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Status and Stability of NH3, HCl, and Hg Calibration Gases

HCl Gas Delivery Panel Systems

Albert Guitjens – Market Development Technologies Manager

Safety Message

- ***Never pick up a cylinder by the cap***

R&D Key Figures

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9 R&D locations

3 continents

278
Million €
innovation budget

1100
researchers
35 nationalities

~300
new patents

** 2014 key figures*

A Global R&D Network

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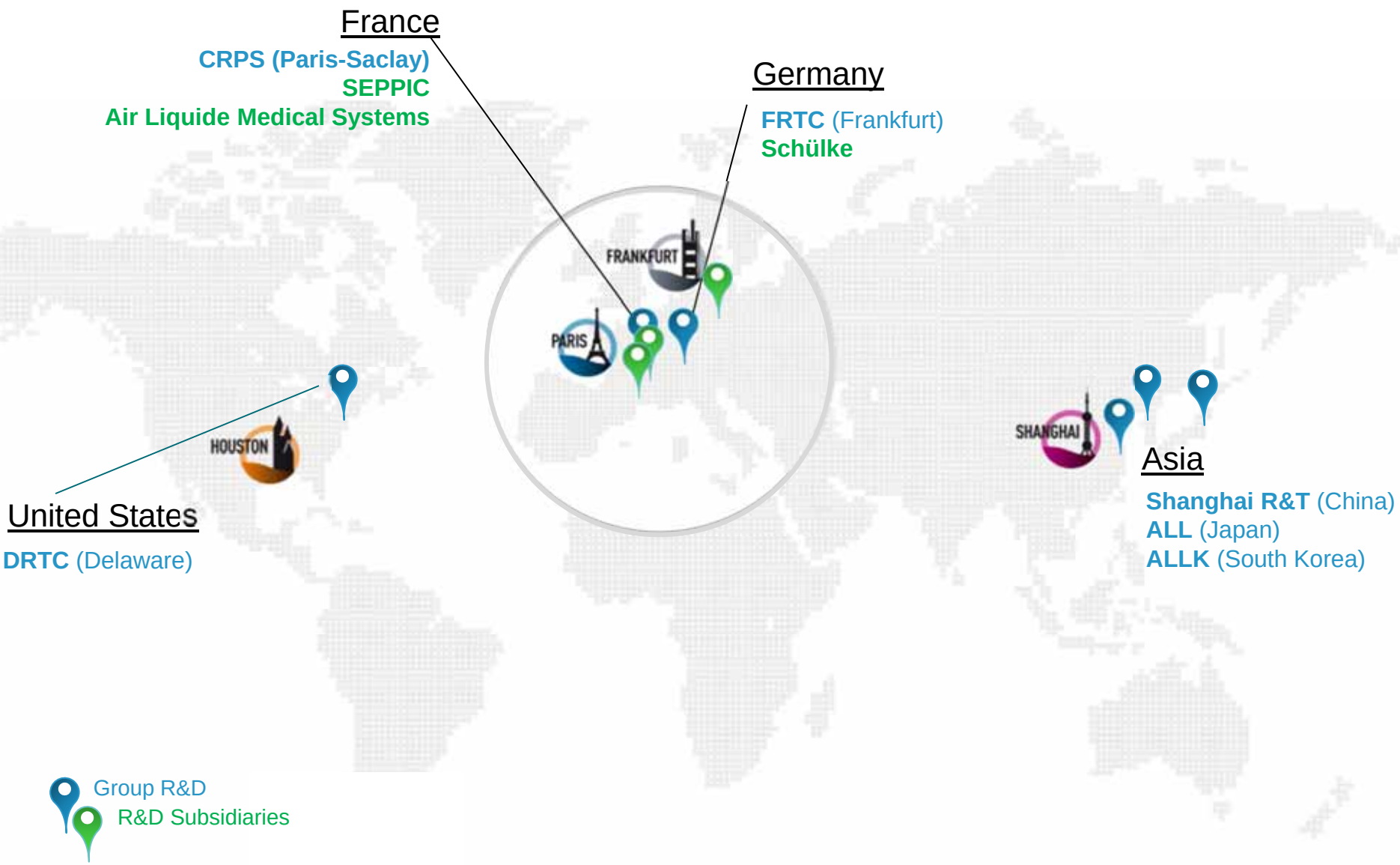


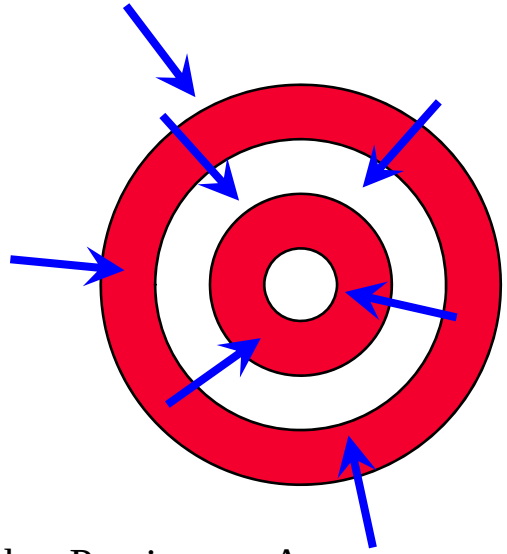
Background – Gas Mixtures, Analytical Accuracy, and Traceability

