

Selecting Accurate Calibration Gases - Beyond The Obvious

Air Liquide America Specialty Gases



Or,
**Bad Calibration Gas -
Why Should I Care?**

Air Liquide America Specialty Gases



Outline

- The Meaning of Accuracy
- The Cost of Inaccuracy
- Achieving Accuracy in Calibration Mixtures
- The Dollarized Advantage of Accuracy

The Dollarized Advantage ...



- Cal Gas Accuracy Affects Operating Cost
- Small Improvements in Cal Gas Accuracy
Can be Worth **Big \$\$** in Cost Avoidance
- Accurate Cal Gases Yield True Cost Savings

Calibration Gas Certificates

- **Concentration: "100 ppm NO in N₂"**
 - ▣ Measured Concentration of Component

- **Accuracy: "+ / - 1%"**
 - ▣ Estimated Deviation from True Value

- **Traceability: "NTRM-1684"**
 - ▣ Citation of Reference Standard(s) Used



The Meaning of Accuracy

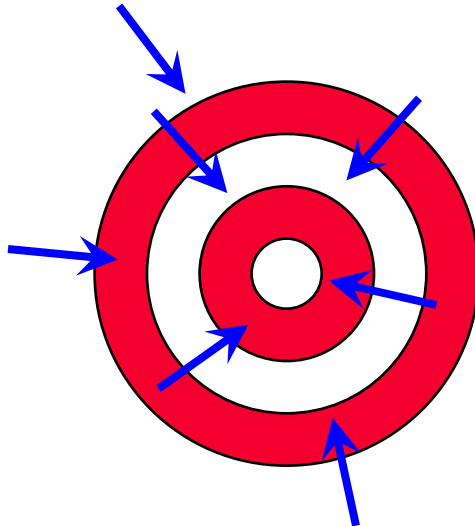
■ Accuracy

- ▣ A statistical estimate of how closely a measured value approaches the **“true value”**.

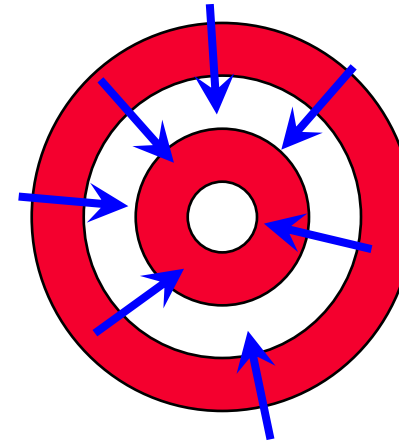
■ “+ / - 1% Accuracy”

- ▣ “Our certified value is within 1% of the **true value**, having evaluated all known sources of underlying measurement uncertainty.”

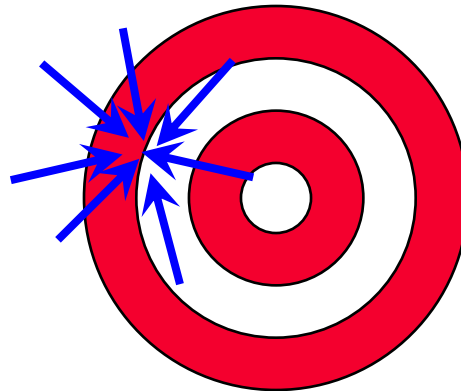
Accuracy vs. Precision



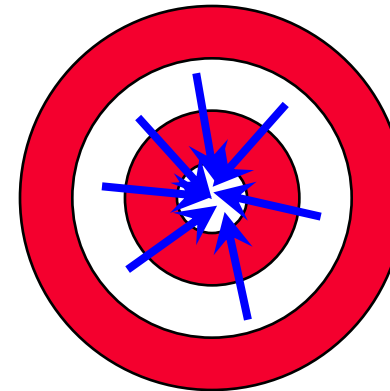
■ Neither Precise nor Accurate



■ Accurate, But Not Precise



■ Precise, But Not Accurate



■ Precise and Accurate

Sources of Cal Gas Error

■ “Basic” Uncertainty Sources

| | |
|------------------------|------------|
| ▣ Reference Material | 0.5 - 1.5% |
| ▣ Analyzer Calibration | 0.1 - 0.8% |
| ▣ Analyzer Precision | 0.1 - 0.5% |

■ “Extra” Uncertainty Sources

| | |
|----------------------------------|-----------|
| ▣ Bad Cylinder Prep | 0 - 5% |
| ▣ Contaminated Raw Materials | 0 - 10% |
| ▣ Analyzer Interferences | 0.1 - 5+% |
| ▣ Correction Factors | 0.1 - 2% |
| ▣ GMIS / “Daisy Chain” Standards | 0.5 - 2% |

