The Preparation of Low Concentration Hydrogen Sulfide Standards

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RECHERCHE ET DEVELOPPEMENT

Previous Focus

■ **Low level H_2S gas mixtures (<10 ppm) can exhibit reactivity to materials**

   ✓ Reactivity may be observed in flowing systems

   - Long contact times
      - *Low flow rates in tubing*
   - Small contact amounts
      - *Injection of sample into carrier gas stream*

   ✓ Non-flowing systems

   - Long contact times between gas and material
      - *Storage*
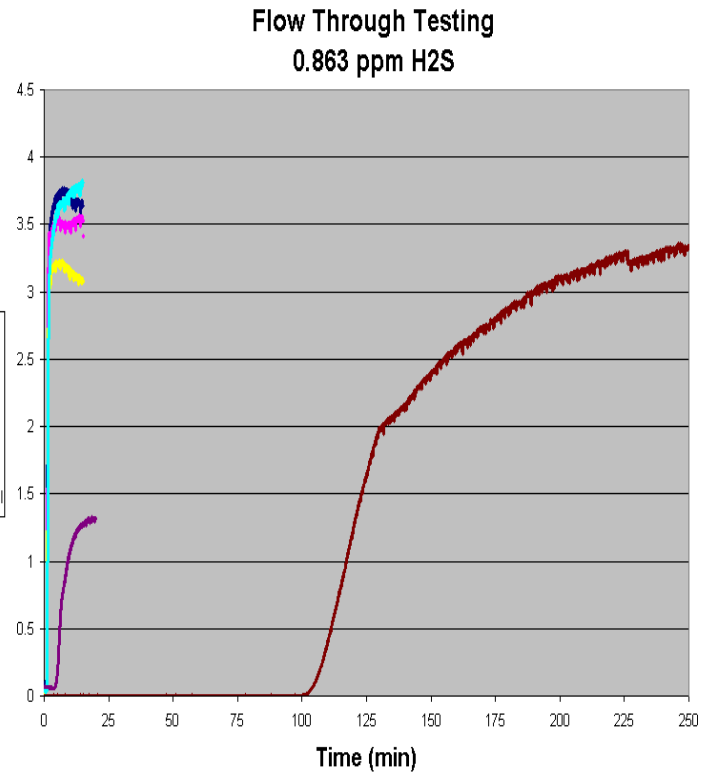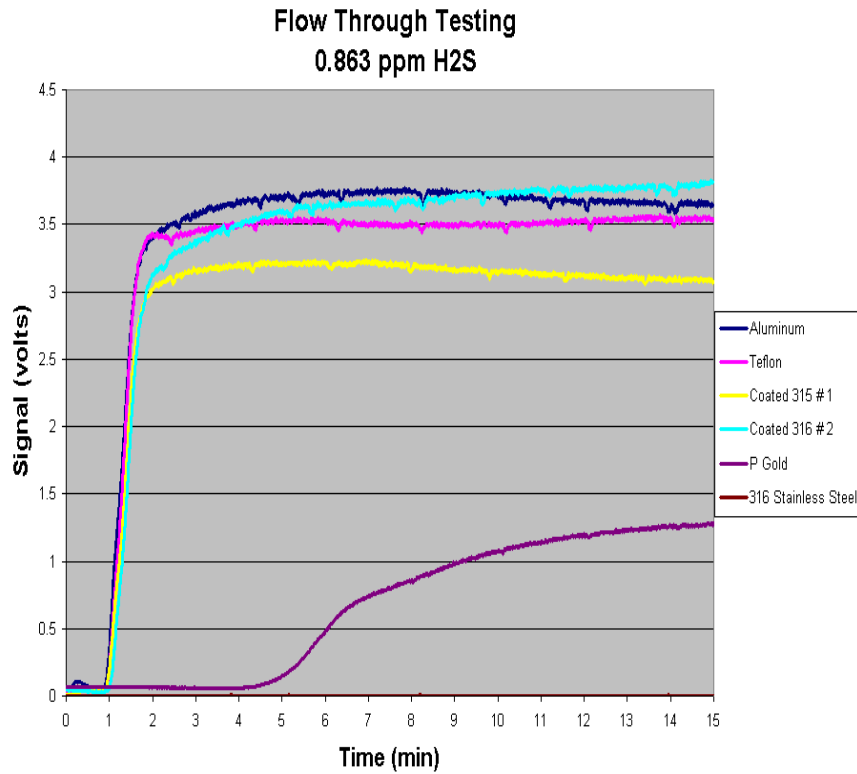
6 feet – ¼ inch tubing