Tighter gas specifications and tougher regulations require elimination of any possible source of errors (artifacts) for improved measurements through accurate and consistent analysis

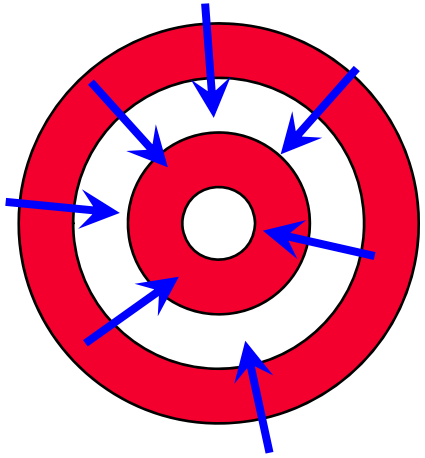
Analytical instrumentsfor reliable analysis, gas distribution equipment for consistent gas delivery, cylinder treatment technology and gas mixtures for accurate calibration are important to the process.

Gas manifolds and gas delivery systems are critical to protect the purity and integrity of the gases in use.

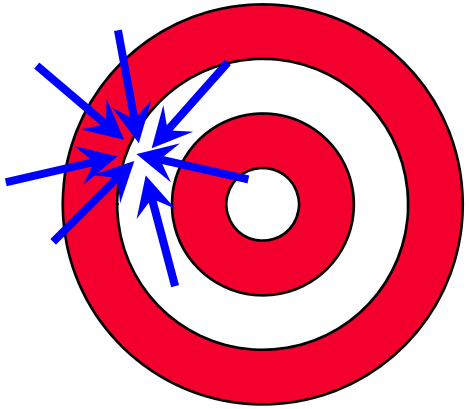
Accuracy vs. Precision



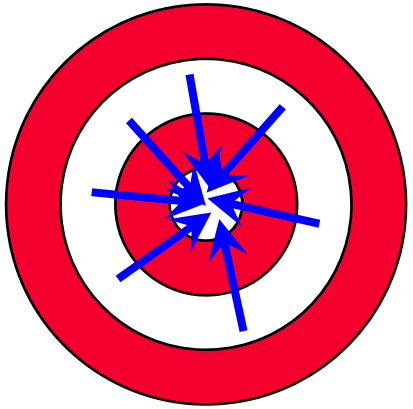
- Neither Precise nor Accurate



- Accurate, But Not Precise



- Precise, But Not Accurate



- Precise and Accurate

Calibration Gas Certificate Claims

- Concentration: ”100 ppm NO in N_2”
  - “Certified” Concentration for the Component
  - Estimate of the “True Value” (but not “the” True Value)

- Accuracy: “+ / - 1%”
  - Estimated Maximum Deviation from the True Value
  - Roll-up of All Known Sources of Error

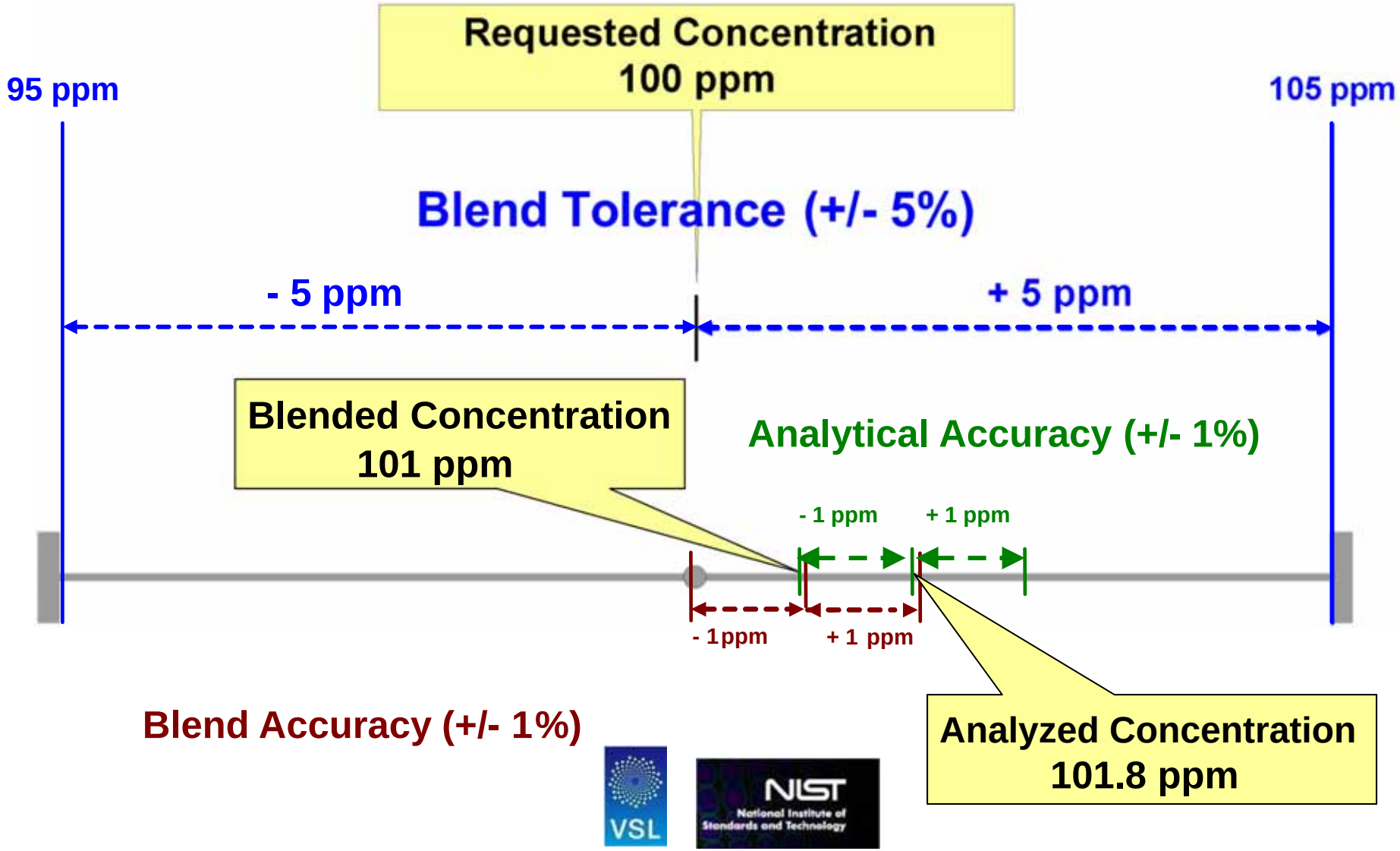
- Traceability: “NTRM-1684”
  - Citation of Reference Standard(s) Used
  - “Anchor” for the True Value and the Minimum Accuracy

