Troubleshooting AutoGC Systems

Jonathan. Meyer
carol@orsat.com

Orsat, LLC
www.orsat.com
Recording Gas pressures and flows
- Documents gas usage which can diagnose potential leaks in the system
- Keeps system from running out of necessary support gases
- Diagnose low recoveries when canisters get low or are changed
- Diagnose some instrumental failure due to insufficient input pressures

Recording system performance
- QC standards
- Changing response factors
- Failures, error messages or lost data

Recording method changes
- Documenting the reprocessing of data
- Changes in response factors from curves

Less common documentation
- Reasons for data loss
- Unusual site activities
- Manifold cleaning
Using Rhone Web Pages
The Importance of Logbooks
Using Rhone Web Pages

The Importance of Logbooks

<table>
<thead>
<tr>
<th>Canister Installation</th>
<th>Hardware Changes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Update information below when canisters are installed/replaced; please include &quot;CC&quot;, &quot;ALM&quot;, etc. on cylinder information if applicable</td>
<td>Update information below as needed. Select the checkboxes as appropriate when CTS, LCS, Blank, or Audit Failures occur. **Please note that Propane and Benzene % Recovery boxes may be used even if the QC did not fail.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>QC Sample Check</th>
<th>Preventive Maintenance (PM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Update information below as needed. Select the checkboxes as appropriate when CTS, LCS, Blank, or Audit Failures occur. **Please note that Propane and Benzene % Recovery boxes may be used even if the QC did not fail.</td>
<td>Please document start date/time and end date/time of PM</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Preventive Maintenance (PM)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual Routine PM</td>
<td>Start date:</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Preventive Maintenance (PM)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual Routine PM</td>
<td>Start date:</td>
</tr>
</tbody>
</table>

2018 TCEQ Operator Training

September 26, 2018
Using Rhone Web Pages
The Importance of Logbooks
Using Rhone Web Pages
The Importance of Logbooks
Viewing Logbook allows filtering for specific types of information:

- Pressures
- QC checks
- Canister installation
- Calibrations
Using Rhone Web Pages
Logbook Review

Validators and Service techs use logs for troubleshooting failures
Site Visits and Rhone Logbook Entries

- Every visit remote or on site
- Record your observations of system performance
  - Important record for documenting problems
  - Helps with troubleshooting
  - Record as many parameters as possible
  - Note any changes
- Don’t forget to check
  - System clock on time
  - Record any power failures
  - Note if TD drier is changing color
The causes of failing QC checks should be evaluated as soon as they are noted.

- Review chromatogram to determine if the failure resulted in the collection of ambient air
- Check canister pressures and valves
- Check blender set points
- Check sample pump
- Re-run QC run to confirm failure is systemic

Common Failures
- QC sample looks like ambient air
- Blank failures
  - High propylene
  - High heavies from CVS
- Low CVS recoveries
- Low LCS recoveries
Oracle Database
• Populated daily

LEADS Database
• Populated hourly
QC Checks loaded into the Oracle Database can be reviewed from the Validation Pages
Retention Time Standard
• Run Weekly
• All targets should be identified
Using Rhone Web Pages
Quality Control Checks

CVS and LCS Standards
Detail Report
Using Rhone Web Pages
Quality Control Checks

CVS Control Chart Report - Percent Recoveries

<table>
<thead>
<tr>
<th>Compound</th>
<th>Date and Hour</th>
<th>Date and Hour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>03/08/15</td>
<td>03/09/15</td>
</tr>
<tr>
<td>Ethylene@</td>
<td>96.7</td>
<td>98.1</td>
</tr>
<tr>
<td>Propane@</td>
<td>102.7</td>
<td>101.4</td>
</tr>
<tr>
<td>n-Butane@</td>
<td>107.6</td>
<td>107.5</td>
</tr>
<tr>
<td>Acetylene@</td>
<td>74.0</td>
<td>74.9</td>
</tr>
<tr>
<td>n-Pentane@</td>
<td>105.5</td>
<td>106.2</td>
</tr>
<tr>
<td>1,3-Butadiene@</td>
<td>104.1</td>
<td>104.4</td>
</tr>
<tr>
<td>2-Methylpentane</td>
<td>103.5</td>
<td>103.7</td>
</tr>
<tr>
<td>n-Hexane@</td>
<td>98.5</td>
<td>98.5</td>
</tr>
<tr>
<td>Benzene@</td>
<td>97.3</td>
<td>99.1</td>
</tr>
<tr>
<td>Toluene@</td>
<td>93.9</td>
<td>94.2</td>
</tr>
<tr>
<td>p-Xylene + m-Xylene@</td>
<td>87.9</td>
<td>89.8</td>
</tr>
<tr>
<td>n-Propylbenzene@</td>
<td>91.6</td>
<td>92.4</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene@</td>
<td>77.1</td>
<td>79.6</td>
</tr>
</tbody>
</table>

