min (out)

(\(< 0.2 \text{ mL/min}\))
He

24.2 mL/min N\(_2\)

Helium OFF, Nitrogen ON at 80 psig
# D4815 – Helium and Nitrogen Carrier Gas Operating Conditions

<table>
<thead>
<tr>
<th></th>
<th>Helium GC Conditions</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Col1: TCEP Micropacked</td>
<td>5.0 mL/min (17.8 psi)</td>
<td>5.0 mL/min (16.7 psi)</td>
</tr>
<tr>
<td>Col2: PDMS Capillary</td>
<td>3.1 mL/min (14.7 psi)</td>
<td>3.1 mL/min (13.8 psi)</td>
</tr>
<tr>
<td>Split Flow</td>
<td>70 mL/min</td>
<td>70 mL/min</td>
</tr>
<tr>
<td>TCEP Backflush Time</td>
<td>0.24 min.</td>
<td>0.24 min</td>
</tr>
<tr>
<td>TCEP Reset Time</td>
<td>0.84 min.</td>
<td>0.84 min</td>
</tr>
<tr>
<td>Valve Oven Temp</td>
<td>60° C</td>
<td>60° C</td>
</tr>
<tr>
<td>Column Oven Temp</td>
<td>60° C</td>
<td>60° C</td>
</tr>
</tbody>
</table>
D4815 – Helium and Nitrogen Carrier Gas
MTBE in Gasoline

MTBE

Helium Carrier Gas

Nitrogen Carrier Gas

Min.
D4815 – Helium and Nitrogen Carrier Gas
Ethanol in Gasoline

Helium Carrier Gas

Ethanol

Nitrogen Carrier Gas

Min.
## D4815 – Helium and Nitrogen Carrier Gas Results from 3 Gasoline Samples

<table>
<thead>
<tr>
<th></th>
<th>Gas1 wt% MTBE</th>
<th>Gas2 wt% Ethanol</th>
<th>Gas3 wt% Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Helium</td>
<td>Nitrogen</td>
<td>Helium</td>
</tr>
<tr>
<td>run1</td>
<td>13.146</td>
<td>13.186</td>
<td>6.007</td>
</tr>
<tr>
<td>r (calc)</td>
<td>0.019</td>
<td>0.014</td>
<td>0.024</td>
</tr>
<tr>
<td>r (ASTM spec)</td>
<td>0.212</td>
<td>0.212</td>
<td>0.179</td>
</tr>
</tbody>
</table>
Summary

• New Large Valve Oven for the 7890B GC
  – greater capacity and flexibility for GC methods using complex valve configurations
  – allows multiple ASTM methods to be configured on a single GC
  – reduces costs and saves lab space

• New Weigh Station for Agilent Sample Prep Work Bench
  – automates gravimetric and volumetric sample prep
  – reduces reagent use and the need for volumetric glassware
  – eliminates manual weighing errors
  – same or improved analysis results compared to tedious manual prep

• New 7890B Helium Conservation Module
  – allows easy switching to alternative nitrogen carrier gas
  – reduced helium consumption when GC is idle
  – no effect on analysis results