The Meaning of Accuracy

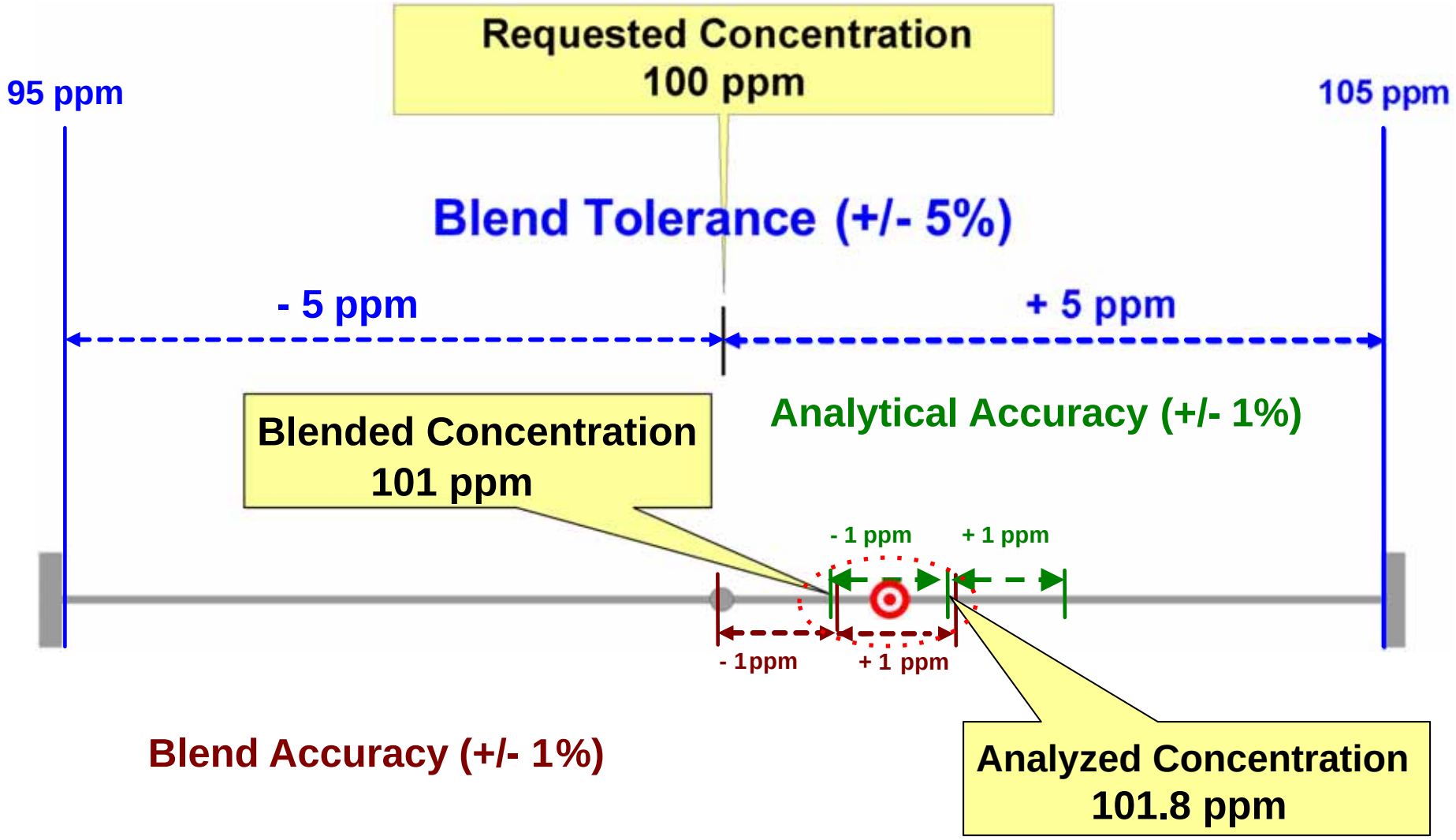
- Accuracy
  - A statistical estimate of how close an analyzed value is to the “True Value”
  - The “True Value” cannot be known without consuming the entire sample

