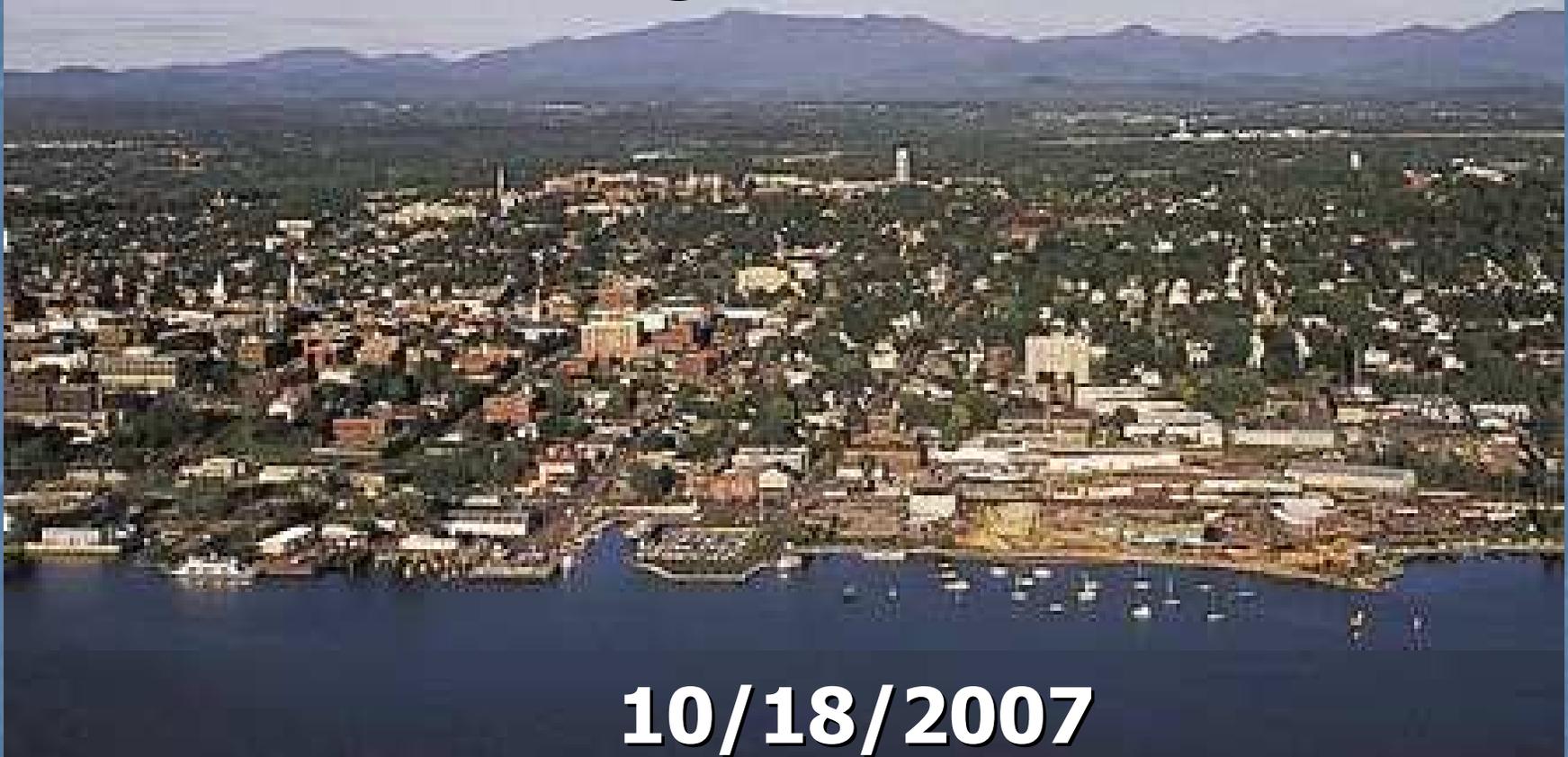# Semi-continuous Benzene Monitoring in Burlington, Vermont

10/18/2007

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Vermont APCD Air Toxics Project Manager

Overview:
Syntec Spectras GC955 Series 600 BTEX Analyzer

- General Information
- Design Specifications
- Principles of Operation
- Installation
- Operation
- Calibration
- Auditing
- Data handling/validation
- Quality assurance
- Results
- Issues/Concerns: "Bumps in the Road"

