

# Semi-continuous Benzene Monitoring in Burlington, Vermont



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**National Air Monitoring Conference**  
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# Background

- Vermont DEC Awarded EPA Grant in 2006
  - Local-Scale Air Toxics Ambient Monitoring Program Grant  
*RFA OAR-EMAD-05-18*
- Grant Study Objectives
  - To assess spatial and temporal characteristics of benzene in Burlington, Vermont
  - Evaluate and validate a benzene dispersion model
- Short-term Benzene Concentrations Beneficial
  - Semi-continuous analyzer viable alternative to canisters/tubes



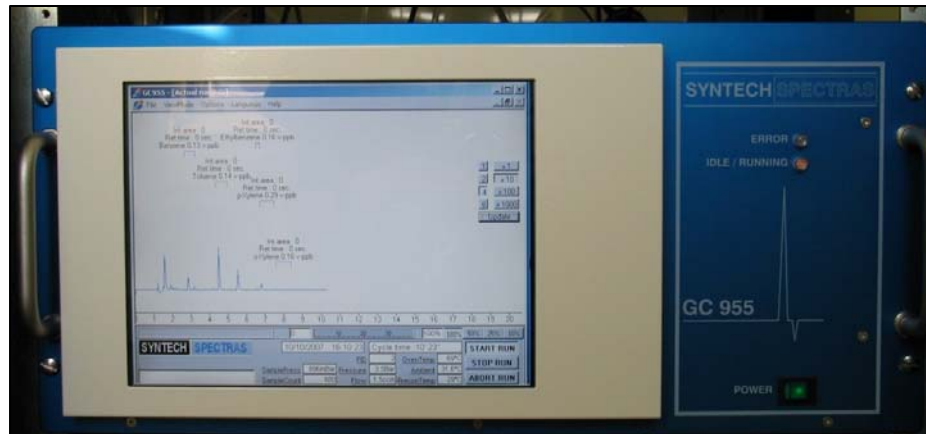
# Overview

- Design Specs
- Installation
- Calibration
- Data Handling, Validation & Reporting
- Quality Assurance
- Summary of 1-Hour Benzene Results
- Comparisons to TO-15 (24hr & 6hr canisters)
- Summary & Observations



# “Syntec Spectras GC955 Series 600 BTEX Analyzer”

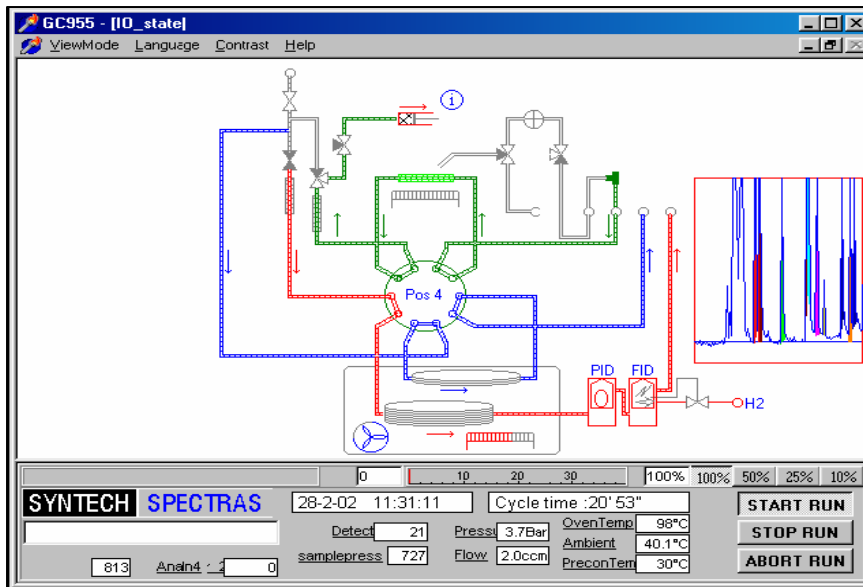
- Designed to measure “BTEX” compounds in air
  - benzene, toluene, ethylbenzene and xylenes
- Computer Controlled Gas Chromatograph-PID
  - Embedded-PC running proprietary software
  - *Windows XP, 40 Gigabyte HD, PC-Anywhere*
  - 19” Standard Instrument Rack Mount
  - 10” integrated monitor, External keyboard & mouse
- Manufactured by *Synspec* (The Netherlands)
  - U.S. Distributor: Wilbur Technical Services, LLC



# Design Specifications



**GC955 Inside Top view**



- Carrier gas- N<sub>2</sub> (Ultra High Purity)
- Preconcentrator- *Tenax GR*
- Column: 15 m x 0.32mm (ID)
  - 95% dimethylpolysiloxane; 5% diphenylpolysiloxane
  - 2-meter “stripper” column
  - 13-meter “analysis” column
- PID- 10.6 eV, 50 µl measurement cell
- 15-minute analysis run time per Sample
- “Semi-continuous”; allows for simultaneous collection of next air sample while previous sample is analyzed
- Design keys
  - 10-port valve
  - Preconcentrator
  - Precision sampling piston

# Installation

- **Burlington Monitoring Shelter**
  - In downtown city parking lot on corner of 2 busy streets
  - Across street from a gas station and newspaper publisher, next door to fire station
- **Connected to Common Glass Sample Manifold**
  - 1/8" Silco-coated stainless tubing
  - 2 $\mu$  sintered-stainless particulate inlet filter
- **Internet Connection via Dedicated DSL Line**
  - Allows offsite communication, data review/download
  - Remote control via *PC-Anywhere*