2018 TCEQ Operator Training
September 26, 2018
Using Rhone Web Pages
Quality Control Checks

Blank Control Chart
Using Rhone Web Pages
Data Collection - Is it running?
Using Rhone Web Pages
Data Collection - Is it running?
## Dallas Hinton St. [E] Monthly Summary

Air Monitoring Comparison Values (AMCVs) are used to evaluate the potential for effects to occur as a result of exposure to concentrations of constituents in the air. AMCVs are based on data concerning health effects, odor, and vegetation effects. They are not ambient air standards. If predicted or measured airborne levels of a constituent do not exceed the comparison level, adverse health or welfare effects would not be expected to result. If ambient levels of constituents in air exceed the comparison levels, it does not necessarily indicate a problem, but rather, triggers a more in-depth review. If you have any questions about the potential for health, odor, or vegetation effects from exposure to the reported concentrations, please contact the Toxicology Section by telephone at (512) 236-3800 or by email at tox@tceq.texas.gov.

Use the controls below to select a different date or site. Click on the Generate Report button once you have made your selections.

### September 2018

<table>
<thead>
<tr>
<th>Day</th>
<th>Morning</th>
<th>Afternoon</th>
<th>Local Standard Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Propane (ROC C) measured in parts per billion - Carbon</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8:29</td>
<td>8:53</td>
<td>2018 TCEQ Operator Training</td>
</tr>
</tbody>
</table>

### September 26, 2018

- TCEQ Operator Training

- **September 26, 2018**: This is the date mentioned in the document.
Using Rhone Web Pages
Data Collection - Is it running?
Troubleshooting Failures
No Data - AutoGC is Not Running
Totalchrom Errors

- **Not Ready - No Method**
  - Power failure has interrupted connection between Totalchrom and the interface
    - NCI902 interfaces can be backed up to eliminate this for momentary power outages
    - Integral interface in GC cannot be backed up.

- **Port Comm error**
  - May be the result of a power failure
  - Sometimes the result of operator activity on computer during Totalchrom activities
  - Requires refresh of configuration

- **End of Sequence**
  - System stops at midnight
No Data - AutoGC is Not Running
Turbomatrix Errors

- If possible check the TD log before resetting the TD
- System Faults
  - Air pressure too low
  - Carrier pressure too low
- Peltier at -58°C
  - Peltier at -58°C - Heated zones have shut down
  - Valco valve A failure
  - Oven position error
  - Duty cycle errors
- TD Ready to Inject
  - Check to see why GC is not ready
  - Check to see that Totalchrom is ready.
No Data - AutoGC is Not Running
GC Errors

- One or both FIDs are not lit
  - Only applies to PPC FID GCs
  - Check H2 and air sources
- Oven PRT error on GC
  - Reset GC - could be the result of poor power failure
  - Call Orsat if this continues to happen
- GC fails to reach starting temperature
  - Trailer is too hot, check AC
  - Check TD log for deviations
- TD does not recognize that GC is ready
  - Check Ready out signal cable from GC to TD
- GC shows Not Ready - EXT (NCI902 interface only)
  - Check IF ready out cable to GC Ready In
- TD and GC are running but Totalchrom is not collecting data
  - Check GC start out cable to NCI902 Interface start in.
Factors Affecting Data Validity

- Timing Issues resulting in invalid data
- Sampling Issues
  - Ambient data which appears suspect
  - May or may not be associated with failing QC
- Chromatographic Issues
  - Baselines
  - Noise
  - Contamination
- Failing QC
  - CVS and LCS standards
  - RTS spikes
  - Blanks
Causes of Invalid Sampling Times

- Power failures
  - Vigilance during rainy periods
  - Using Smart home switches to reset TD
  - Using Totalchrom to reset timing

- Creeping sample times
  - Check TD log
    - Deviation - GC not Ready
    - Duty cycle errors
  - Peltier not cooling to -30 in a timely fashion
  - Trailer too warm
Valid Sample Timing

