Evaluating Performance of Measurement Systems Configured for TO-15 Toxic Organics in Ambient Air and Other Bulk Gases

Randall Bramston-Cook
and
Edward Bramston-Cook

Lotus Consulting
Long Beach, California

Selected Targets for **California Human Health Screening Levels for Vapor Intrusion**

Chemical	Indoor – Residential (nmol/mol)	Soil Gas – Commercial (nmol/mol)
Benzene	0.026	38.5
Carbon Tetrachloride	**0.0095**	13.5
Naphthalene	0.014	20.2
Tetrachloroethene (PCE)	0.060	89
1,1,1-Trichloroethane (TCA)	420	**511,000 [sic]**
Vinyl Chloride	0.012	17.5
Xylenes	168	200,000

California PUC Target Levels for Toxics in Biomethane

Constituent of Concern	Trigger Level (µmol/mol)	Upper Action Level (µmol/mol)
total Dichlorobenzenes	0.95	24
Ethylbenzene	6.0	150
n-Nitroso-di-n-propylamine	**0.0061**	0.15
Vinyl Chloride	0.33	8.3
Hydrogen Sulfide	22	1,080
Methacrolein	0.37	18
Alkyl Sulfides	12	610
Toluene	240	**12,000 [sic]**

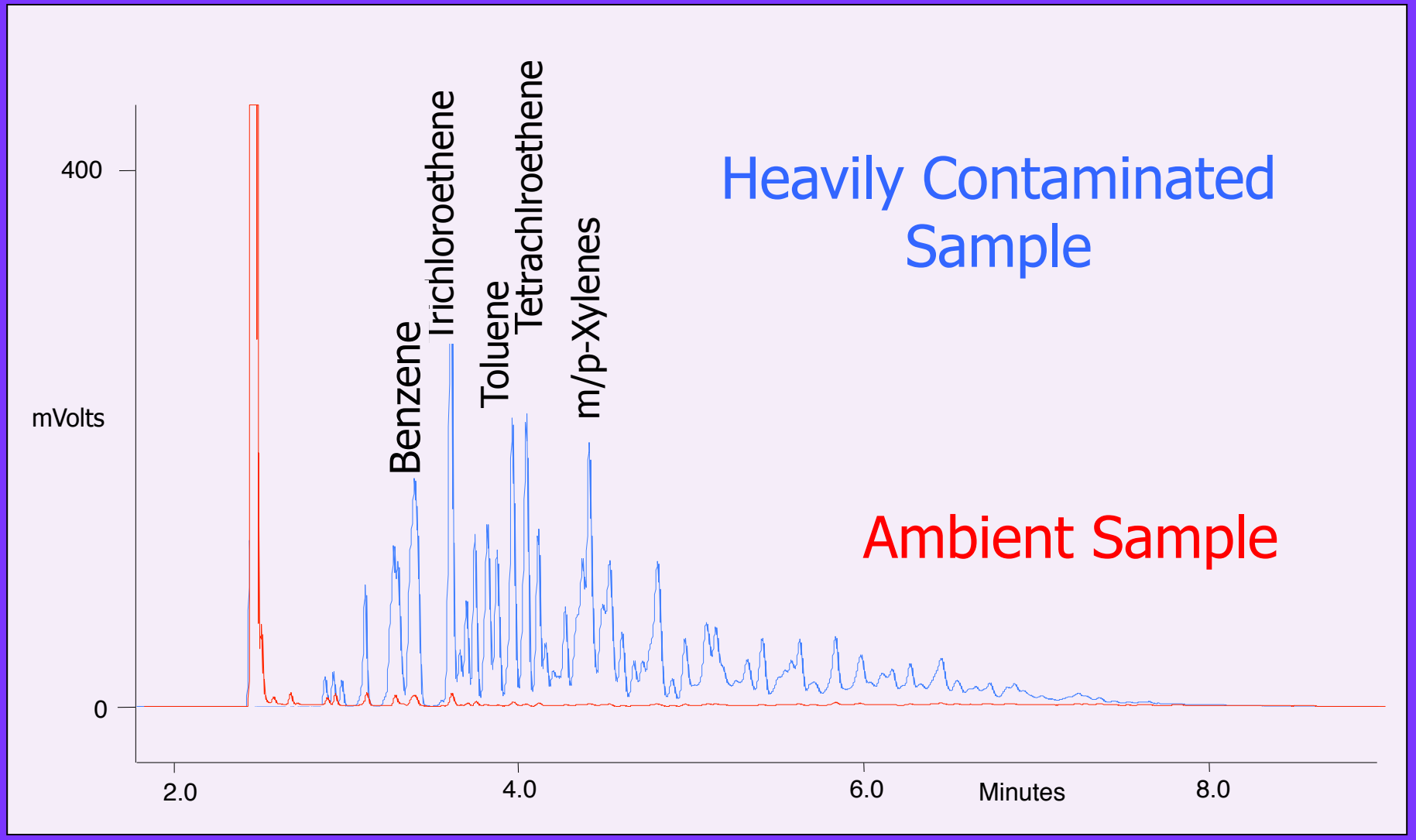
Translation of Units to IUPAC Molar Concentrations

Ratio of Analyte to Total	Invalid Reporting Units	Molar Units for Gases
1:100	%	cmol/mol
$1:10^{6}$	ppm	µmol/mol
$1:10^{9}$	ppb	nmol/mol
$1:10^{12}$	ppt	pmol/mol
$1:10^{15}$	ppq	fmol/mol
$1:10^{18}$	---	amol/mol (atto)