# Calibration Equipment

- Software Calibration “mode”
  - Linear /non-linear
  - optional “auto-linearization” function
  - Retention times verified/edited
- BTEX Calibration Gas
  - *Spectra* or *Scott*
  - 0.6 or 1 ppmv
  - 5% analytical accuracy w/ 1-yr cert.
- Zero Air
  - *TEI* Model 111
- Dilution Calibrator
  - *Enviro* Model 6103
    - 0-10 sccm gas MFC
    - 0-20 lpm Air MFC

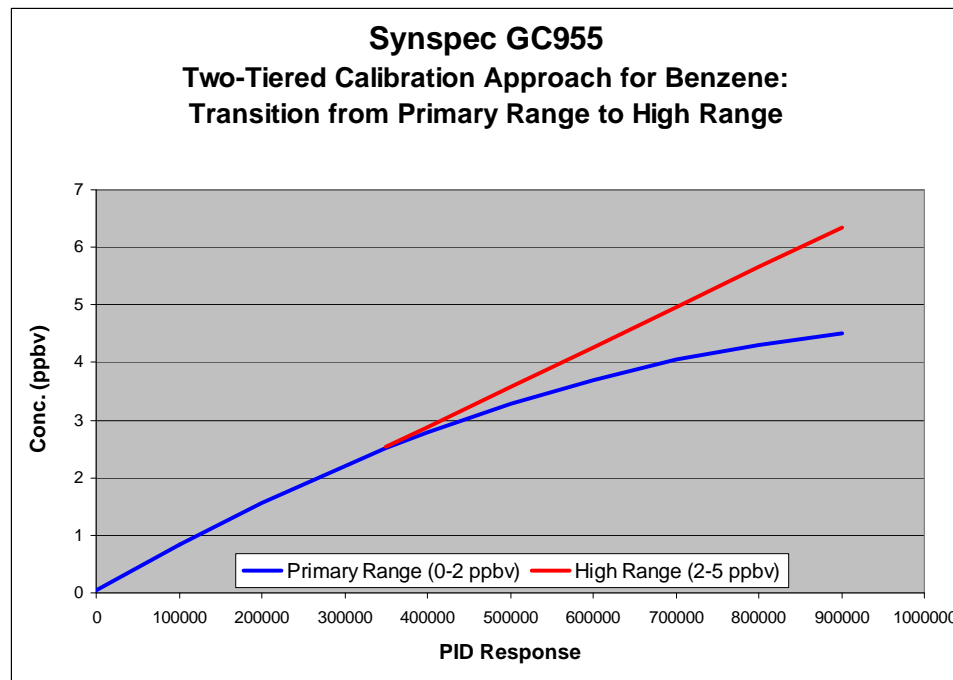
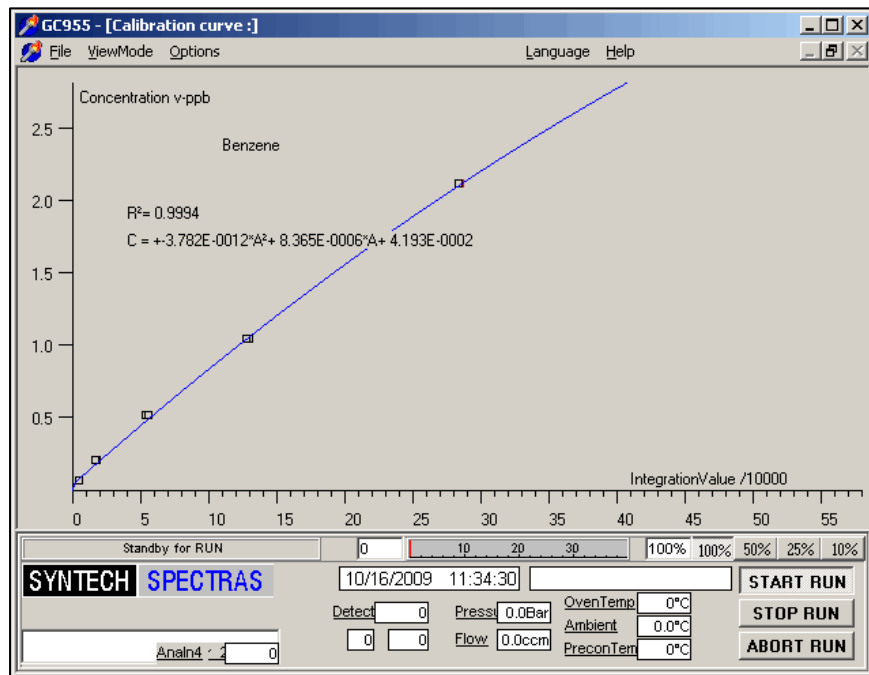


# Synspec Benzene Calibration

- Six-point Calibration – Input Levels: 0.07, 0.2, 0.5, 1, 2, 4 ppbv
- Two-tiered Approach
  - Primary Range 0-2 ppbv (98% of measured values)
  - High Range 2-5 ppbv
- Non-linear Regression (software auto-linearization not utilized)
  - $R^2=0.9994$
  - Method detection limit =0.04 ppb (y-intercept)