- “Accuracy + / - 1%”
  - “Based on our analysis, with all of the underlying sources of uncertainty evaluated, our reported value is within 1% of the true value”

Common Mixture Specifications



Interlocking Specifications



Traceability Types

- Weight
  - Gravimetrically preparing a gas mixture using a high accuracy scale calibrated by “NIST” Weights.
- Gaseous
  - Standard Reference Material (SRM) – High accuracy gas standard manufactured by NIST. Produced in 5.9 liter aluminum cylinders.
  - NIST Traceable Reference Material (NTRM) – produced by a gas manufacturer with defined traceability to NIST standards. Typically in 29.5 and 47 liter aluminum cylinders.
  - Research Gas Material (RGM) – produced by a gas manufacturer with NIST defined stability criteria and analyzed and certified by NIST.
  - Gas Manufacturing Intermediary Standard (GMIS) – A reference standard produced from an NTRM or SRM.

NIST/VSL Traceability

- Direct calibration of an instrument with gas reference material from a recognized metrology organization.

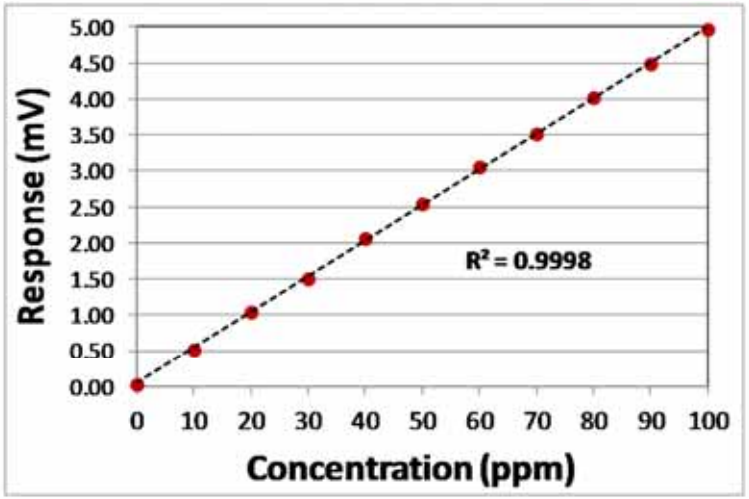
"True Value" and NIST Traceability

		Calibration Points										
Concentration	(ppm)	0	10	20	30	40	50	60	70	80	90	100
Response	(mV)	0.024	0.512	1.040	1.503	2.063	2.544	3.057	3.516	4.021	4.488	4.968

"NIST" Ref Standards (Certified Mixtures)

Analytical Instrument

Instrument Response Data



Calibration Curve (NIST Traceable)

+ / - 1.0 %

NIST Traceable Product

Key Gas Considerations

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Selecting the right equipment	• Pressure regulator, valve....
Verifying materials compatibility	• Stainless, steel, brass, plastic....
Purging the transfer line	• To avoid contamination
Passivating the transfer line	• For reactive components
Service & maintenance	• To maintain the quality

Selection of the Right Equipment

- Single-Stage vs Two-Stage Pressure regulators
  - Single stage reduces the cylinder pressure to the delivery pressure in one step.
  - Two stage reduces the cylinder pressure to the working level in two steps.
  - Two stage is unaffected by changes in the cylinder pressure and provide precise control of the gas being delivered.

- Minimize the gas transfer lines
- Select appropriate fittings and transfer lines
  - Compression, NPT, orbital welding

Material Compatibility

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- What material to use for transfer lines, regulators & other equipment?

Metals
Brass, 303 SS, 316SS, Aluminum, Copper, Monel

Plastics
PCTFE, Teflon, PVC, Polycarbonate

Elastomers
Kalrez, Viton, Buna-N, neoprene, Polyurethane

Use of incompatible gas with the equipment may cause a leak, damage the system and cause personnel injury.