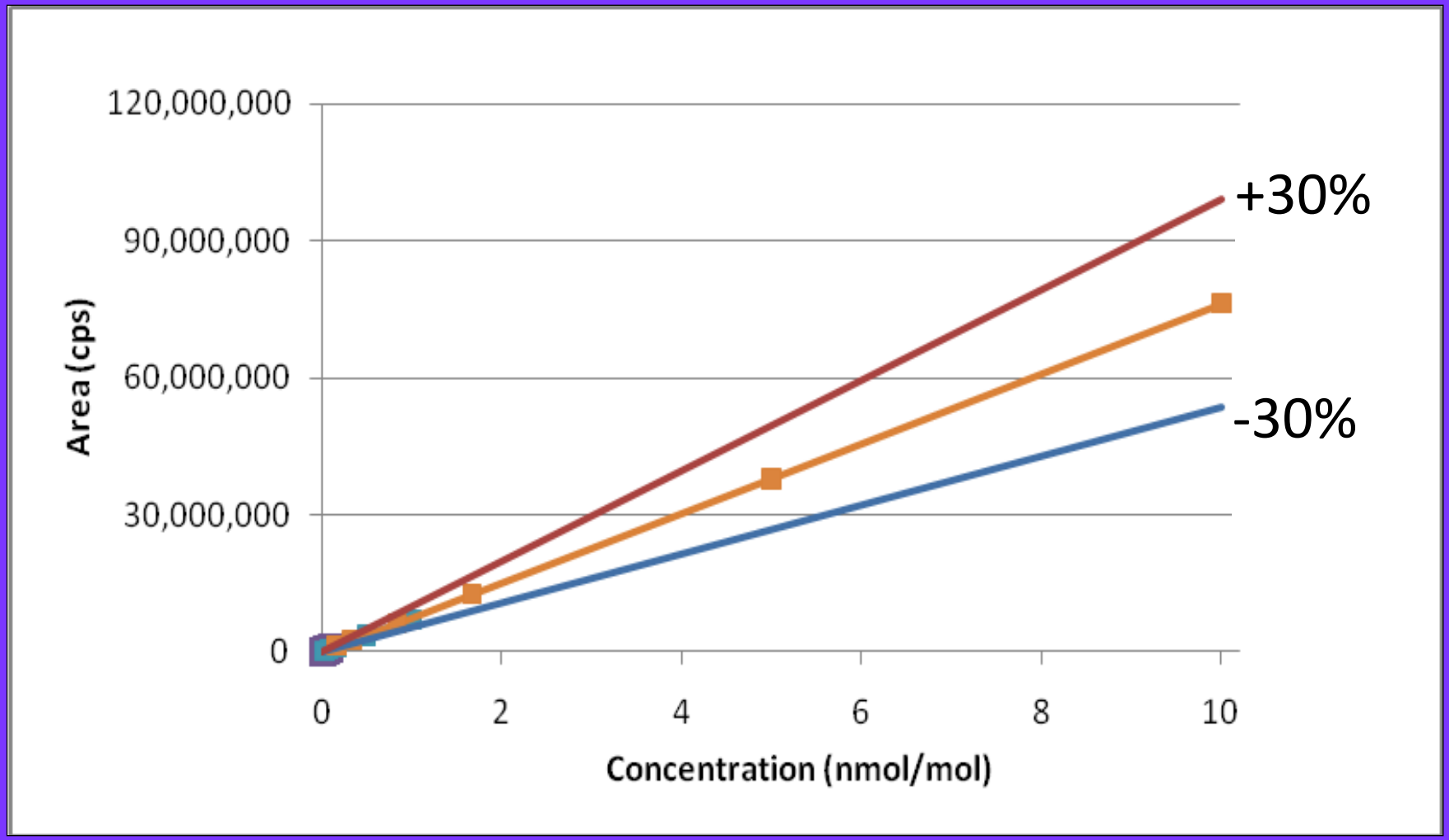
Prescreen with FID

- Target concentrations widely variable
- Many GCMS system limited to linear range < 1,000
- Misguess on expected level mandates tedious reruns
- Rapid prescreen anticipates contamination level