[0-2 ppbv Calibration]

[2-5 ppbv Calibration Transition]





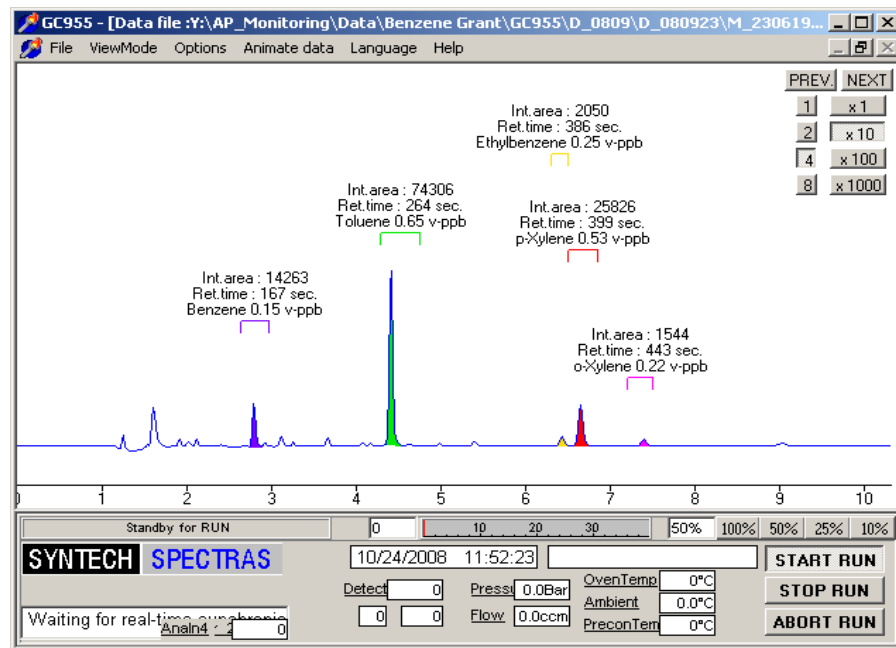
# Data Handling

- Chromatograms
  - Each 15-min sample analysis run is saved to a separate binary file
  - Files can be viewed on analyzer or desktop (running Synspec program) for review and validation
- Output File of Results
  - Results of each analysis written to a text file (PID response, ppbv, retention time, operating parameters)
  - Text file is retrieved using PC-Anywhere and imported to *EXCEL* and *ACCESS* for review and validation
  - 15-min values used to generate 1-hour averages
    - 75% data averaging rule (minimum of 3, 15-min values for 1-hr avg.)



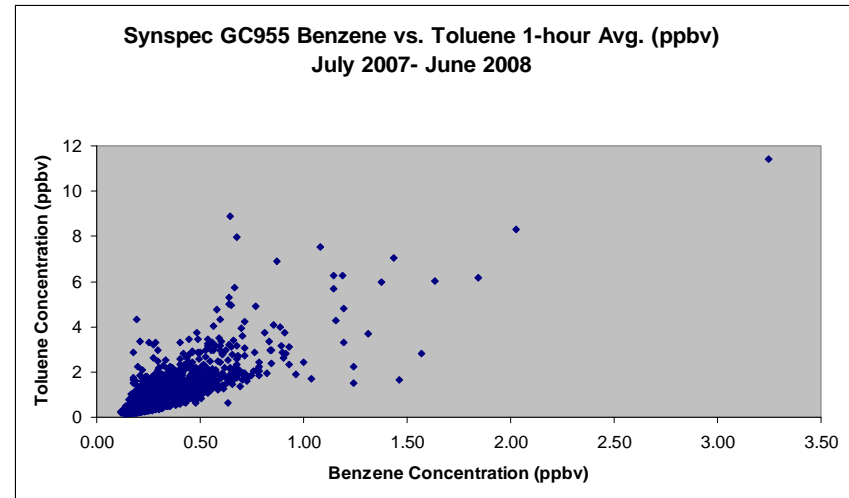
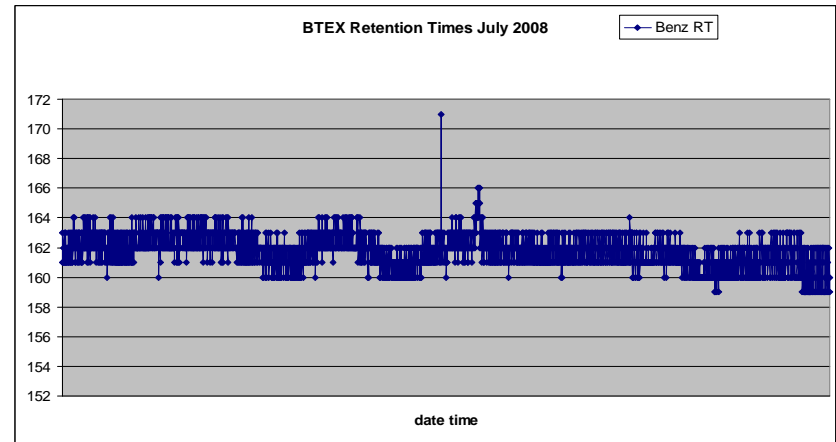
# Data Validation