General Information
Syntec Spectras GC955 Series 600 BTEX Analyzer

- Manufacturer: Synspec
  - Located in the Netherlands
- US Distributor/Customer Support
  - Wilbur Technical Services, LLC (NH)
- Base unit cost ~ $35k
- Burlington first ambient installation in USA
  - >800 Analyzers deployed in many EU countries to meet ambient Benzene monitoring Requirements
- Computer controlled-embedded PC running proprietary software
  - *Windows NT,* 40 Gigabyte HD
  - 10" integrated monitor
  - External keyboard & mouse
  - Various communication/data options (USB, modem, ethernet etc..)
  - *PC-Anywhere* (remote control)
- Standard 19" rack mount/110v
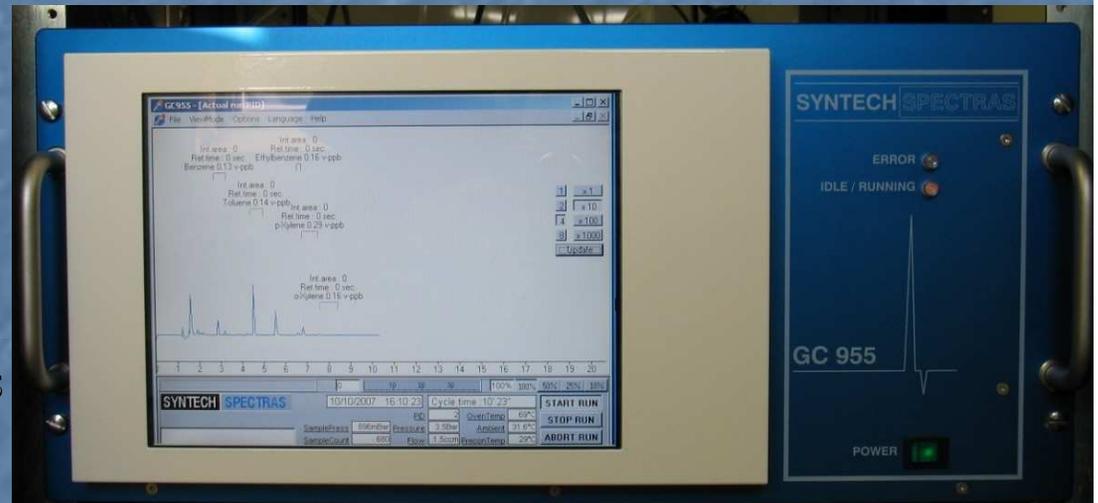
Design Specifications

GC955 Inside Top view

- Specifically for ambient air measurement of benzene, toluene & xylenes (others cpds/configurations available)
- Carrier gas- N_2
    - Ultra High Purity (Grade 5, 99.999%)
    - 50 psig, 1.5 ccpm
- Preconcentrator-Tenax GR
- 2-phase GC capilllary column (in oven)
    - AT-5, .32mm ID
    - 2-meter "stripper" column isolates BTEX compounds
    - 13-meter "analysis" column
- PID- 10.6 eV, 50 µl measurement cell
- "Semi-continuous"; 15-minute run time
- Analog or digital data options
- Range: up to 300 ppbv
- Synspec's reported detection limit
    - benzene: 0.03 ppbv (0.1 µg/m^3)

Principles of Operation
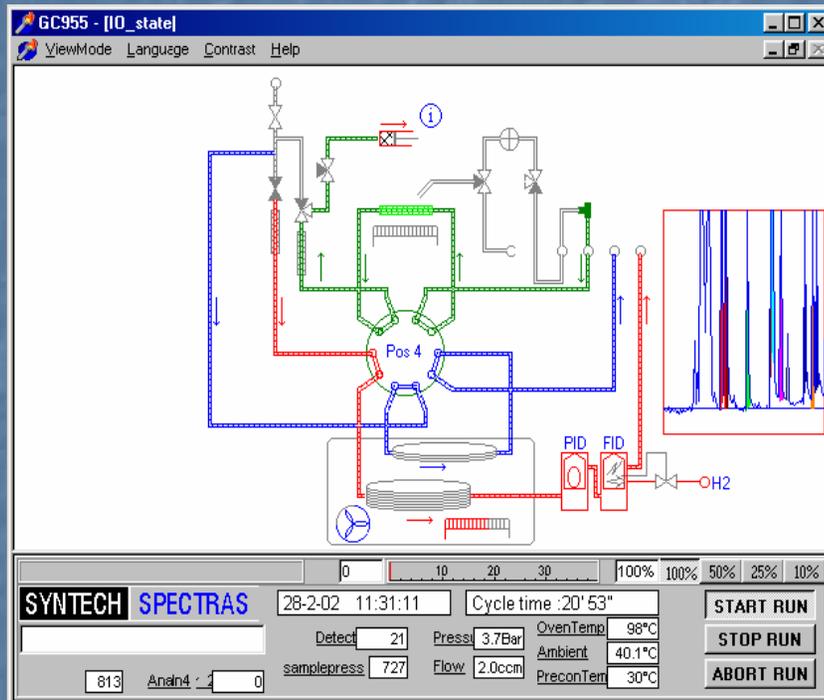
- 2 main operating modes:
  - Sample Injection
  - Sampling/Analysis
- Design keys
  - 10-port valve, preconcentrator and sampling piston/cylinder
    - allows for simultaneous collection of next air sample while analysis of previous air sample is occurring

Sample Injection Mode
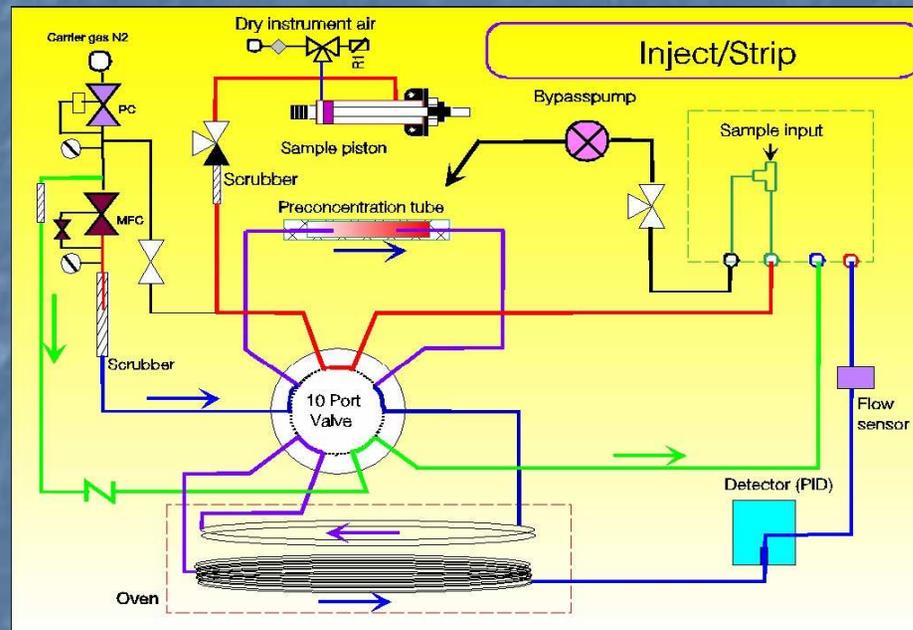
- Sample collected on preconcentrator during previous 15-minute period is thermally desorbed into stripper column and then into analysis column
- Bypass pump operates for brief period before next sample collection
  - Flush sample piston/cylinder and SS sample inlet line
  - provide fresh air sample to "T" at back of analyzer