FID Chromatograms of Sample Prescreens



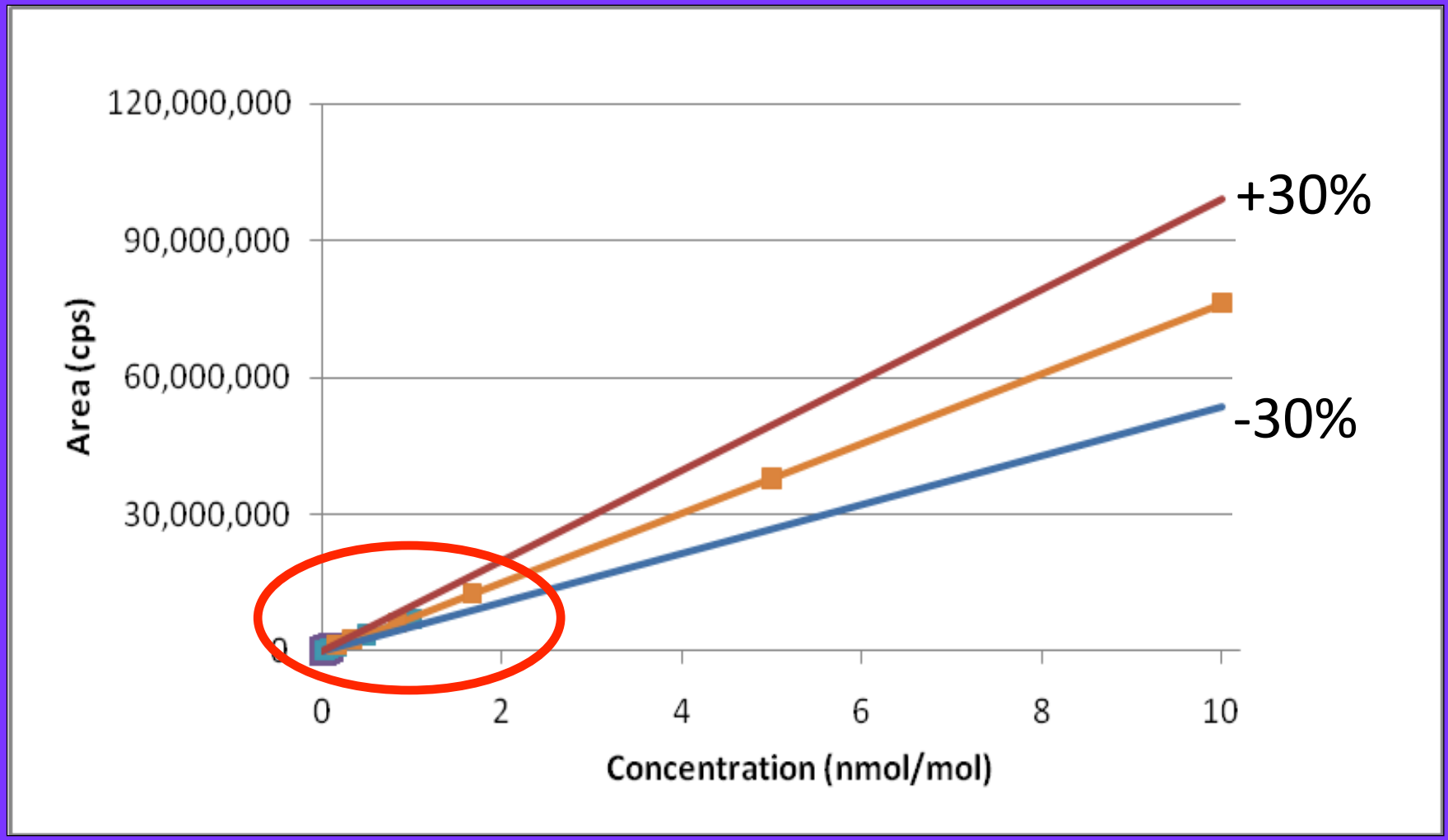
Typical Cartesian Calibration Plot



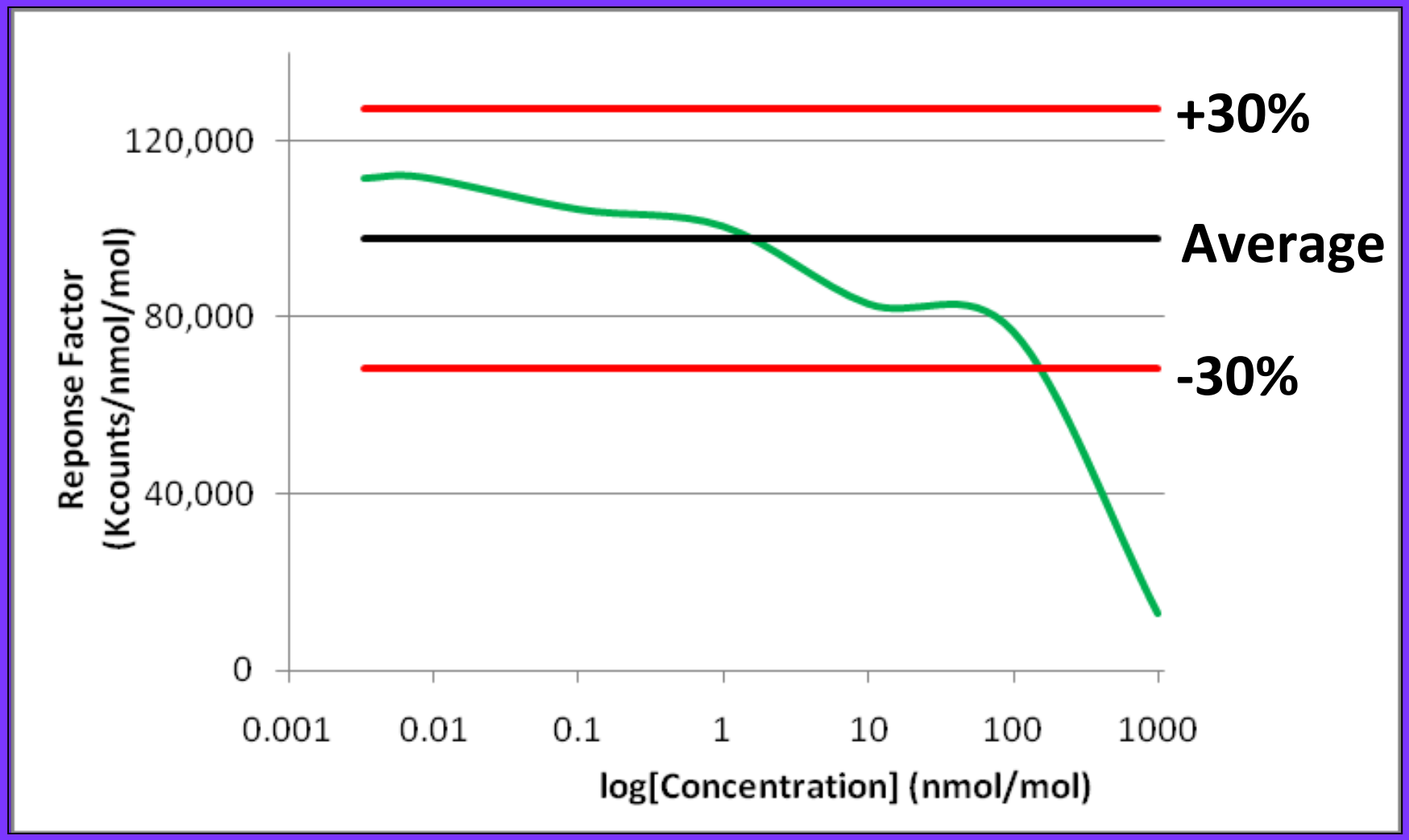
Cartesian Plots

- Heavily weighted visually to high concentrations
- Difficult to see deviations at low concentrations
- Severely limited display of wide dynamic range