- Performance Audits
- Review Text File With Excel/Access
  - Missing/suspect values
  - Retention time/operating parameter verification
  - Flagging/validation
- Review Chromatograms of Selected Runs
  - Verify retention time, peak area, identification, concentration



# Data Validation (continued) & Reporting

- Visually Review Results Graphically
  - Time series, fingerprint plots
  - Scatter plot of benzene/toluene ratios for review of suspect values



- Valid 15-minute Results Reported to AQS

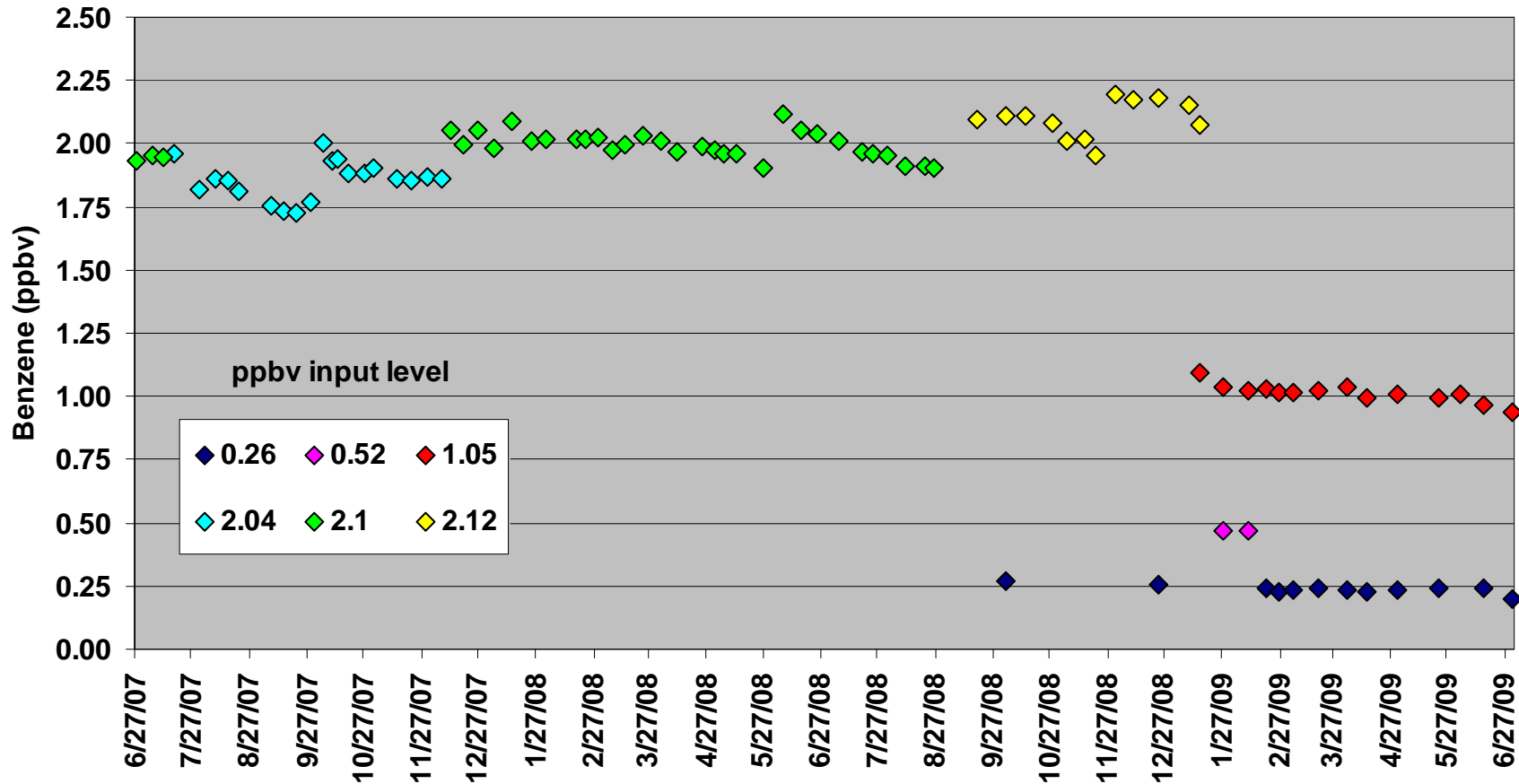


# Quality Assurance

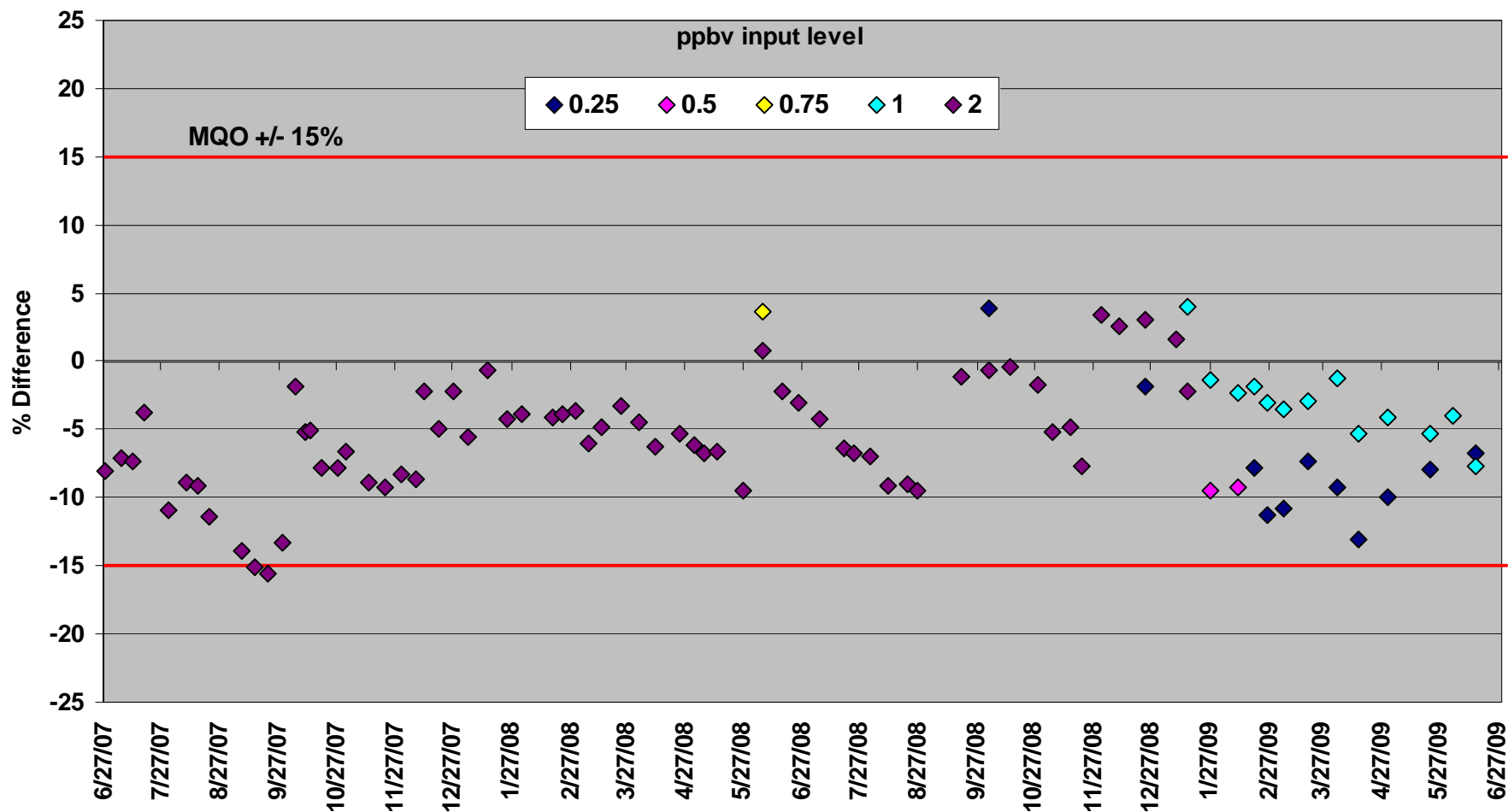
- QAPP approved by EPA-New England
- Routine performance audit
  - MQO +/-15% Difference
- Biannual independent accuracy audit
  - “second source” gas standard
  - Independent dilution calibrator, zero air system
  - MQO +/-20% Difference
- Data capture
  - Quarterly DQO: 75%