Sampling/Analysis Mode

- During each 15-minute run….
  - Sampling cylinder/piston draws total ~35 cc of ambient air sample through preconcentrator at set intervals
    - ~150 cc total during 15-minute cycle
- Once BTEX cpds make it thru stripper column (after injection mode)……
  - 10-port valve switches and back flushes remaining VOCs from stripper column…..
- While BTEX compounds continue on thru analysis column to the PID for measurement at specific retention times
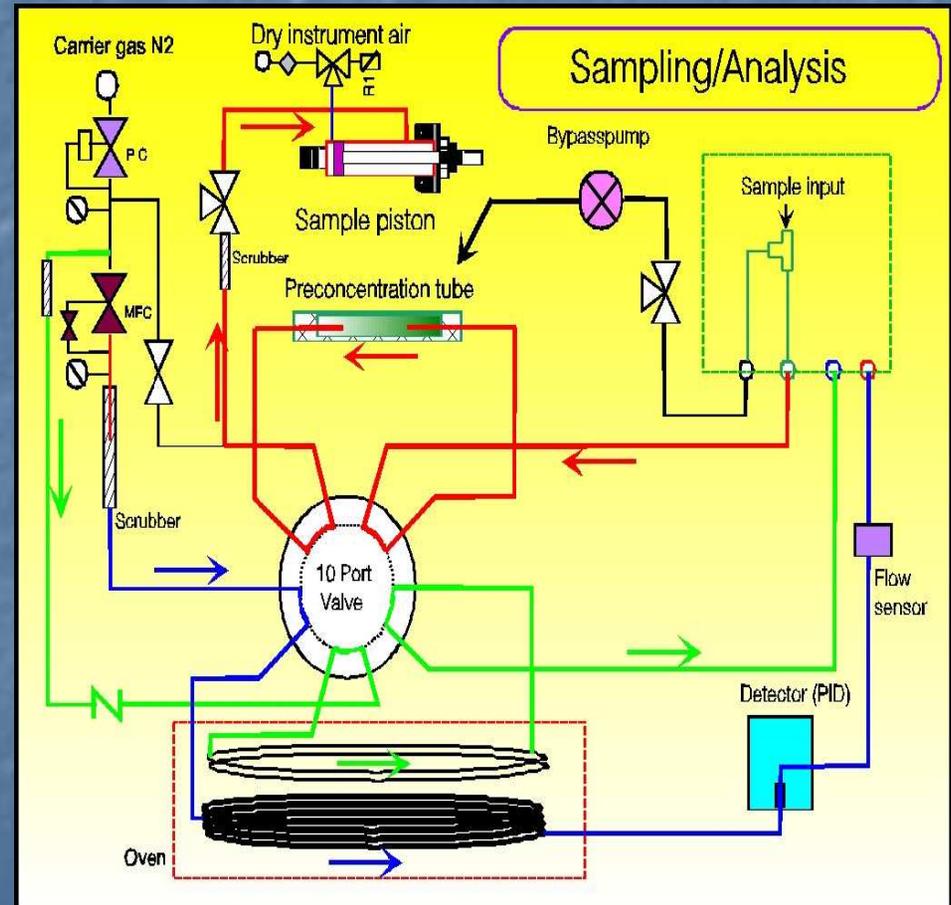
Installation

- Rack mounted in monitoring trailer
- Connected to common glass manifold
  - 1/8" SS tubing
  - 2μ sintered SS inlet filter
- 3 Channel analog output connected to ESC data logger

- Internet connection via dedicated DSL line
  - Allows offsite communication, data review/download
  - Remote control via PC-anywhere
- LAN connection with trailer PC