Typical Cartesian Calibration Plot



Plot of Response Factor versus log[concentration] for Propene



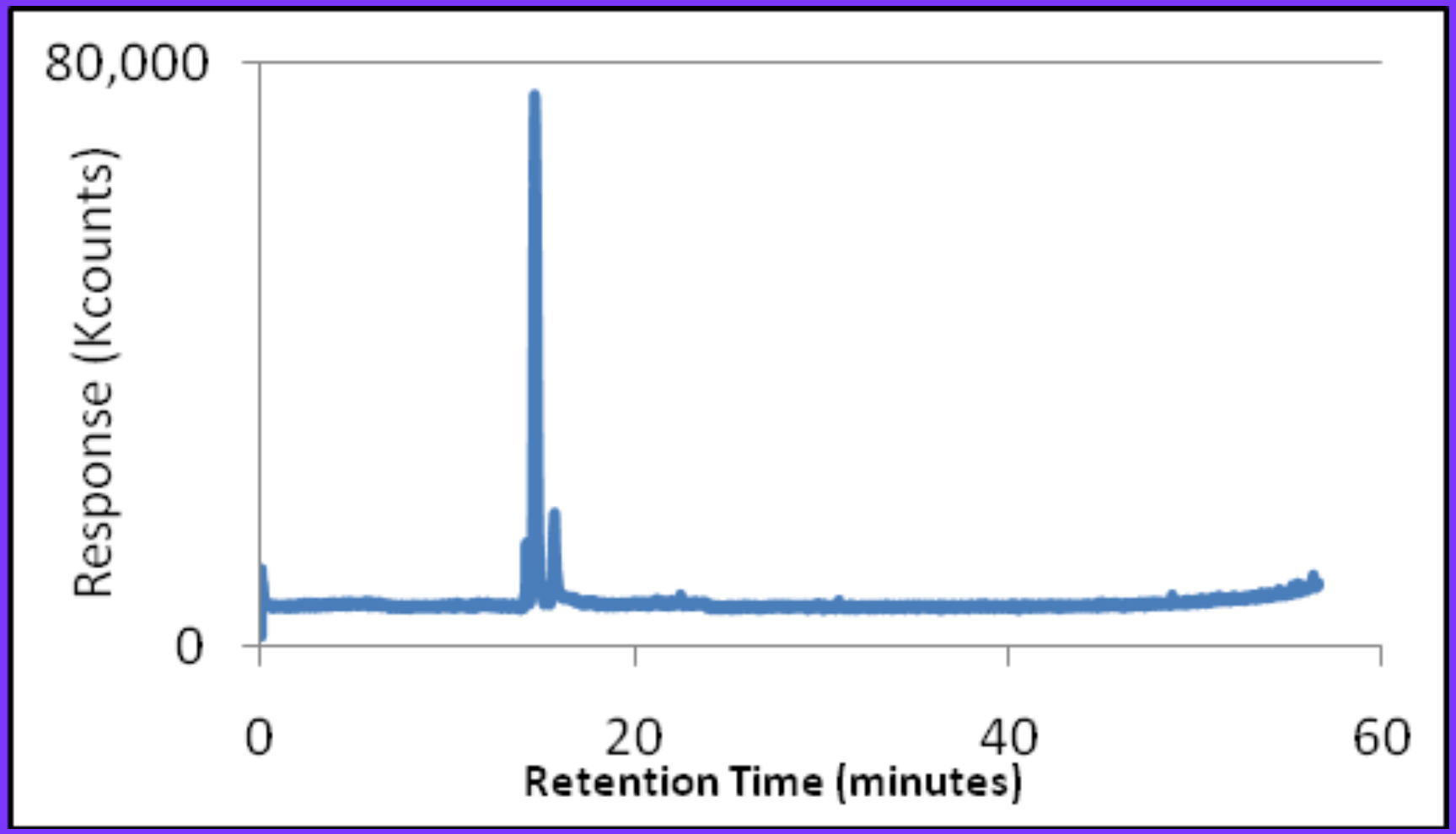
Response Factor versus log[concentration]

- Equal Weighting to low and high levels
- Easy to assess linearity over huge range
- Accurate assessment of TO-15 linearity mandate

Nitrogen Blank

- System contributions to low level measurements
- Possible sources:
  - Backflow of high concentration samples
  - Impure purge and carrier gases
  - System contamination
  - Thermal degradation of Tenax
- Must be lower than Detection Limits

Total Ion Chromatogram of Nitrogen Blank



Typical Levels in N_2 Blank

Analyte	Blank Levels (pmol/mol)
Propene	0.10
Ethanol	0.52
Benzene	0.15
Hexachlorobutadiene	0.14

Sample Carryover

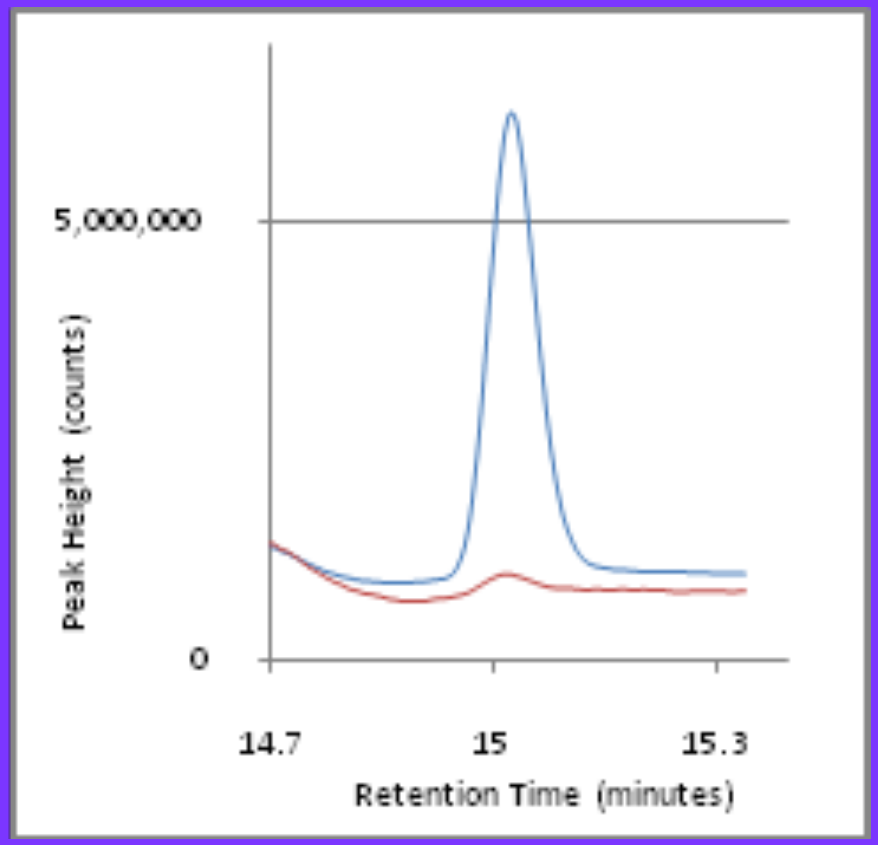
- Can add to subsequent low level samples
- Sources:
  - Unswept dead volumes
  - System contamination from high sample
- Continuous purge of all sample lines
- No cold spots