## Synspec GC955 Performance Audit Responses for Benzene at Various Inputs Levels (ppbv) July 2007 - June 2009



# Synspec GC955 Performance Audit Results for Benzene at Various Input Levels (% Difference) July 2007 - June 2009



**CV= 5.2% (Based on Equation 2 from 40CFRPart58, App.A)**



# Synspec GC955

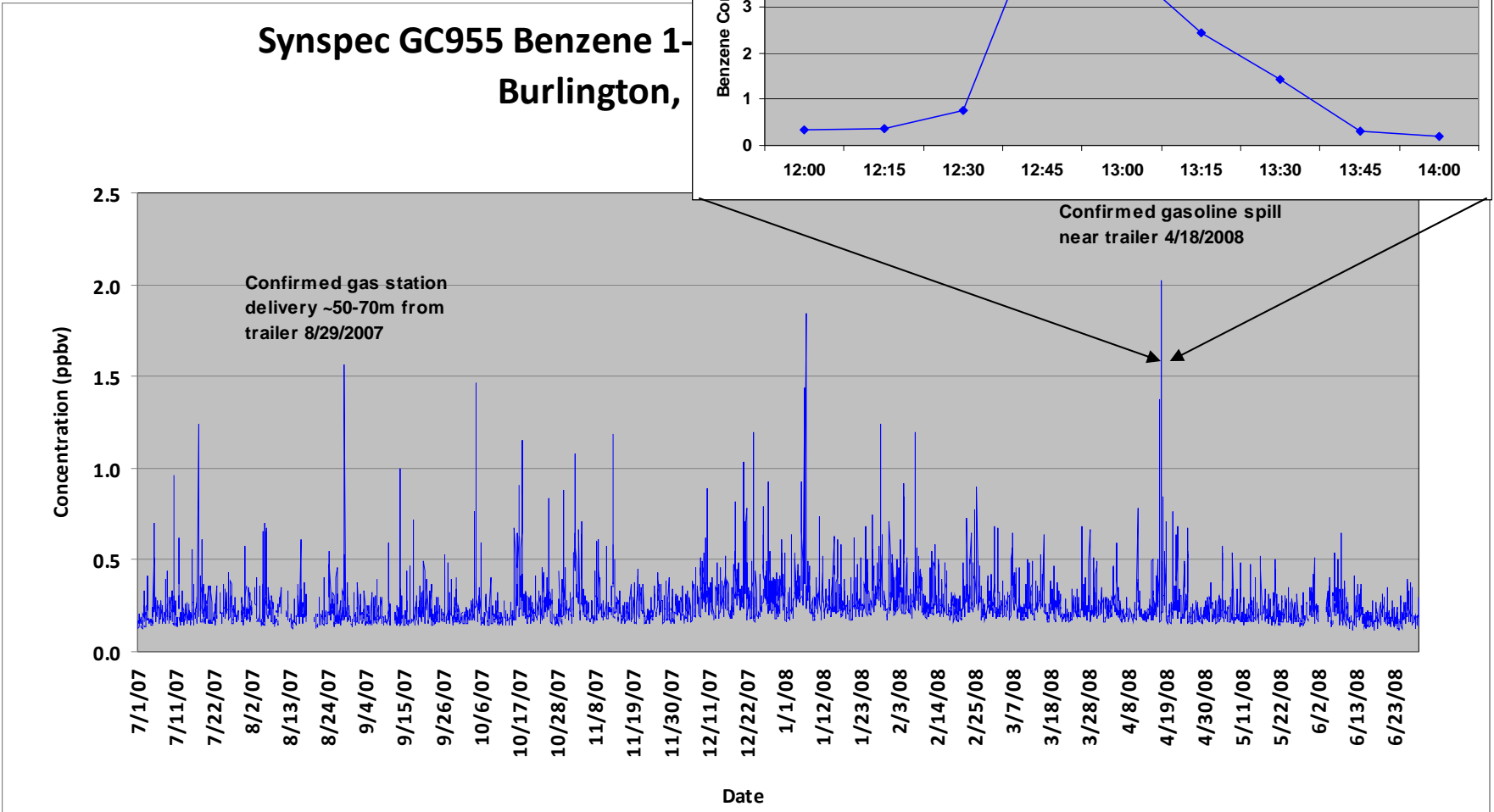
## Independent Accuracy Audit Results for Benzene

	Input (ppbv)	Response (ppbv)	% Diff.
<b>8/31/07</b>	<b>2.71</b>	<b>3.01</b>	<b>11.1</b>
<b>4/24/08</b>	<b>3.00</b>	<b>3.01</b>	<b>0.3</b>
<b>8/3/08</b>	<b>2.02</b>	<b>2.00</b>	<b>-1.0</b>
<b>5/12/09</b>	<b>1.08</b> <b>0.54</b>	<b>1.01</b> <b>0.50</b>	<b>-6.5</b> <b>-7.4</b>