Operation
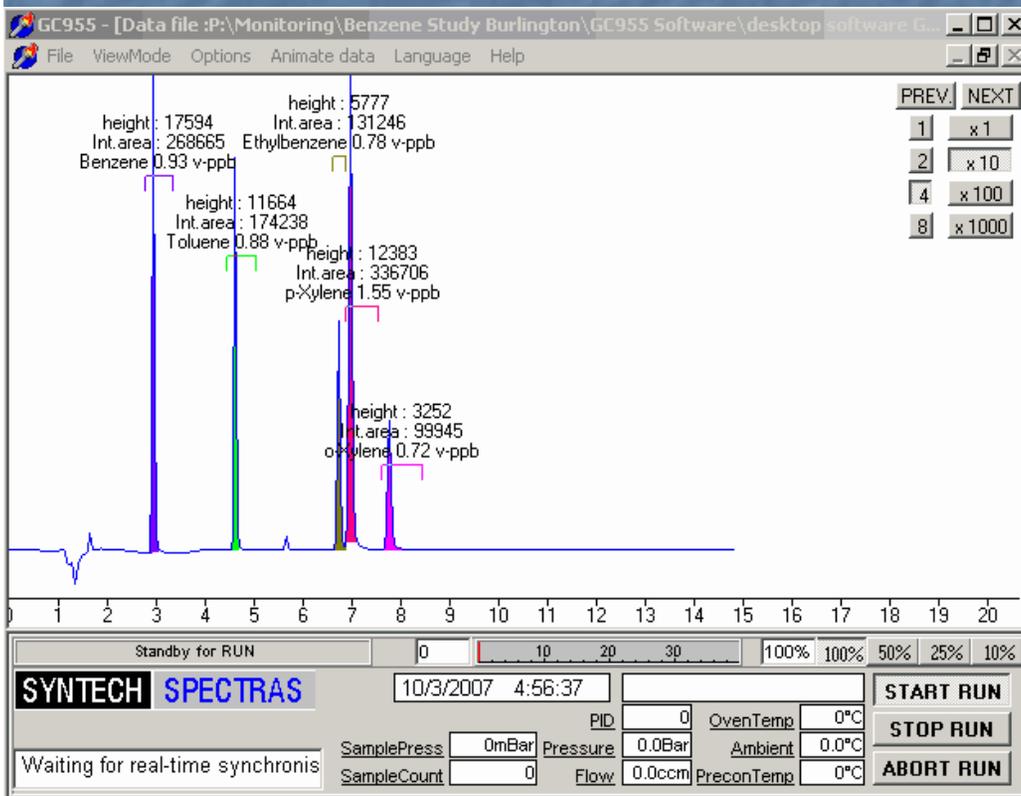
- Analyzer is pre-configured at factory for application/method
  - Run time, retention times, GC oven program, carrier gas flow, peak integration style etc....
- Easy to operate:
  - GC955 auto-starts run on power-up
  - Windows/menu-based operation
- Main run window indicates chromatographic results for current run
  - Retention times, conc., peak area
- Also displays real-time operating parameters at bottom
  - N_2 Flow & pressure, preconcentrator & oven temp, PID, sample pressure
- Pull-down menus provides access to:
  - Calibration results
  - Operational state
  - Configuration settings

Calibration

- Desired Range: 0-5 ppbv
  - Software has integrated calibration "mode"
    - results are stored and used to calculate current calibration relationship for each VOC
    - Linear and non-linear regression options available
    - Software has optional "auto-linearization" function for addressing non-linear PID response at lower levels.
- Retention times verified/edited

- BTEX cylinder gas: 1ppmv – *Spectra Gas*
- Onsite Zero Air System: *TEI* Model 111
- Diluter: *Environics* Model 6103 (trace level)
  - 0-10 sccm gas MFC; 0-20 lpm Air MFC