Minimizing Cal Gas Error

■ “Basic” Uncertainty Sources

- ▣ Reference Material (U_s) 0.5%
- ▣ Analyzer Calibration (U_c) 0.4%
- ▣ Analyzer Repeatability (U_p) 0.2%

■ “Propagation of Error” Calculation

- ▣ Accuracy = $\pm \sqrt{(0.5)^2 + (0.4)^2 + (0.2)^2} = \pm 0.71 \%$

- Control the Main Uncertainty Contributors
= Control the Overall Cal Gas Accuracy

Air Liquide Toolbox for Accuracy



- **Cylinder Preparation**
- **Raw Material Advantage**
- **Blending Advantage**
- **Instrumentation Advantage**
- **Reference Standards Advantage**
- **Traceability Advantage**

Cylinder Preparation Advantage



■ ALTech[®] and Aculife[®] Cylinder Treatments

- ▣ Metal Surface Finishing
- ▣ Physical Treatments (Evacuation and Baking)
- ▣ Gas / Gas Mixture Treatments
- ▣ CVD and Chemical Modifications of Surface

■ Results

- ▣ Rigorous Exclusion of Oxygen and Moisture
- ▣ Elimination of Component “Stick” and “Drop Out”
- ▣ Stability of Reactive Mixtures e.g., Low NO_x

Raw Material Advantage



- **World-Wide Sourcing of Pure Materials**
- **In-House Purification of Raw Materials**
- **In-House Manufacture of 99.995% NO**
 - ▣ Only Such Plant in North America
- **100% Analytical QC of Blend Components**

Air Liquide Blending Advantage



■ Acublend[®] Dynamic Blending

- ▣ Dynamic Blending with “Real-Time” Analysis
- ▣ Calibrated Process Analyzers / NIST Traceable
- ▣ Accuracy to +/- 1%
- ▣ Cylinder-to-Cylinder, Batch-to-Batch Reproducibility
- ▣ “Zero” Blend Tolerance

■ GravStat[™] Gravimetric Blending

- ▣ Statistically Controlled Gravimetric Blending
- ▣ Calibrated Scales / NIST Traceable (by Weight)
- ▣ Accuracy to +/- 0.1% or Better
- ▣ Statistical Calculation of Concentration and Accuracy