# Benzene 1-Hour Average Local Scale Grant Study

Based on 15-minute values; 94% Valid Data

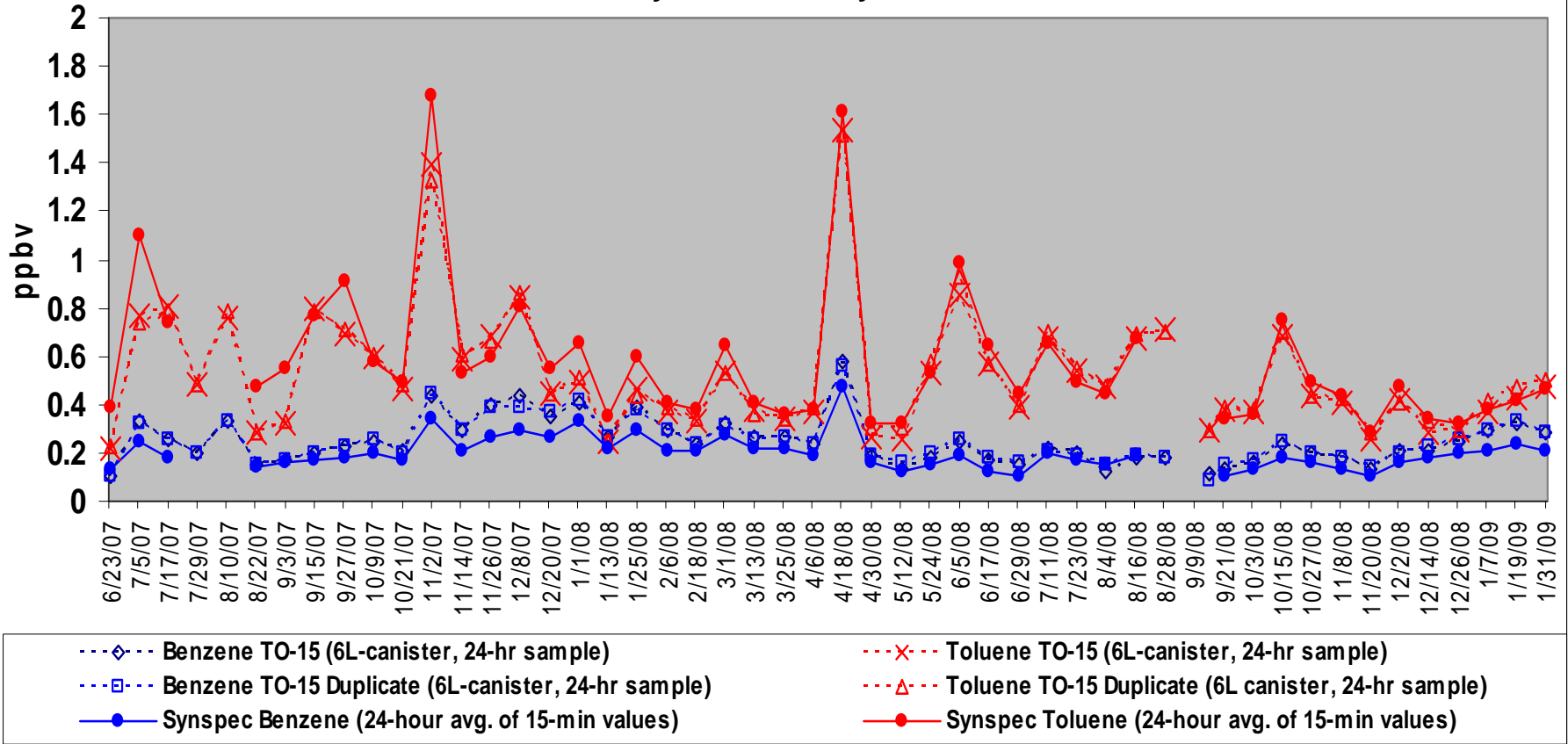




# Comparison of Synspec GC955 to TO-15 Canisters

## Benzene and Toluene 24-hour Averages Collocated (1/12th day) at Burlington, Vermont

### July 2007-January 2009



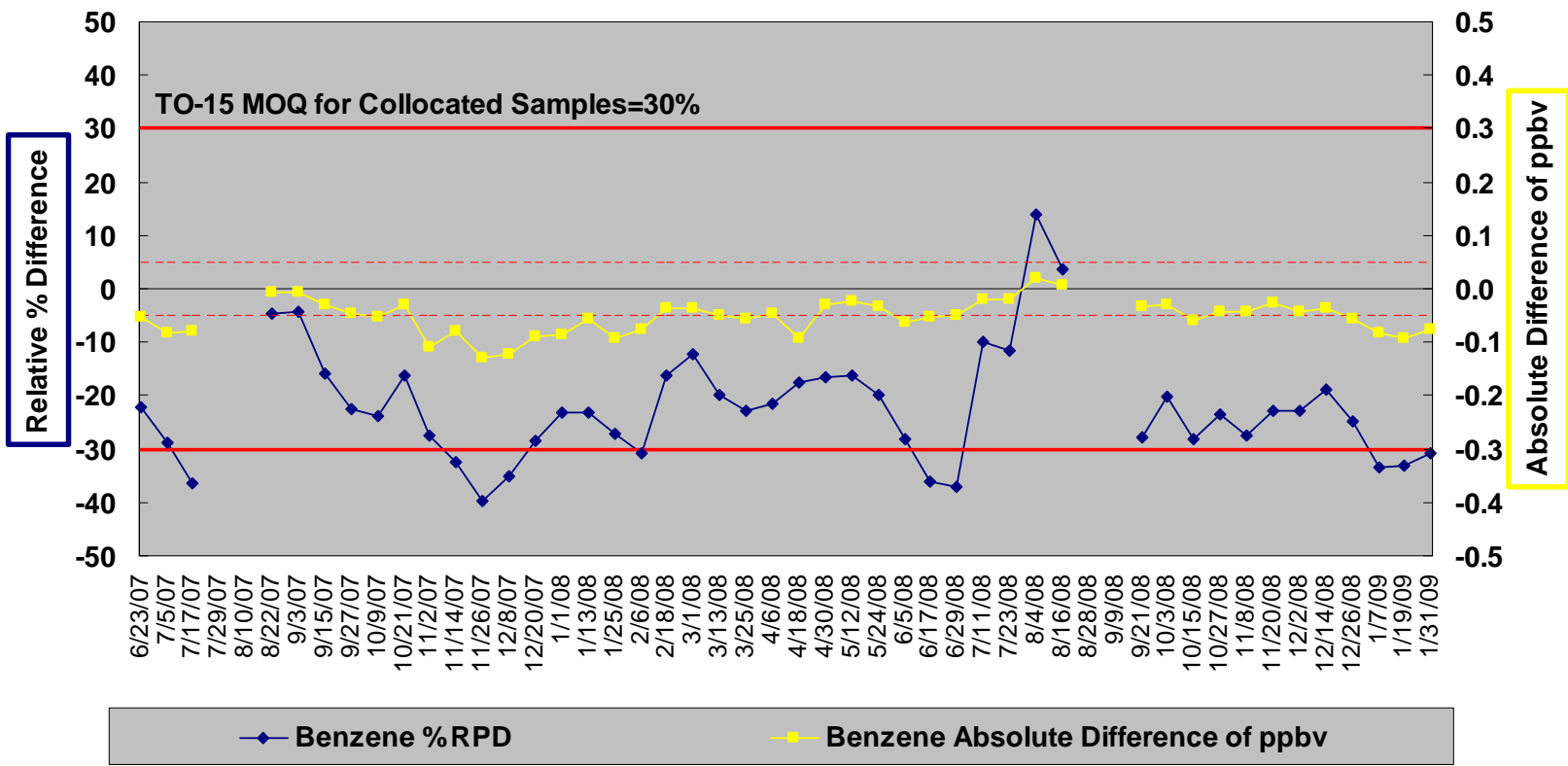
**Synspec 24-hr averages based on average of 96 separate 15-minute values for each 1/12<sup>th</sup>-day run day; TO-15 results based on individual GC/MS analysis of 24-hour canister sample**