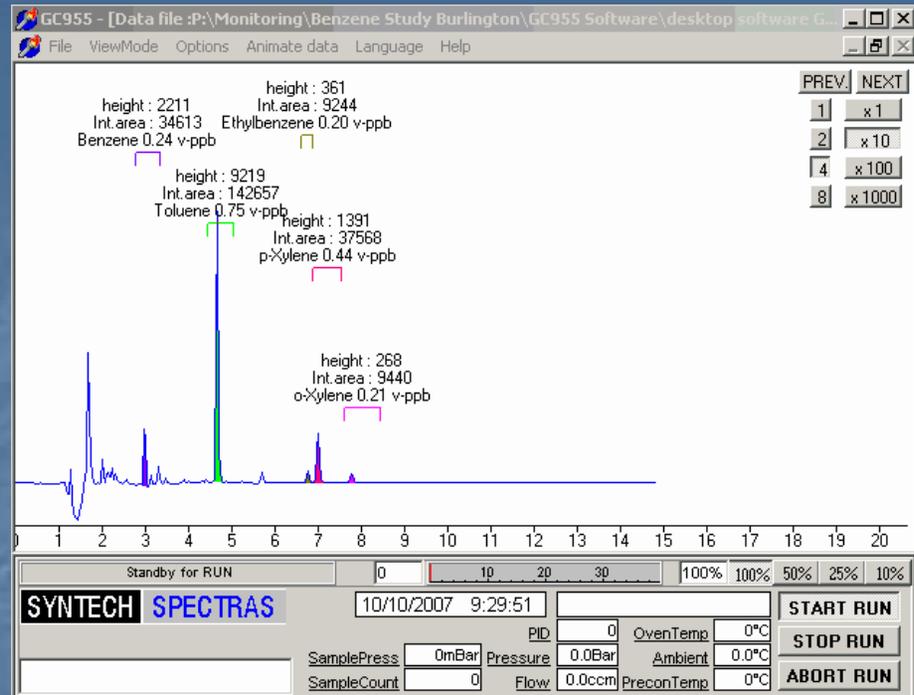# Benzene Calibration
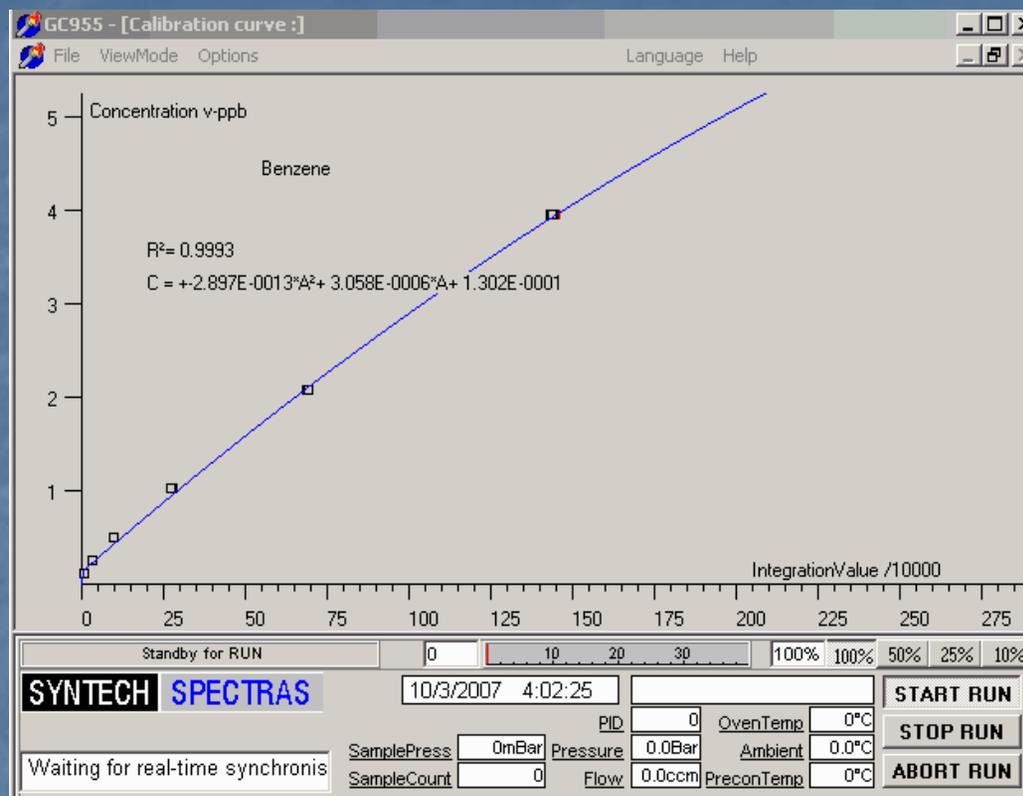
- 6-point calibration
  - ppbv input levels 0.1, 0.25, 0.5, 1, 2, 4
  - Multiple 15-minute runs at each input level incorporated into curve
- Non-linear option used as best fit for desired range and accuracy at low level (auto-linearization for PID not activated at this time)
  - R^2=0.9993
  - y-intercept becomes lowest reportable level (0.13 ppbv ≈ lowest calibrant)
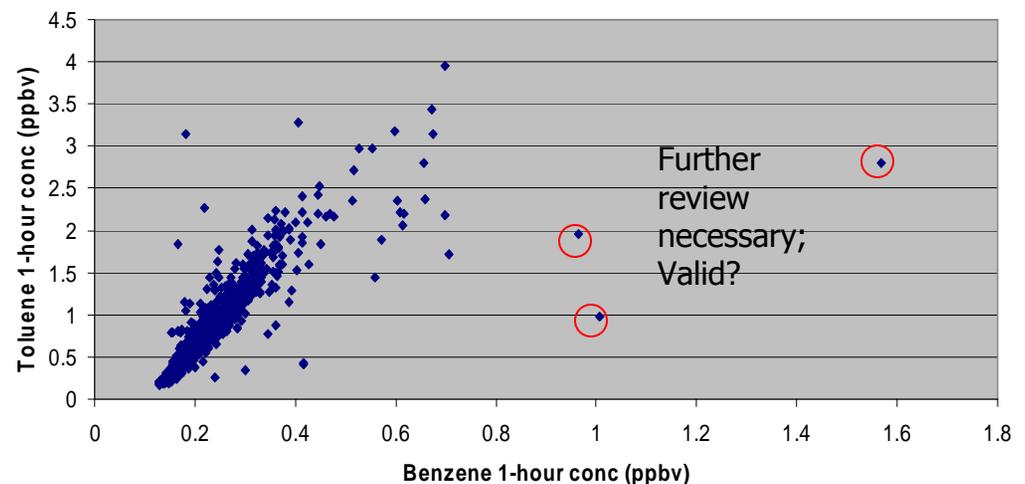
Data Handling

- GC run time is synchronized with 15-min computer clock intervals (optional)
- Chromatogram results from each 15-minute sample run saved to unique data file
  - Saved files can be loaded and reviewed in main screen for review and final validation
- ppbv results for each 15-minute sample are written to a text file
  - Each text file contains 1 month of data
    - also contains RT and peak area
  - Text file is retrieved using PC-Anywhere
    - Other options are flash drive or FTP from trailer LAN
- Text file imported to *EXCEL* and *ACCESS* for review, processing, validation etc…..
  - 15-min values used to generate valid 1-hour averages
    - 75% data averaging rule used (minimum of 3, 15-min. values)
- Analog output to ESC datalogger provides external backup DAS option (limited to 3 compounds)
  - Provides real time access via network and additional flagging capability

Data Validation

- Daily review of hourly averages in ESC
  - Verify flags for maint./auditing
  - Assess data representativeness
  - Investigate missing, suspect or elevated values
- Review audit field sheets for performance w/in DQOs
- Text file of 15-min results reviewed and download to Excel/Access for:
  - processing, further review, flagging, generation of 1-hour avgs., validation
- Review chromatograms of randomly selected runs and ones for suspect or elevated values
  - Verify retention time, peak area, concentration
- Review results graphically
  - Time series, Fingerprint plots
  - Scatter Plot of benzene/toluene ratios for review of suspect values:

GC955 - [Data file :P:\Monitoring\Benzene Study Burlington\GC955 Software\desktop software G...