Typical Carryover after 1 µmol/mol

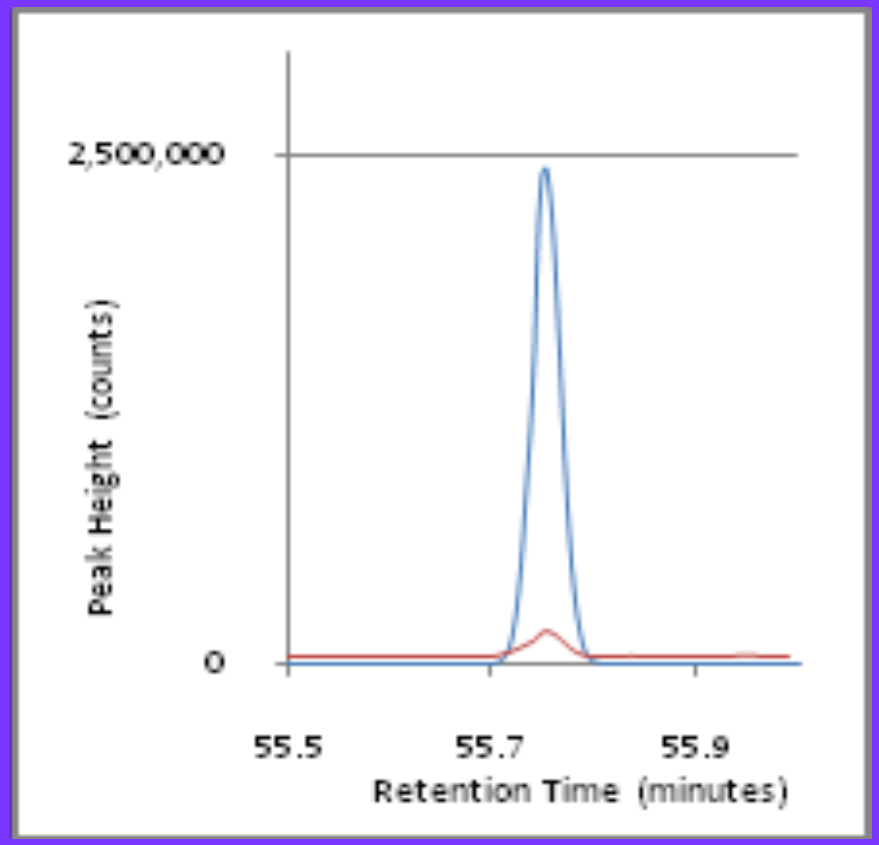
Analyte	Carry-over
Propene	< 0.008%
Ethanol	< 0.112%
Benzene	< 0.015%
Hexachlorobutadiene	< 0.007%

SIM Chromatograms at 3.3 pmol/mol, with N_2 Blanks

Propene



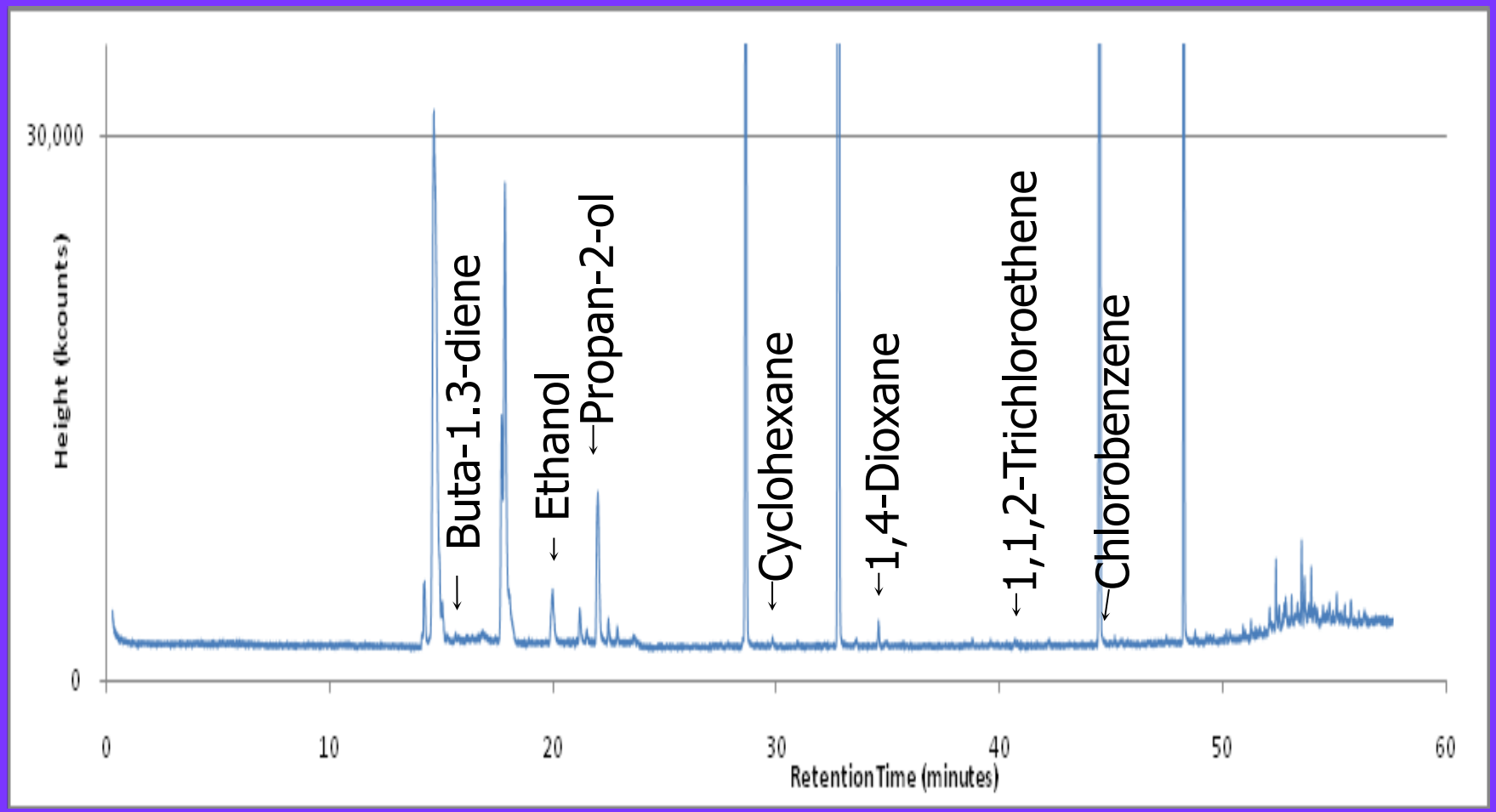
Hexachlorobutadiene



Typical Detection Limits

Analyte	Detection Limit (pmol/mol)
Propene	0.4
Ethanol	3.8
Benzene	0.9
Hexachlorobutadiene	2.5