<table>
<thead>
<tr>
<th>Name</th>
<th>Date Modified</th>
<th>Size</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPSD07K.raw</td>
<td>4/7/2009 10:48</td>
<td>2 KB</td>
<td>TotalChrom Raw File</td>
</tr>
<tr>
<td>RPSD07K.raw</td>
<td>4/7/2009 10:48</td>
<td>2 KB</td>
<td>TotalChrom Raw File</td>
</tr>
<tr>
<td>RPSD07J.TXO</td>
<td>4/7/2009 10:36</td>
<td>3 KB</td>
<td>TXO File</td>
</tr>
<tr>
<td>RPSD07J.rst</td>
<td>4/7/2009 10:36</td>
<td>18 KB</td>
<td>TotalChrom Result File</td>
</tr>
<tr>
<td>RPSD07J.TXO</td>
<td>4/7/2009 10:36</td>
<td>3 KB</td>
<td>TXO File</td>
</tr>
<tr>
<td>RPSD07J.rst</td>
<td>4/7/2009 10:36</td>
<td>19 KB</td>
<td>TotalChrom Result File</td>
</tr>
<tr>
<td>RPSD07J.raw</td>
<td>4/7/2009 10:36</td>
<td>36 KB</td>
<td>TotalChrom Raw File</td>
</tr>
<tr>
<td>RPSD07I.TXO</td>
<td>4/7/2009 09:36</td>
<td>3 KB</td>
<td>TXO File</td>
</tr>
<tr>
<td>RPSD07I.rst</td>
<td>4/7/2009 09:36</td>
<td>18 KB</td>
<td>TotalChrom Result File</td>
</tr>
<tr>
<td>RPSD07I.TXO</td>
<td>4/7/2009 09:36</td>
<td>3 KB</td>
<td>TXO File</td>
</tr>
<tr>
<td>RPSD07I.rst</td>
<td>4/7/2009 09:36</td>
<td>20 KB</td>
<td>TotalChrom Result File</td>
</tr>
<tr>
<td>RPSD07I.raw</td>
<td>4/7/2009 09:36</td>
<td>36 KB</td>
<td>TotalChrom Raw File</td>
</tr>
<tr>
<td>RPSD07I.raw</td>
<td>4/7/2009 09:36</td>
<td>36 KB</td>
<td>TotalChrom Raw File</td>
</tr>
<tr>
<td>RPSD07H.TXO</td>
<td>4/7/2009 08:36</td>
<td>4 KB</td>
<td>TXO File</td>
</tr>
<tr>
<td>RPSD07H.rst</td>
<td>4/7/2009 08:36</td>
<td>24 KB</td>
<td>TotalChrom Result File</td>
</tr>
<tr>
<td>RPSD07H.TXO</td>
<td>4/7/2009 08:36</td>
<td>3 KB</td>
<td>TXO File</td>
</tr>
<tr>
<td>RPSD07H.rst</td>
<td>4/7/2009 08:36</td>
<td>23 KB</td>
<td>TotalChrom Result File</td>
</tr>
</tbody>
</table>

DTS between xx:28 – xx:48

Stability should be < 1 minute change per day – requires resetting TD every 20 days
Review Ambient Data
Issues related to invalid ambient data

- Unusually low levels or inconsistent levels which are not associated with met changes

Examples:
  - All ambient look like blanks
  - All ambient look like CVS or partial CVS
  - Contamination

Checks
  - Sample pump and sample flow on TD
  - Manifold fan motor operational
  - DVI’s on rear of TD have power (should be battery backed up)
  - Use Hands-on in Totalchrom to check blender valve functionality (relay 5 reset)
Chromatographic Issues
Contamination

Contamination of BP Chromatogram from Piston Flow measurement of Sample Flow on Turbomatrix
Chromatographic Issues

Baselines

- **Flat Baselines**
  - Check FID’s are lit
  - Check FID connections to IF
  - Check AZ set to ON on GC
  - Check ATTN and Range on GC at 1

- **Wavy (rolling) Baselines**
  - Insure AC not disturbing FID’s
  - Check Compressor and inline air regulator settings
  - Check Zero Air pressure and change filter if necessary
  - Check or change GC air regulator

- **Ramping Baselines**
  - Replace FID ferrule for offending column
  - Possible damaged detector (see noise)

*Beware of Auto scaling!*
Chromatographic Issues
Spikes, ticks, noise and other humpy-do’s