File   ViewMode   Options   Animate data   Language   Help

PREV NEXT
1   x 1
2   x 10
4   x 100
8   x 1000

height : 2211
Int.area : 34613
Benzene 0.24 v-ppb

height : 361
Int.area : 9244
Ethylbenzene 0.20 v-ppb

height : 9219
Int.area : 142657
Toluene 0.75 v-ppb

height : 1391
Int.area : 37568
p-Xylene 0.44 v-ppb

height : 268
Int.area : 9440
o-Xylene 0.21 v-ppb

Standby for RUN   0   10   20   30   100% 100% 50% 25% 10%

SYNTECH SPECTRAS   10/10/2007 9:29:51   START RUN
                                           STOP RUN
PID   0   OvenTemp   0°C   ABORT RUN
SamplePress   0mBar   Pressure   0.0Bar   Ambient   0.0°C
SampleCount   0   Flow   0.0ccm   PreconTemp   0°C

Synspec GC955 Benzene vs. Toluene
Burlington 1-hour Avgs. from 6/20/07-8/31/07
(ppbv, n=1544)

Toluene 1-hour conc (ppbv)

Further review necessary; Valid?

Benzene 1-hour conc (ppbv)

Quality Assurance

- QAPP approved by EPA-New England
- Weekly precision audit
  - Mid-range input level; DQO +/-15%
- Monthly zero/span check
  - 80-100% of range input level; warning:+/-10%, control:+/-20%
  - Zero: ≤ lowest reporting limit (y-intercept)
- Biannual accuracy audit (second source standard)
  - Multiple mid-range inputs; DQO +/-20%
- Data capture
  - Quarterly DQO: 75%
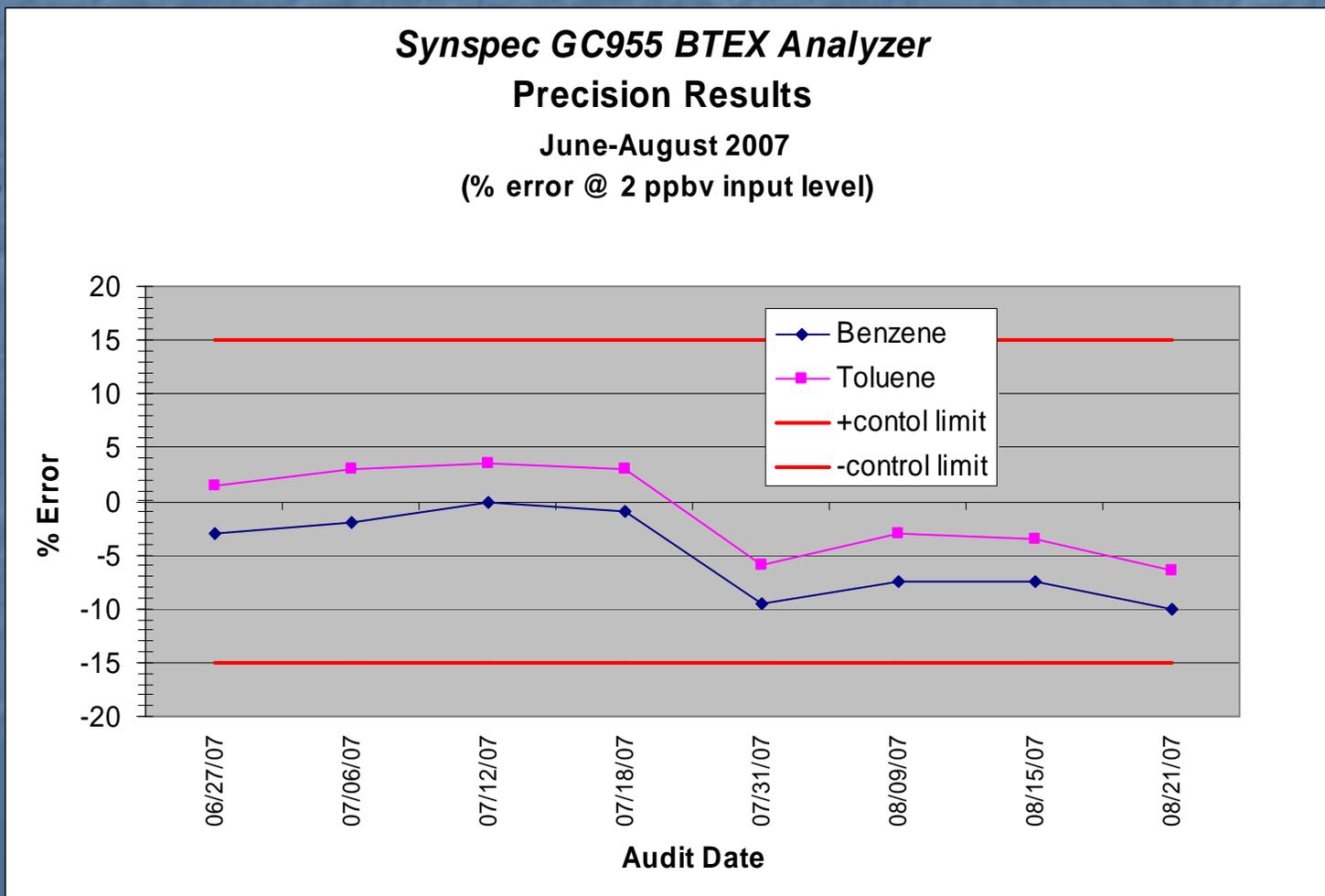
Quality Assurance Results
(6/20/07- 8/31/07)