# Comparison of Synspec GC955 Benzene Results to TO-15 Canisters

## Relative % Difference & Absolute Difference of ppbv

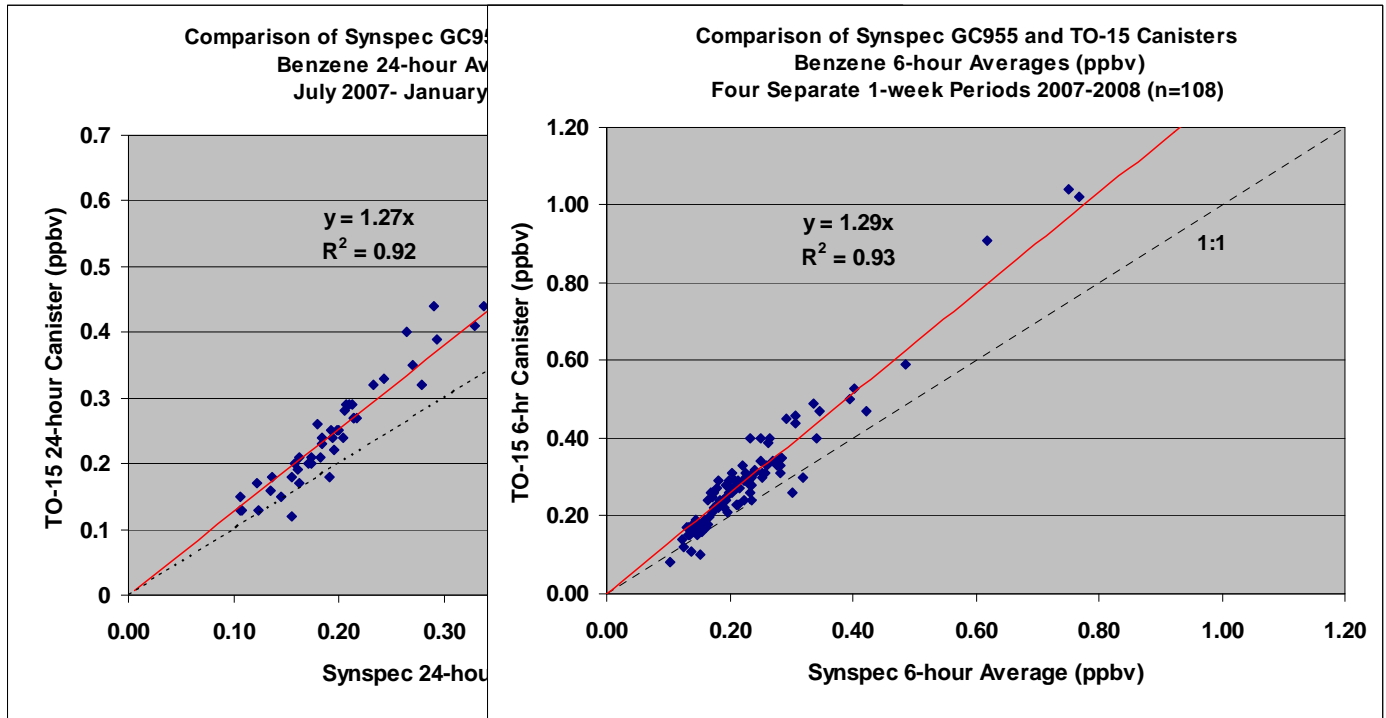
### 24-hour Averages Collocated (1/12th day) at Burlington Site July-2007 thru January-2009



**Mean Absolute Difference = -0.05 ppbv**  
**CV = 17%** (Based on NATTS Equation 2.1.2)



# Synspec GC955 Compared to TO-15 Canisters (Continued)



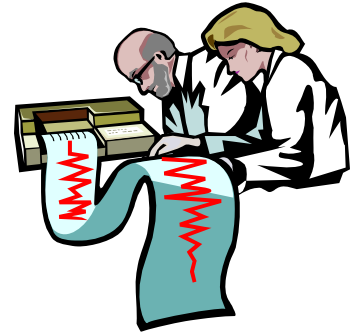
# Summary & Observations

- **Synspec is an Enhancement to Air Toxics Monitoring program**
  - Well designed and reliable
  - Consumables & maintenance reasonable
  - Provides real-time, short-term benzene concentrations
  - Analytical precision, accuracy and sensitivity comparable to TO-15
  - Collocated results compare well with TO-15 & NATTS performance-based criteria
- **Performance & Data Quality/Learning Curve**
  - Requires time for analyzer and software familiarity
  - Trace level dilution calibrator improves low-level performance
  - Data review/validation more time intensive compared to “criteria” analyzers
- **Further Development & Study**
  - Continue to improve low-end sensitivity and accuracy
  - Evaluate implementation of “auto-linearization” program function
  - Streamline data management, review and validation techniques



# Acknowledgements

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- Michael Rijpkema, Synspec
- Wouter Lautenbach, Synspec



# Thank you, Opryland!

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