- Excessive moisture can cause particulate release on PLOT columns
- Dirty or “wet” detectors can cause excessive noise and must be cleaned or parts replaced
- Sawtooth pattern is often associated with replacement of H2 cylinders - exercise GC regulators and cylinder regulator.
- Vibrations such as opening and closing doors or compressors starting and stopping can cause spikes - check that detector collectors are tight and GC lid is screwed down
- Spikes related to heaters or other equipment must be determined by finding the source - sometimes related to poor connections on the IF
- Some excursions, dips and such are associated with compressor cycling and must be determined by association and observation.
Baseline Ramp caused by detector ferrule. Follows temperature profile
Contamination possibly from leak detection solutions.
Chromatographic Issues
Baselines

New System
Ambient Air

Dean’s switch at cut time
Complaint: wandering baseline

1/8/2007
Chavez
PLOT
(scaled to 20 mV fs; 8 mV offset)
Chromatographic Issues

Baselines

1/8/2007
Chavez
BP1
(scaled to 20 mV fs; 8 mV offset)

Complaint: wandering baseline
Chromatographic Issues
Baselines

1/20/2007 Clinton PLOT (scaled to 20 mV fs; 8 mV offset) FOR COMPARISON
Chromatographic Issues
Baselines

1/26/2007
Chavez
PLOT
(scaled to 20 mV fs; 6 mV offset)

Detectors capped off – no column
Chromatographic Issues
Baselines

Tics every 4 minutes (10-12/chromatogram)
Backpressure pulses from TOC PSA switching
Chromatographic Issues
Baselines

Nederland 1/30/2007
3 mV fs

PLOT

BP1
Chromatographic Issues
Baselines - Power Issues

FID Disconnected

Sample

PLOT FID1
BP1 FID2
PLOT FID1
BP1 FID2
Chromatographic Issues
Baselines - Hydrogen Change

FID A

FID B
Quality Control Failures
CVS Failures Low or High for all Components

- Confirm by re-run
- Check blender settings
- Check canister pressure
- Check actual sample flow on TD
- Run LCS to determine if it is also low - if yes
  - Check OTSP compared to previous recorded value
  - Check TD sample flow compared to previous recorded value
Quality Control Failures
CVS Failures - No Peaks

- Check to see if ambient air has peaks - If none:
  - Check FID’s are lit
  - Check sample pump is operational
  - Check BP1 column flow at Deans’ switch - broken or plugged at TD or at Deans switch

- No peaks on PLOT column
  - FID A out
  - Dean’s switch fails to activate (peaks before P+ on BP1 column)
  - PLOT column broken or plugged - check for flow
  - FID A connection to IF lost

- No peaks on BP1 column
  - FID B out
  - Restrictor broken or plugged - check for flow
  - FID B connection to IF lost
Quality Control Failures
LCS Failures - CVS is OK

▶ No peaks or small peaks
  ▶ No can or valve closed (gauge suspect?)
  ▶ Can empty - power failure - DVI’s on battery back up
▶ Looks like RTS or Ambient
  ▶ Is can attached?
  ▶ Check DVI is powered
  ▶ Use Hands-on to check relay connectivity to IF
    ▶ Relay 3 should be RTS
    ▶ Relay 4 should be LCS
    ▶ Relay 6 should be calibrant port
    ▶ Relay 7 should be sample
▶ Additional peaks in chromatogram
  ▶ Contamination
  ▶ Leaks in sample system
Quality Control Failures
Individual Peaks Failing in LCS or CVS

- Check for RT shifting resulting in mis-ID
- Acetylene
  - After trap change
  - Check Ethane recovery - if low as well
    - Check Desorb vent flow <10 sccm
    - Check sample flow with piston flowmeter
  - Replace canister
- 2-Methylpentane
  - Integration parameters - may not be biggest peak
  - Optimize method
- 1,2,4 - Trimethylbenzene (see blanks)
  - Check sample line heaters
  - Canister filling issues
  - Adsorption problems - trap incorrectly installed
  - Trap failures, dirty filter disks
  - Contaminated Dean’s switch
Quality Control Failures

Trap Failures

Results in differential response

Type 1 - Mixing (most common)
- Losses of Hexane, Benzene and Toluene
- Peak shapes for early components on BP column poor, tailing

Type 2 - Trap material moves out of heated zone
- Losses of Xylene, N-propylbenzene, 1,2,4-TMB
- Peak shape for late components may or may not be poor

Generally limited to BP column recoveries
Trap Failures
BP Column Before and After Failure