Instrumentation Advantage



■ Interference-Free™ Instrument Platform

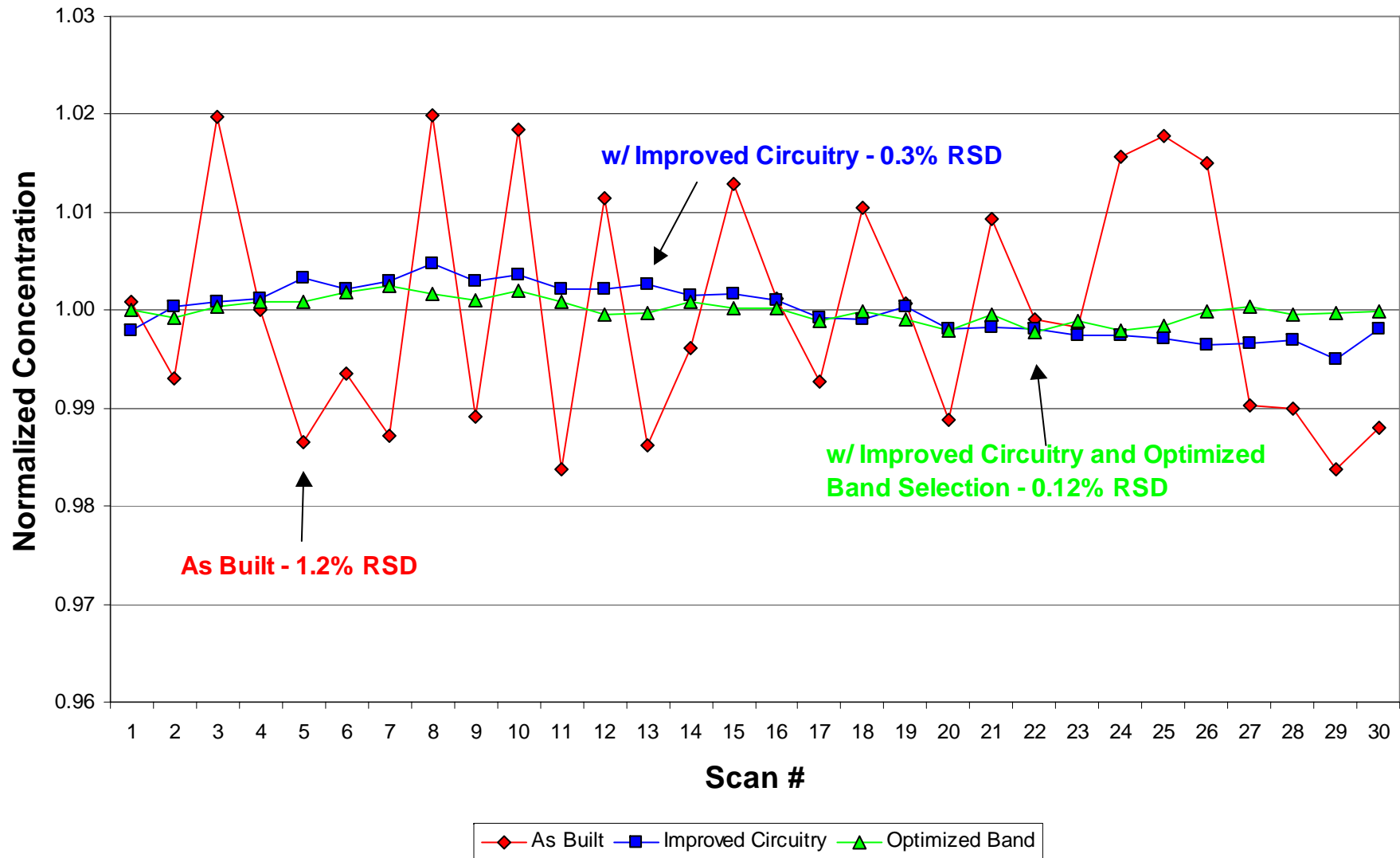
- ▣ \$2 MM Investment to Standardize All FTIRs
 - Full Automation of All FTIR Systems
 - Identical Systems in All ALASG Regions
- ▣ Development of Low Noise Circuitry
- ▣ 6 Months R&D on Improved Accuracy Analysis

■ Active Instrumentation R&D Program

- ▣ Evaluation of Newer Technologies (QCL, TDL, CRDS)
- ▣ Direct Collaboration with Instrumentation Developers

Air Liquide FTIR Optimization

Engineering Improvements on FTIR Precision



Air Liquide Standard Advantage



■ Large Inventory of Reference Standards

- ▣ SRM, NTRM and RGM Reference Standards (NIST)
- ▣ Individually Certified NIST SRMs
- ▣ PRM and CRM Reference Standards (NMI)