Permeation Data of Various Materials

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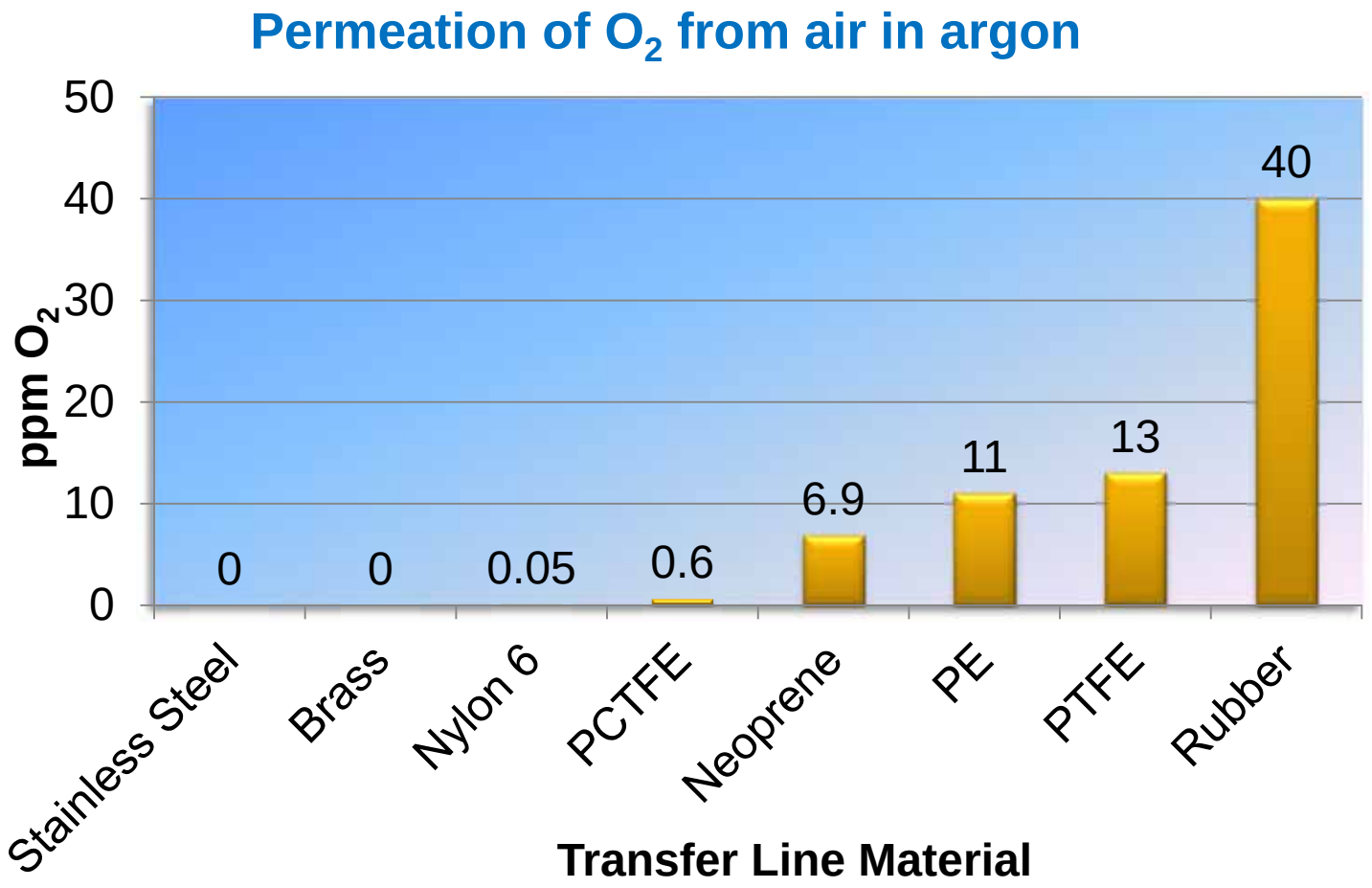
Permeation and diffusion phenomena are due to the difference of partial pressure of the gases inside and outside of the line



80 mL/min

10 bar

L = 1m

d = 6 mm

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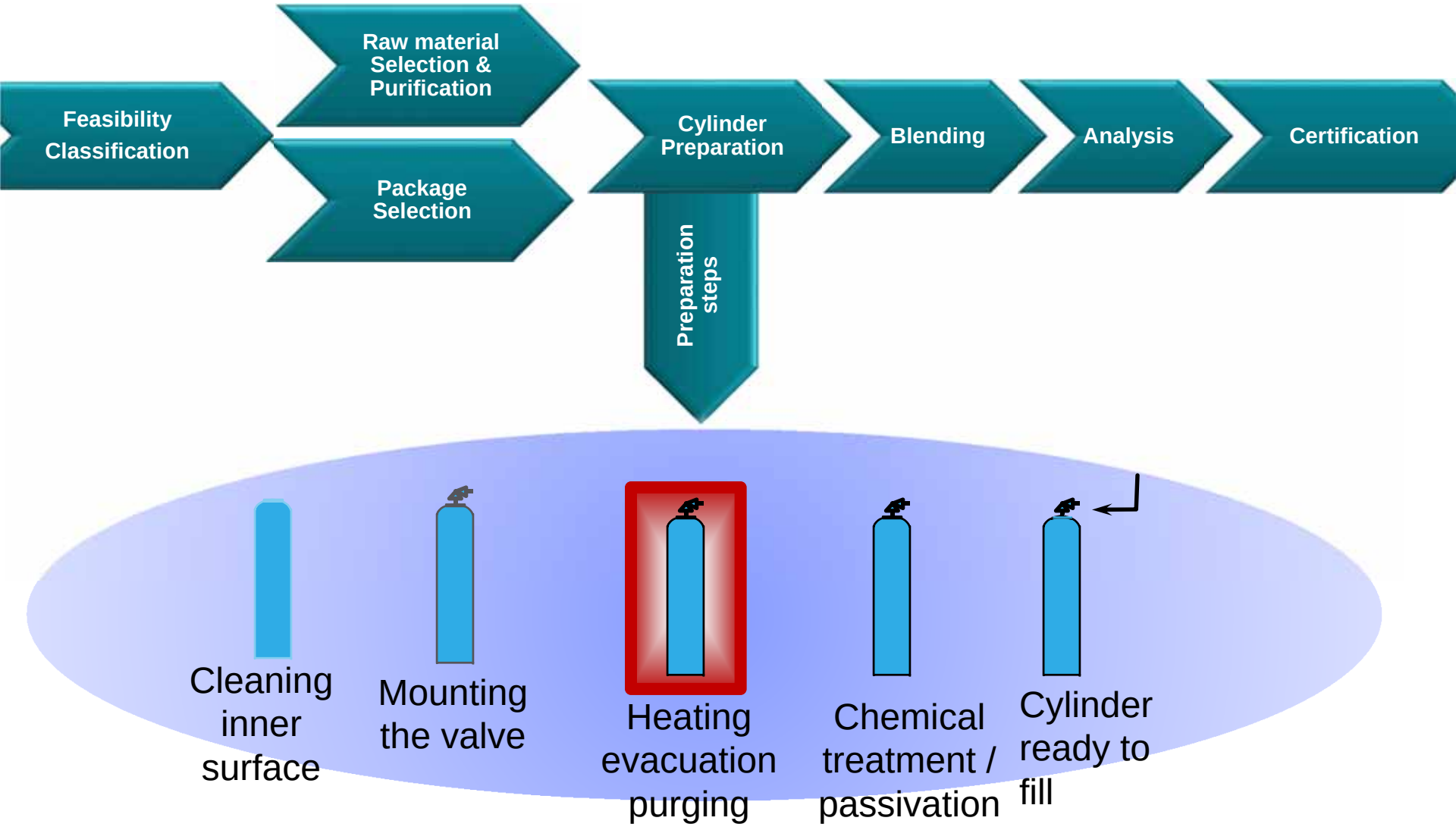
Efficient purging and leak tight condition are two of the most critical aspects to eliminate air contamination from the system