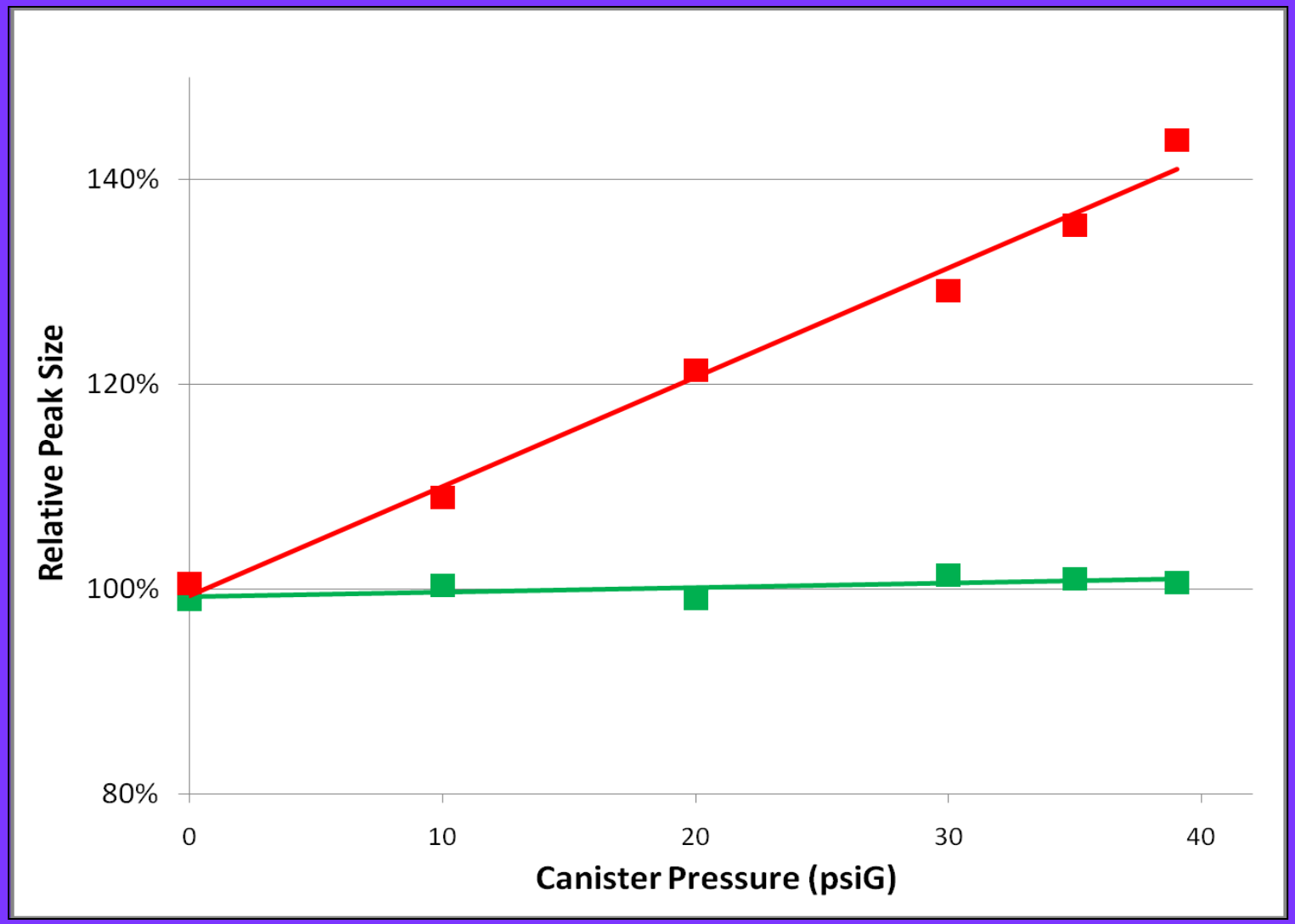
Detected Analytes in Internal Standard



Detected Analytes in Int Std

Analyte	Concentration (pmol/mol)
Buta-1,3-diene	20
Ethanol	72
Propan-2-ol	203
Cyclohexane	18
1,4-Dioxane	66
1,1,2-Trichloroethene	17
Chlorobenzene	18

Peak Size **without** vs **with** Regulator



Effects without Regulator

- High pressure canisters read too high
- Control samples show “degradation” over time, but return to “high” values after recharge