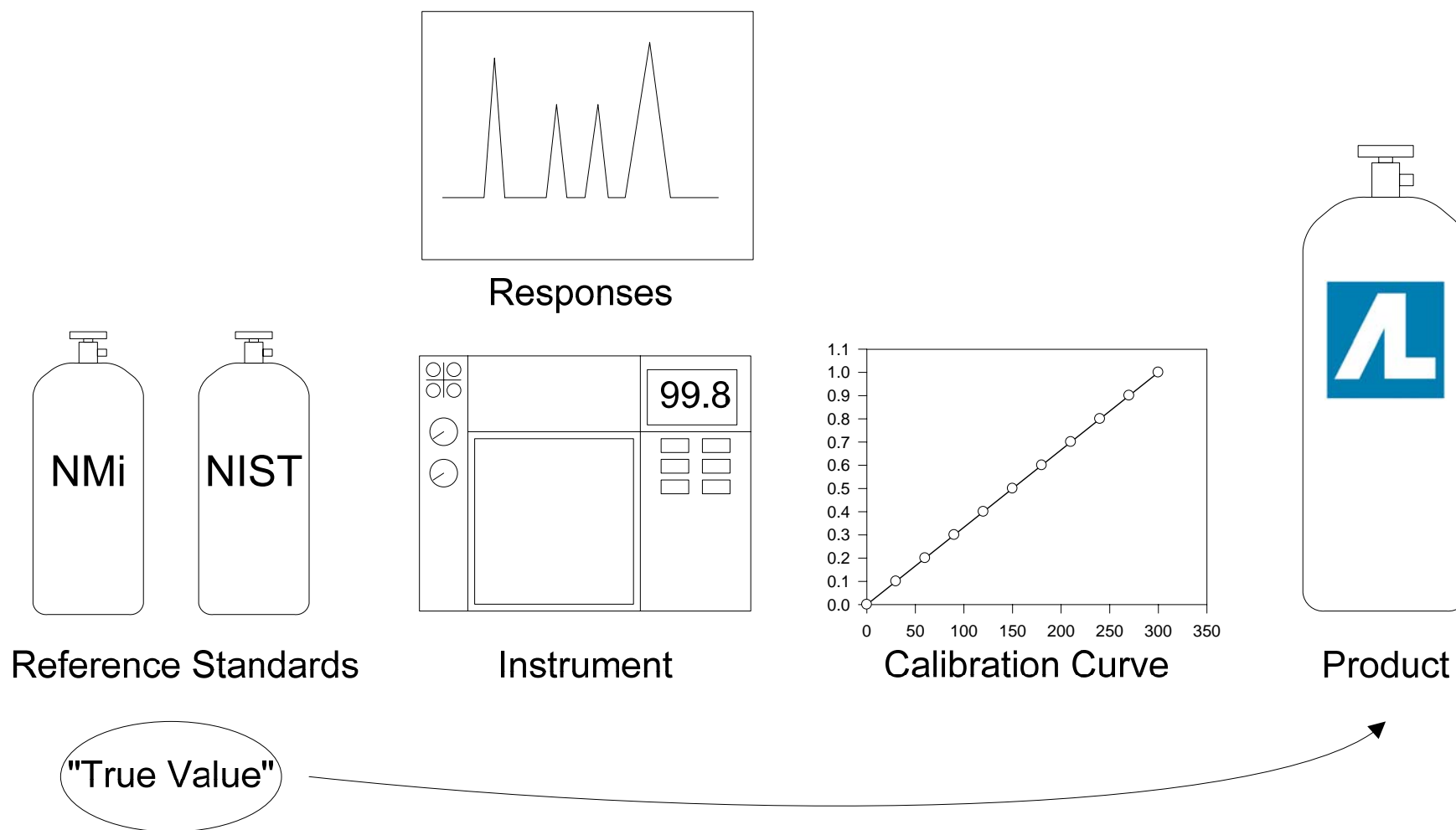
■ NIST Contractor for SRMs

- ▣ NIST SRM / NTRM Lot Control Standards
- ▣ NIST Primary Standards

■ Strong Metrology Institute Relationships

- ▣ NIST / NMI / NPL
- ▣ Declaration of Equivalence

Direct Analytical Traceability



Potential Cost of Inaccuracy

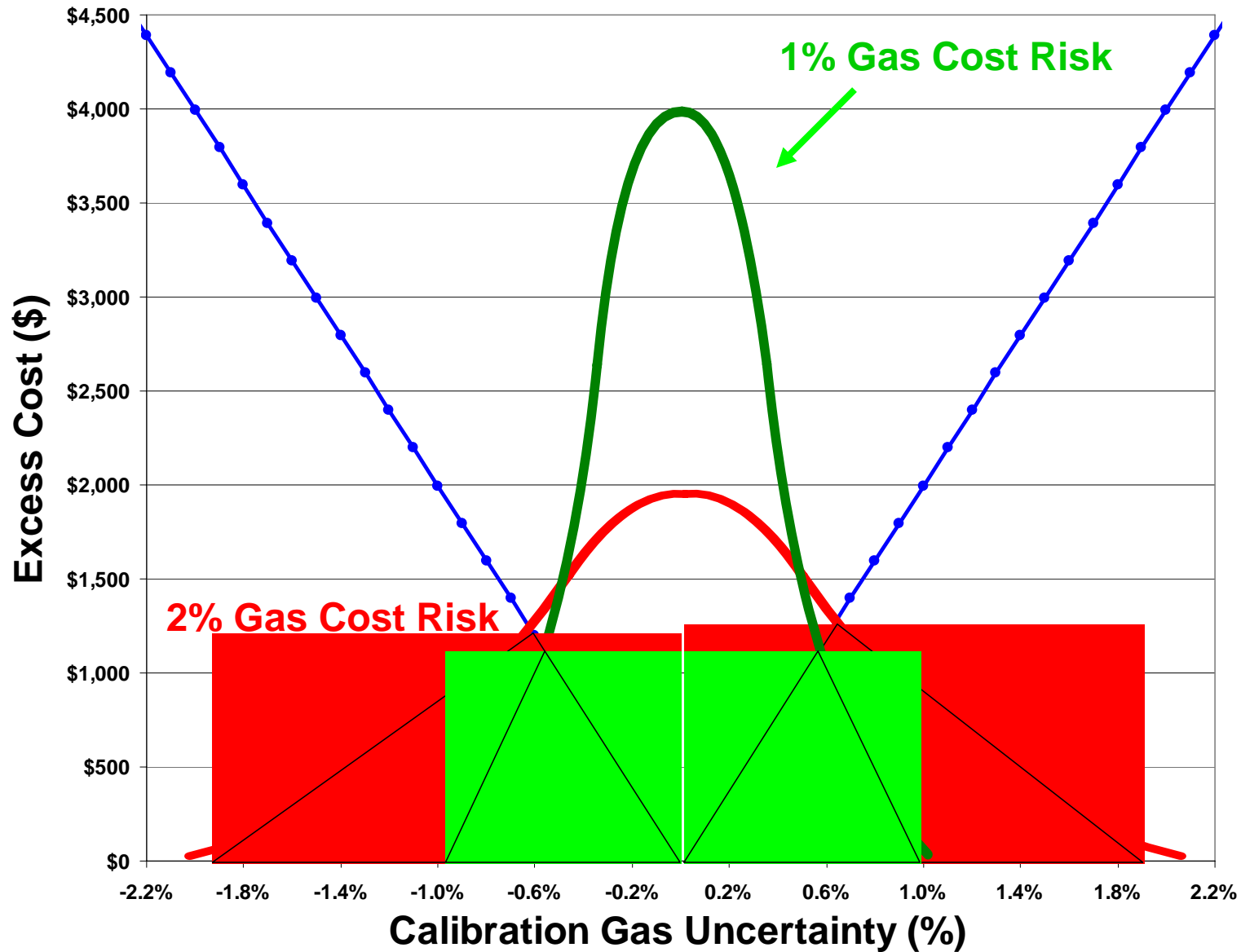


■ Customer Model Case

- One Emissions Test Cell
- Average Value per Operating Hour = \$1500
- Operating Regime 40 Hours per Week (8 x 5)
- Total Value of Business = \$3,000,000

| Source of Cost | Excess Cost |
|---|--------------------|
| Potential Vehicle Recalls (Voluntary and Mandatory) | \$ 110,000 |
| Emission Test Cell Down Time | \$ 48,000 |
| Emergency Technical Troubleshooting | \$ 17,680 |
| Excess Cylinder Inventory | \$ 17,120 |
| Emergency Gas Purchases | \$ 5,840 |
| Poor Supplier Service | \$ 960 |
| Grand Total - Annual Cost of Inaccuracy | \$ 199,600 |

Cost Risk of Cal Gas Accuracy



Cost Exposure Calculation

■ 1% Accuracy Gas

- ▣ "Over": $0.5 \times 1 (\%) \times \$1,000 (\$) = \500
- ▣ "Under": $0.5 \times 1 (\%) \times \$1,000 (\$) = \500
- ▣ Total Cost Exposure = \$1,000

■ 2% Accuracy Gas

- ▣ "Over": $0.5 \times 2 (\%) \times \$1,250 (\$) = \$1,250$