- Generally overlooked in many gas processes.
- More important when using reactive gases / components
- System is usually purged to remove contaminants from air and water vapor
- Before initial & subsequent system start up and changing out cylinders
- Purge the installation by **compression and release cycles**

Mixture Manufacturing



Manufacturing Methods

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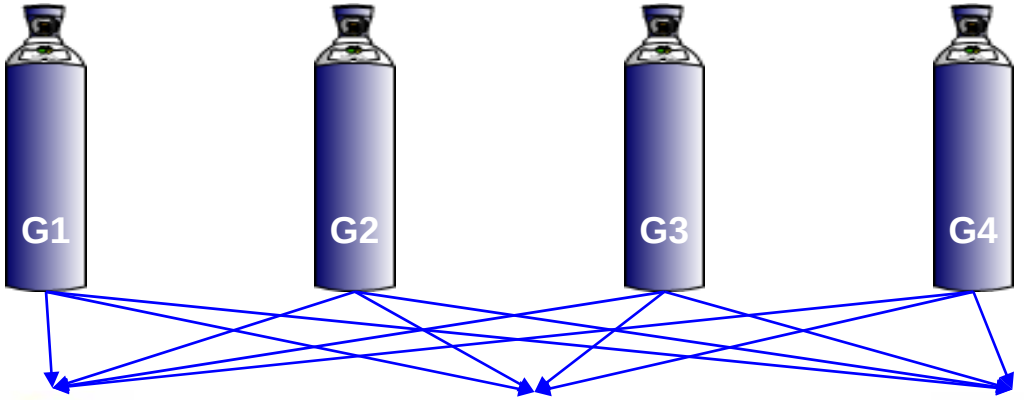
Sources
(pure gases or pre-mixes)



Blending
(filling method)

$\int_o^T vdt$

Manometric — Dynamic — Gravimetric

Calibration mixtures

Analysis
(after or during filling)

ISO 6146 — ISO 6143 — ISO 6142

Dynamic Blending: Acublend® Technology

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- This process allows blending, mixing, compression and analysis of the gas mixtures in a single operation.
- The cylinders produced from this process are completely homogeneous from top to bottom, from cylinder-to-cylinder, and even from batch-to-batch.
- Instantaneous and average compositions calculated and displayed continuously.

Stability of Calibration Mixtures

- Decomposition of the calibration mixture is one of the most common reasons for the analytical value to change over time.
- Under the conditions in the cylinder, the probability of different molecules reacting increases with
  - Cylinder pressure
  - Cleanliness of cylinder
  - Reactivity of the inner surface
  - Reactivity of the mixture components between themselves and with the cylinder
- Both the concentration and chemical nature of the calibration mixture dictate the relative importance of these criteria