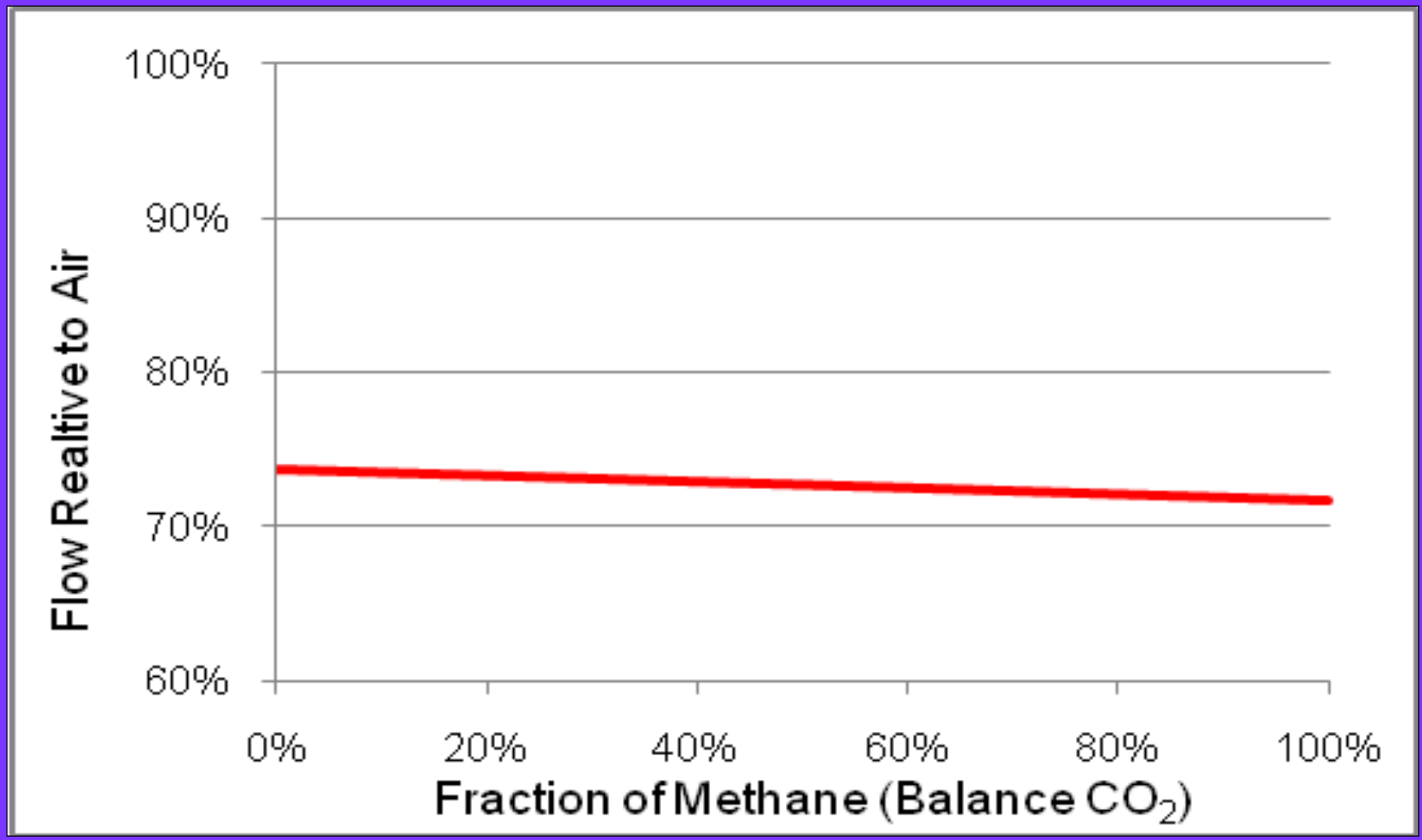
Samples Below Atmospheric

- Volume improperly measured by MFC
- Lab air can be sucked into sample loading process

Mass Flow Controller Performance

- Calibrated to specific bulk gas - typically air
- Change in bulk composition will impact measured flow
- Corrections possible if bulk gas is known and predictable
- Standards usually not matching sample matrix

Relative MFC Flows with varying CH_4/CO_2, Relative to Air



Mass Flow Controller Performance

- Biogas - varying levels for CH_4 and CO_2
- Without corrections, biogas/biomethane results reported ***too low***
- Fixed volume sample loop
  - true volumetric measure
  - independent of bulk gas

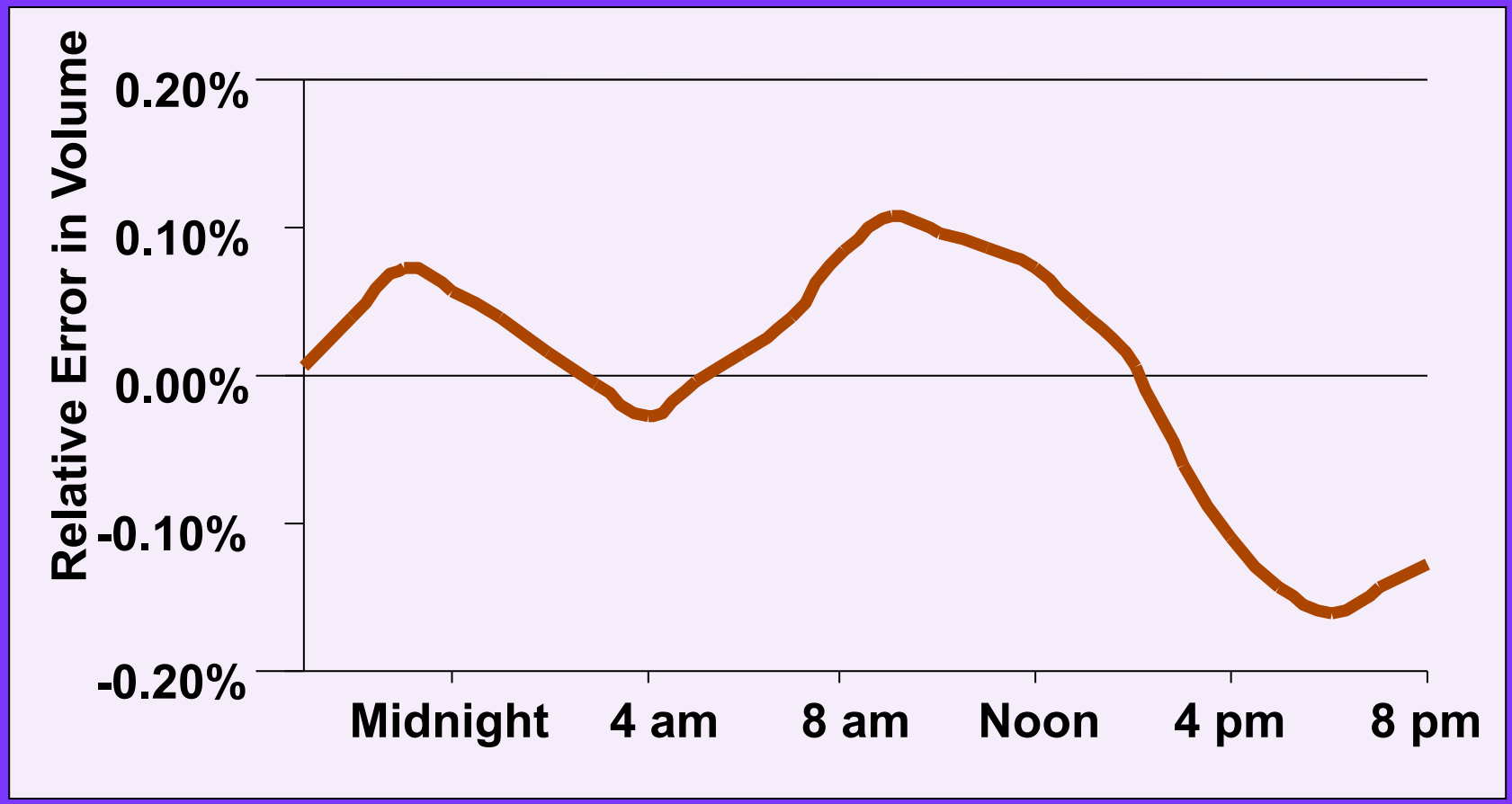
Atmospheric Pressure Effects on Sample Loop Volume