Currently, DQO's Are Being Met

Mean precision error:
- Benzene=-6.5%
- Toluene=-2.5%
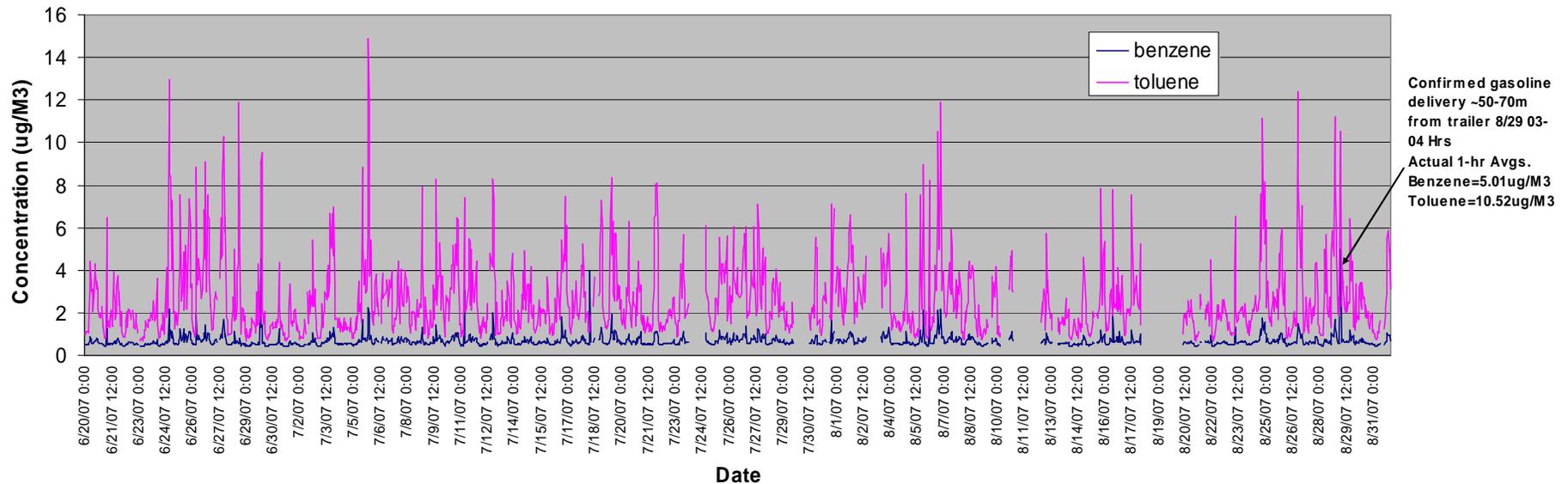
Data Capture
- 15-minute ≈87%

Synspec GC955 BTEX Analyzer
Precision Results
June-August 2007
(% error @ 2 ppbv input level)

Benzene & Toluene
1-hour Averages*

6/20/07-8/31/07

**Burlington Benzene and Toluene 1-hour Avgs.
from 6/20/07- 8/31/07 (ug/M3)**

Confirmed gasoline
delivery ~50-70m
from trailer 8/29 03-
04 Hrs
Actual 1-hr Avgs.
Benzene=5.01ug/M3
Toluene=10.52ug/M3

legend: benzene, toluene

X-axis: Date — *Y-axis:* Concentration (ug/M3)

* final review/validation pending; 1-hour averages only flagged for missing and audit/maintenance periods

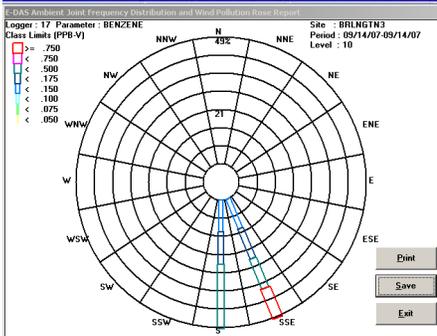# One week in August with confirmed gasoline delivery near site

Burlington Benzene and Toluene 1-hour Avgs. from 8/26/07- 8/31/07 (ug/M3)
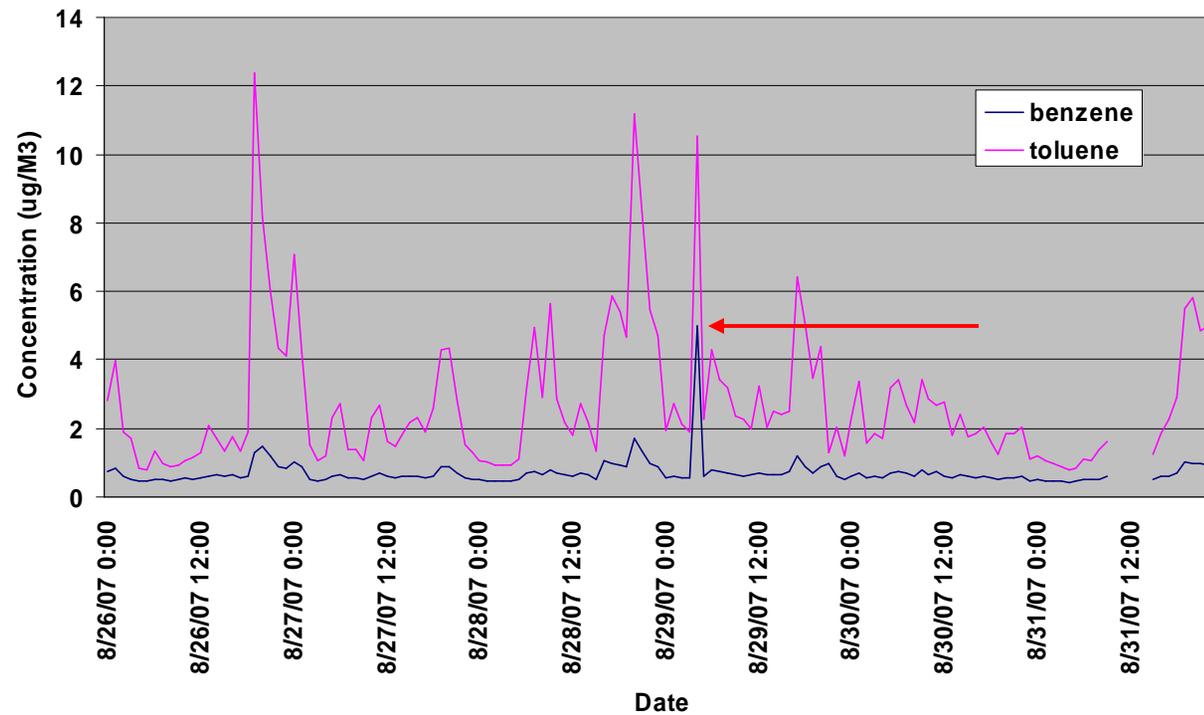
- **Similar period in September with confirmed gasoline delivery near site**