Linear velocity 2 cm/sec

Teflon™ - Du Pont

Previous Focus

■ **Storage of 100 ppb H_2S in 500 mL sample cylinders**

  ✔ 30 day stability test

  - Satisfactory - Sulfinert™, Silcosteel ™ -
    - *No experimentally noticeable loss in concentration*
  - Unsatisfactory -Aluminum, Stainless Steel, Carbon Steel
    - *Immediate loss of total concentration*

™ Restek Corp.

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Present Focus

- **Introducing**

Alphatech ^{TM}

- **New patent pending, commercial cylinder treatment for specialty gas applications**

  - Provides
    - Storage of low level sulfur compounds ($\leq$100 ppb) in a commercial compressed gas cylinder
    - Stability of H_2S for at least 9 months

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Experimental

- **To determine the effectiveness of Alphatech^{TM}**
  - Cylinders prepared, filled, and analyzed

- **Cylinders filled by pressure from source cylinders**
  - 9.9 ppm H_2S
  - 99.999 % N_2

- **Analysis**
  - Utilized 2 different instruments

    (1) Varian 3800 GC (Initial testing instrument)
    - Sievers 355 SCD (Sulfur Chemiluminescence)
    - Restek 1/16" RT-Sulfur packed column

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Experimental

■ Analysis (Con't)

- ✓ (2) Agilent 6890 GC
  - Antek 7090 SCD
  - Restek SPB-1 capillary column

- ✓ Calibration of instruments
  - Calibration curves generated within range of testing
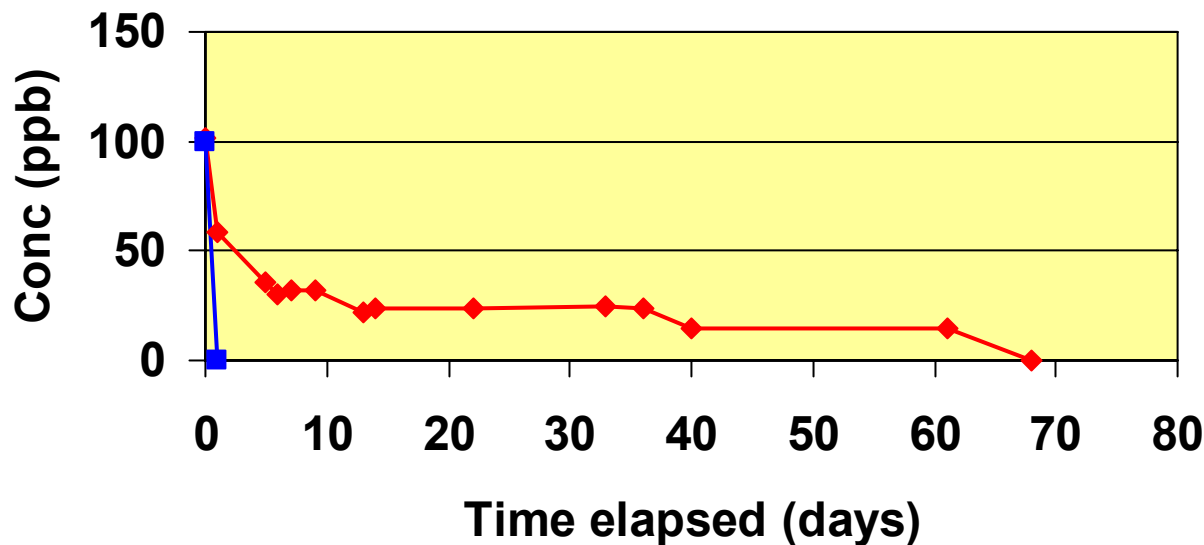   - *Dilution system used to generate four point calibration curve*