- Boyle-Mariotte's Law relates volume and pressure
- Changes in atmospheric pressure can alter volume in loop
- Pressure cycles twice a day

Atmospheric Pressure Effects on Sample Loop Volume

- Extremes:
  - +7% (1968, Agata, Siberia)
  - -14% (1979, Western Pacific)
- Typical variation: 0.25% per day
- Releasing loop pressure to atmosphere minimizes sample pressure effect

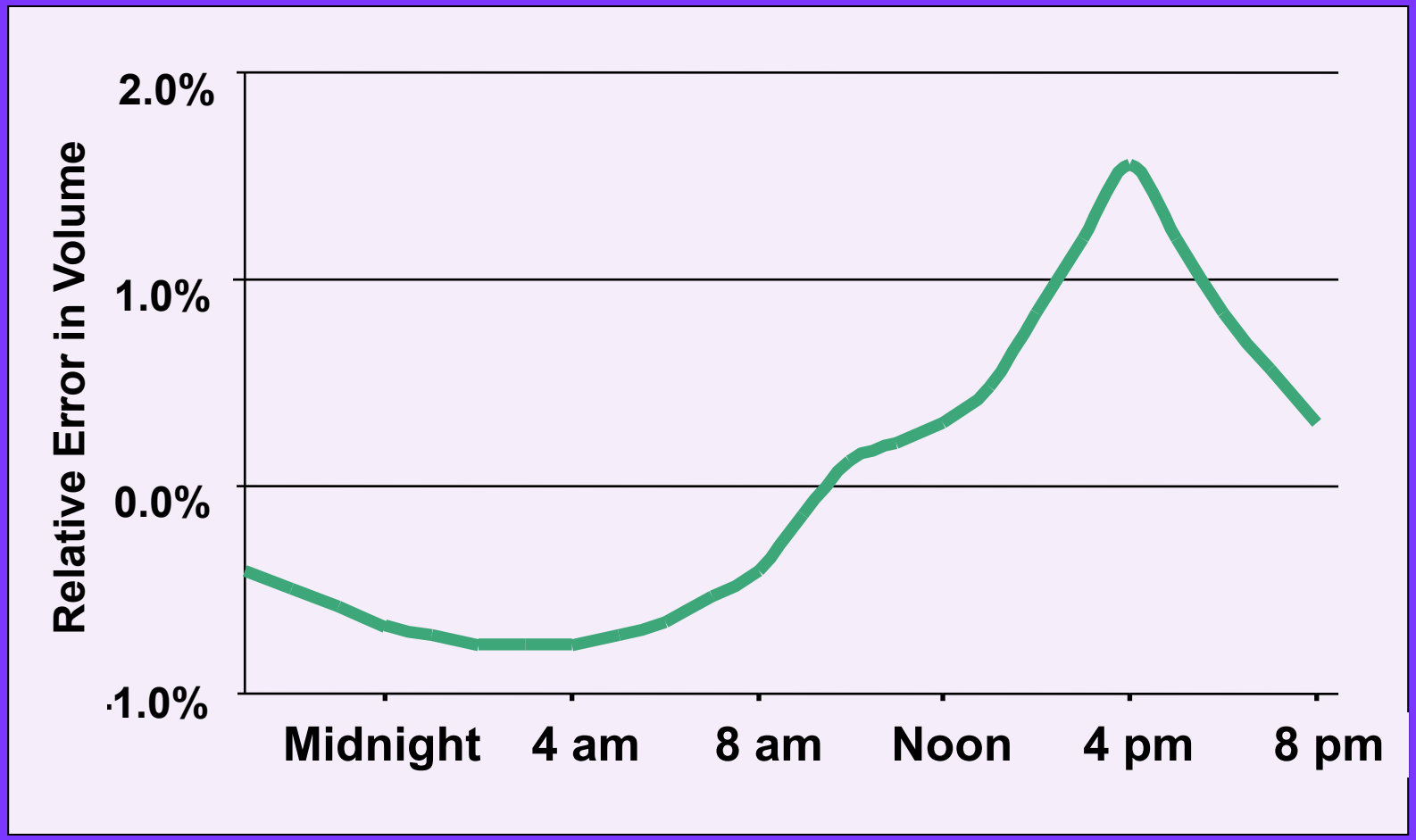
Errors in Sample Loop Volume with Atmospheric Pressure



Effects of Laboratory Temperature on Sample Loop Volume

- Charles-Gay-Lussac's Law - volume to temperature
- Changes in sample loop temperature typically > 2.5%
- Holding loop in controlled oven above ambient minimizes effect

Errors in Sample Volume with Varying Ambient Temperature



Summary

- Dynamic range now capable of measurement over 10,000
- Detection:< single digit pmol/mol
- Nitrogen blanks well below LOD

Summary (cont.)

- Internal standards with added targets - **not** recommended
- Biogas and biomethane accurately analyzed with fixed volume sample loops
- Prescreen with FID avoids sample reruns

Contact Information:

Lotus Consulting - 310/569-0128

randy@lotusinstruments.com

edward@lotusinstruments.com

website: www.lotusinstruments.com