- ▣ "Under": $0.5 \times 2 (\%) \times \$1,250 (\$) = \$1,250$
- ▣ Total Cost Exposure = \$2,500

- Area of a Triangle = $1/2 * \text{Base} * \text{Height}$

Dollarized Value of Accuracy

■ Cost Exposure Related to Gas Accuracy

▣ 1% Gas = \$1,000

▣ 2% Gas = \$2,500

■ Dollarized Accuracy Difference = \$1,500

■ 2% Gas Has 2.5X More Cost Exposure

Key Takeaways



■ Air Liquide Cal Gases are More Accurate

- ▣ Greater Work Input and Attention to Detail
- ▣ Strict Control of Underlying Sources of Errors
- ▣ Assessment of Combined Impact of Errors

■ Proven Track Record

- ▣ Uniformly Positive Customer Results
- ▣ Success in Competitive Tests and Audits

■ Cal Gas Accuracy Directly Equates to Cost

■ Higher Accuracy Cal Gas Saves Money

- ▣ More Accurate Gas Reduces Excess Cost Exposure
- ▣ 2% Gas ~ **2.5X** More Costly to Use than 1% Gas

More Value from Air Liquide Offer



- **Consistent Calibration Gas Accuracy**
- **High Quality Companion Products**
 - ▣ Alphagaz Pure Gases and Support Mixtures
- **Metrology Services**
 - ▣ Cross Reference Service
 - ▣ "ReAL Time™" Gas Subscription Service
- **Equipment and Delivery Systems**
- **Cylinder Inventory Minimization**
- **eScott On-Line Services**
 - ▣ Folio Services, C of A's, MSDS's
 - ▣ Product Ordering and Data Management