Stability of Calibration Mixtures

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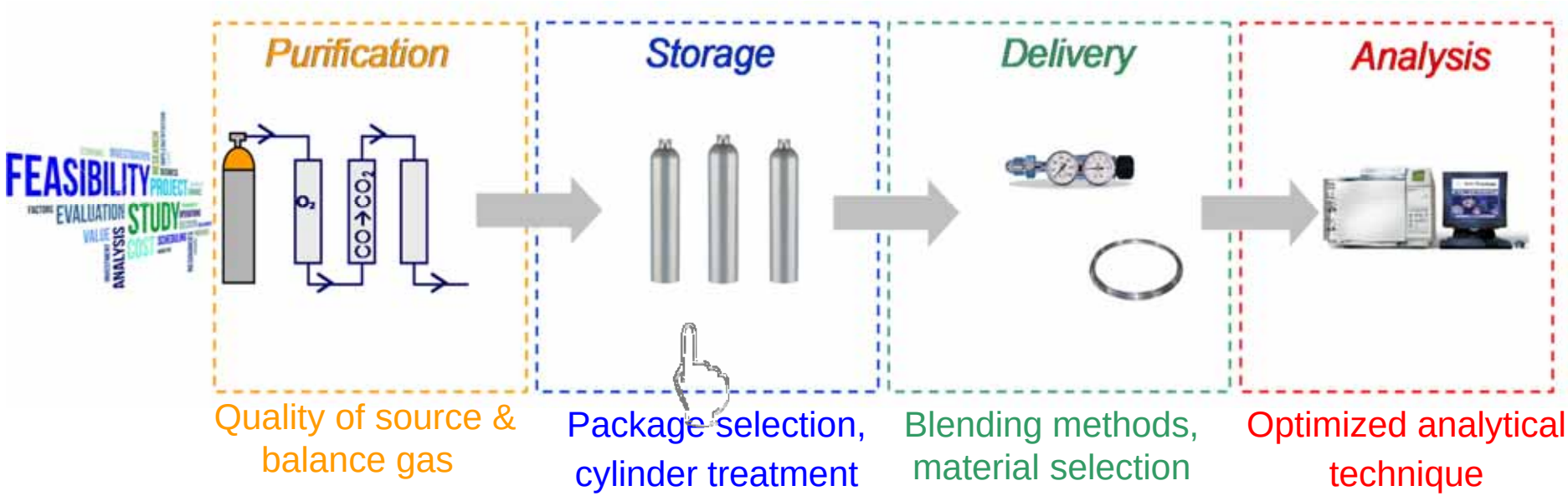

*For providing **stable reactive calibration gas mixtures**,*
*there is **no** universal cylinder treatment,*
*cylinder preparation must be **adapted** to suit the chemical properties of the gases.*

*Air Liquide Specialty Gas manufacturing processes contain **proprietary methodologies** which have been consistently developed and refined*

Shelf Life Studies

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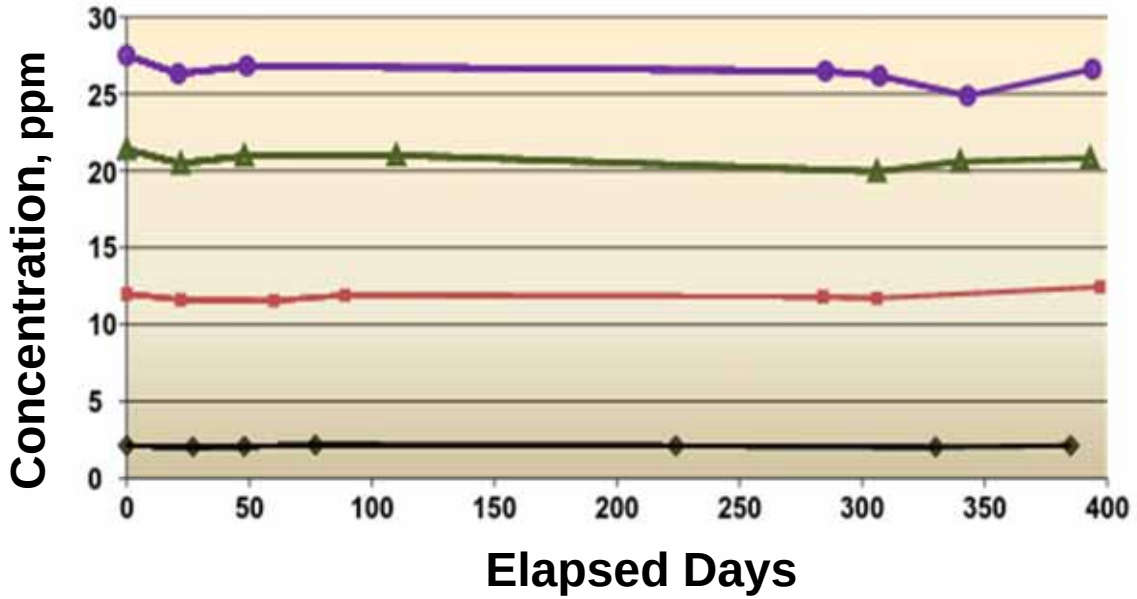
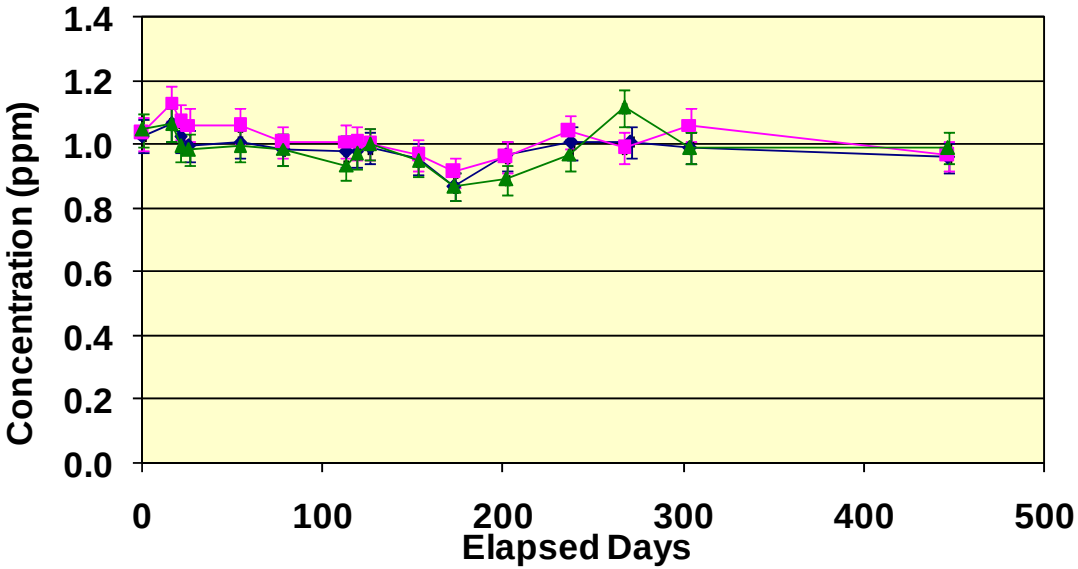
HCHO (Formaldehyde) mixtures, 2-30 ppm in N_2