Before

After
Trap Failures
PLOT Column Before and After Failure

Before

After
Quality Control Failures

Blanks

▶ Failing Totals
  ▶ New trap - mostly on BP1 column
  ▶ System contamination due to trailer activity
▶ Propylene, ethylene or butenes
  ▶ Contamination of Nafion drier from high ambient levels - replace Nafion with conditioned one
▶ CVS/LCS component carry over or ‘memory’
  ▶ Generally last 3 - 4 components on BP1 column
  ▶ Possible adsorption problems
    ▶ Trap material escaped from trap - filter disk
    ▶ PLOT column particulate in restrictor end of Dean’s switch
  ▶ Often related to compressor/TOC failures resulting in high moisture levels in sample and lines.
Quality Control Failures
Retention Time Standard

- Retention time not the same as ambient air
  - RTS times are longer than ambient
    - Canister not humidified enough
    - Nafion not working well
      - Dry air purge not dry
      - Dry air purge not high enough flow (150-250 mL/min)
  - Retention time not stable
- If canister is > 1 year old replace
  - Loss of heavy components
  - Loss of acetylene
Retention Time Shifting
BP1 Column
Retention Time Shifting
BP1 Column
Leak Tests

Sample Leak test

- Will show leaks in sample flowpath associated with TD. Use when:
  - LCS high when CVS is good
  - Contamination in all samples
  - Low values for CVS, when LCS is good
- TD should be in Standby and RTS and LCS canisters closed
- Set Sample/Calibrant valve to Sample
- Remove sample line and cap sample inlet on TD
- Remove poly line from vacuum pump and attach to test manifold*

Pressure Drop Leak test

- Plug both columns at detector (using septa)
- Set TD and Midpoint to 48 psi
- Back off both TD and GC regulators to determine if there are leaks at TD or in Dean’s switch
- Good when one column only is failing CVS and LCS
Leak Tests

Sample System Test Manifold

1. Use Toggle to pressure system up to 60 psig (may require open and close several times)
2. Close Toggle and observe for pressure drop over 5 to 10 minutes.
Leak Tests
Turbomatrix Air Supply Leaks

- In-line flowmeter should read 0.4 to 0.7 slpm
- Make initial observation of flow
  - Turn off TD
    - Removes Nafion flow and air to internal pneumatics on TD
    - Normal drop is only Nafion setpoint - 0.25 slpm
  - Turn off Drier toggle valve
    - Removes pneumatic air to DVI’s
    - Removes pneumatic air to Peltier
    - Normal drop is only peltier flow ~ 0.1 slpm
  - Back off Blender zero gas
    - Normal drop is amount of zero flow from blender spreadsheet ~ 0.1 to 0.15 slpm
- These tests will not identify leaks in compressor, or internal to the zero air purifier or TOC
Leak Tests
Testing Canisters attached to LCS/RTS ports

► Attach new canister and leave valve closed
► Use Hands-on or DVI switches to switch the appropriate relays to select the canister just attached*
► Observe sample flow (actual) on TD
► Sample flow should fall to <0.2 sccm
► Open canister valve to re-establish flow

*Note: You must manually switch both DVI’s to access LCS and RTS ports for each test
System Shut-down

- Power off GC and TD
- Close shut-off valves on Hydrogen cylinders
  - Close cylinder valves on all cylinders
  - Option: Remove regulators and secure cylinders in the event of Hurricane
- Carrier can be left flowing to GC and TD for temporary shut-downs
- Power off Zero Air purifier and TOC gas generator.
  - Close toggle valves to Zero Air, TOC and any auxiliary air cylinder if installed.
  - Close toggle valve on drier to TD.
- If there is an AC failure other electrical equipment such as computers and monitors may need to be powered off to protect them from excessive heat.
- Excessive heat over prolonged periods have been seen to cause issues for standards
System Start-up

- **Startup compressor**
  - note any issues on pressure building like hissing or leaking of shut-off valve assembly or auto drain.

- **Zero Air start-up**
  - Once compressor has reached 100 psig pressure, open toggle valve to zero air purifier.
  - Zero air must be disconnected from GC and allowed to flow at least 4 hours while heating up (use cap or other restriction to limit flow during warm-up)

- **TOC Start-up**
  - Open toggle valve to TOC and observe pressure build on inline regulator.
  - Confirm inline regulator reaches 80 psig. And there is no leaking in the TOC.

- **Re-establish FID flows**
  - Confirm air and hydrogen flows are correct
  - Wait until detectors reach the correct temperature 250 °C
  - Ignite FIDs and observe mV signal for unusual values (-97)

- **Open air line toggle valve on drier to TD and power on TD**