  - ← Visual confirmation of tanker delivery from onsite video cam

 - ← Pollution rose confirming S/SSE winds during highest values

  - ← Benzene time series (ESC) showing elevated levels for Hr 0300-0400

Burlington BTEX Results vs. TO-15 canisters
(Comparison of 24-hour Averages for Benzene and Toluene)
*BTEX 24-hr averages based on mean of 96 separate 15-minute values for each day
*TO-15 results based on analysis of 24-hour integrated whole-air canister sample

Comparison of GC955 BTEX Results to TO-15 Canisters
Benzene & Toluene 24-hour Averages, Burlington VT (ppbv)
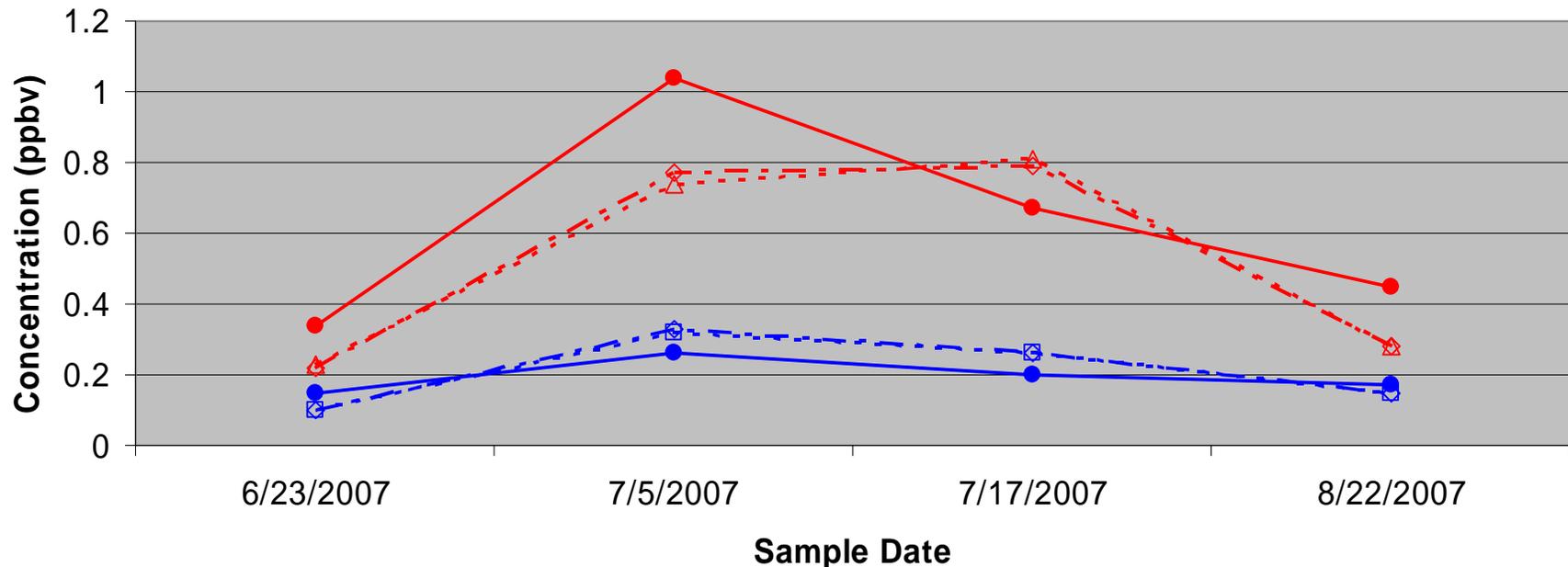
"Bumps in the Road"

- Computer/hardware issues
  - Computer reboots periodically
  - GC955 Analyzer occasionally locks-up due to a Windows error
    - Can create large missing data periods
    - Still under investigation; computer replacement considered
  - Analog output only provides for 3 channels
  - Calibration/audit limitations
    - 0-10 ccpm MFC a necessity
    - Canisters not viable option
    - Tedlar bags ok, not preferred option

- BTEX software issues
  - European date format in data text file requires additional post processing
  - Chromatogram requires *Synspec* software to review and is not a permanent record of results for ppbv value

- Communication/Customer Support
  - Some difficulty/delays dealing with the Netherlands regarding timely corrective actions and answers

Thank you!

- Jenny Berschling (Vermont APCD/DEC Lab)
- John Simone (Vermont APCD)

- John Wilbur (Wilbur Technical Services)

  - For all their effort and invaluable assistance with this project

Contact Information

- Note: Synspec will be in the U.S. next month:
  - What: North American Technical Training Session
  - When: November 7-9, 2007
  - Where: Sheraton in Braintree, Massachusetts
  - Contact: Wilbur Technical Services
- Wilbur Technical Services, LLC
  - John Wilbur (603) 880-7100
- Synspec
  - Michael Rijpkema, Wouter Lautenbach
  - Website: www.synspec.nl
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- Robert Lacaillade, Vermont APCD
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  - (802) 241-3840