NH_3 mixtures, 1 ppm in N_2

Ammonia (NH_3)Gas Mixtures – Specifcations & Traceability

- Traceability Paths:
  - NIST Research Gas Material (RGM) @ 35ppm – 4 years stability (2018)
  - NTRM @ 14.39ppm ±0.17% - 4 years stability (2017)
  - VSL – Primary Reference Materials (PRM) – 60, 100, 200 & 300ppm
  - Gas Manufacturers Intermediary Standard (GMIS)

- Analytical Accuracy: ±1 to ±2%
- Blend Tolerance: @≤10ppm: ±1ppm abs. & >10ppm: ±5% rel.
- Guaranteed Stability: 12 months
- Manufacturing Capability: 2 plants
- Lead-time: 4-5 weeks

HCl CEMS Monitoring – Preferred Mode of Compliance

- For EPA
  - Highly successful pollution abatement platform
  - Proven commissioning and QA practices
  - Established emissions reporting mechanisms

- For Sources
  - Well supported technology and infrastructure
    - Instrument, equipment and software companies
    - System integrators and consultants
    - Specialty gas manufacturers
  - Low risk of non-compliance
  - Side benefit of plant operations control data

HCl CEMS Monitoring – Preferred Mode of Compliance

- PS18 Wording Excerpt

3.18 Reference Gas Standard means a NIST-traceable gas standard containing a known concentration of HCl certified in accordance with an EPA traceability protocol in ***section 7.1*** of this PS.

7.0 Reagents and Standards.

7.1 Reference Gases. Reference gases (e.g., cylinder gases or liquid evaporative standards) used to meet the requirements of this PS must be NIST certified or NIST traceable and vendor certified to ±5.0 percent accuracy. HCl cylinder gases must be certified according to ***Reference 5 in section 16*** of this PS through a documented unbroken chain of comparisons, each contributing to the reported uncertainty. Liquid evaporative standards must be certified using the gravimetrically-based procedures of the latest version of the EPA Traceability Protocol for Qualification and Certification of Evaporative HCl Gas Standards and Humidification of HCl Gas Standards from Cylinders (see EPA–HQ–OAR–2013–0696–0026.pdf).

7.2 Cylinder gas and/or liquid evaporative standards must be used within their certification periods.

7.3 High concentration cylinder gas or liquid evaporative HCl standards may be diluted for use in this specification. You must document the quantitative introduction of HCl standards into the system using Method 205, found in 40 CFR part 51, appendix M, or other procedure approved by the Administrator.

16.0 Bibliography

5. EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, U.S. Environmental Protection Agency office of Research and Development, EPA/600/R–12/531, May 2012.

- Net Impact – *No Available Calibration Gases*

Hydrogen Chloride (HCl)Gas Mixtures – Specifcations & Traceability

- Traceability Paths:
  - NIST Research Gas Material (RGM) @ 8-12ppm – 2 years stability – Currently 1.5 to 11ppm HCl bal N2 as EPA Protocols.
  - 18 RGM candidate mixes at NIST to capture 1.5ppm to ~950ppm.
  - Gas Manufacturers Intermediate Standard (GMIS)
  - ALT114 – Gas Manufacturer's Alternative Certified Standards (GMACS) – 1ppm to 1%
- Analytical Accuracy: ±2 to ±4%
- Blend Tolerance: ±10% rel.
- Guaranteed Stability: 12 months
- Manufacturing Capability: 2 plants
- Lead-times: 3-4 weeks - GMACS & 6-8 weeks EPA Protocols

HCl GMACS - Datasheet

- GMACS Certification Scheme
- HCl Gas Delivery System

Mercury Compressed Gas Standards - EPA

- Mercury compressed gas standards are a viable option
- Availability of Hg concentrations between 1 µg/M^3 to 150 µg/M^3

(Note: concentrations >40 µg/M^3 at reduced pressure)

- Paths to traceability:
  - Elemental Mercury generator NIST certified up to 40 µg/M^3
  - Mercury analyzer is confirmed by NIST as having a linear fit at least up to 200 µg/M^3
- ALT118 / GMACS from USEPA Provides well-defined NIST traceability procedures
- Coordinating with NIST to have fleet of candidate mercury/N2 RGMs certified
- Uncertainties to be well below the required ±5%
- Guaranteed stability: 12 months – White TOP Cylinders
- Manufacturing Locations: 1 plant
- Lead-time: 4 to 6 weeks

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QUESTIONS??