- ✓ Concentration determination
  - Averaging four points
  - Experimental error (~10 %)

Untreated Cylinder

- ■ Typical compressed gas cylinder – Varied behavior
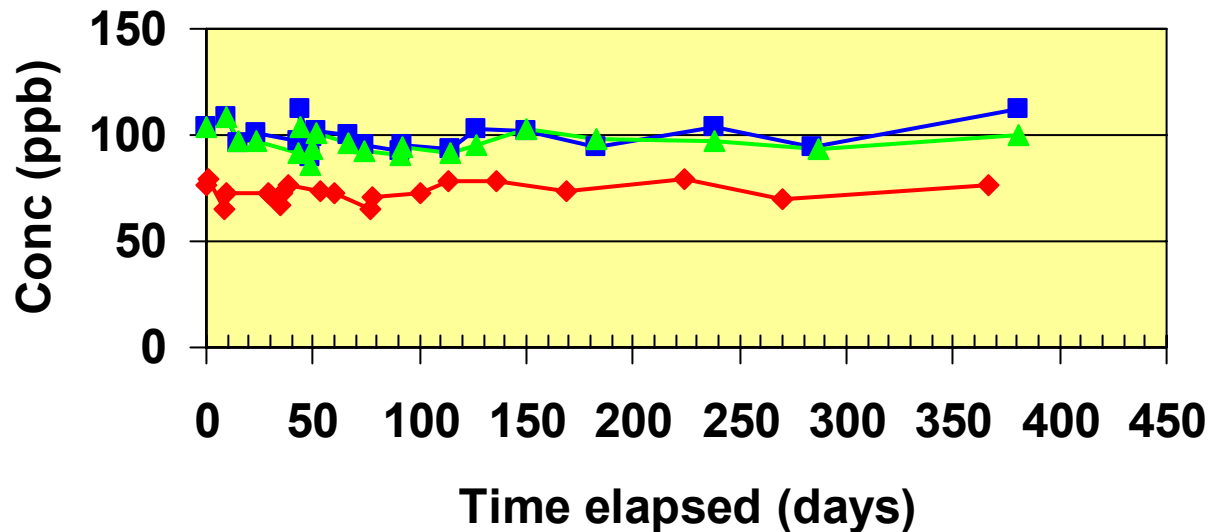 - ✓ New aluminum cylinder – Vacuum baking

Untreated Aluminum Cylinder
100 ppb H_2S

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Alphatech Stability

■ **Treated with Alphatech^{TM} process**

    ✔ Three cylinders − 2 filled simultaneously

ALPHATECH^{TM} Stability Test
H$_2$S in Nitrogen

AlphatechTM Stability

Typical Results

	Initial (calculated)	Final	Avg	RSD
Cylinder 1	79.4	76.4	73.1	5.8%
Cylinder 2	104	111.8	96.6	5.7%
Cylinder 3	104	99.6	99.7	6.4%

→*All cylinders exhibit greater than 9 month stability*

Adsorption

■ **Adsorption of H_2S onto cylinder walls**

  ✔ **Is it occurring in Alphatech^{TM} cylinders?**

  • Difference between fill concentration and first test concentration

    • *Difference observed is within experimental error*

| Fill	Test	% Diff
106.2	111.4	4.90
106.2	105.7	0.47
106.2	108.8	2.45
106.2	111.8	5.27

  • Consistency of concentration at various pressures

    • *Increase in concentration at lower pressures if desorption is occurring*

Consistency of Concentration vs. Pressure

- ## Cylinder depletion

  - ✔ Cylinder filled 97 ppb H_2S in N_2 at production facility using Alphatech^{TM} preparation
  - ✔ 3 % difference between 2150 and 63 psia
   - • Within experimental error

H_2S in Nitrogen
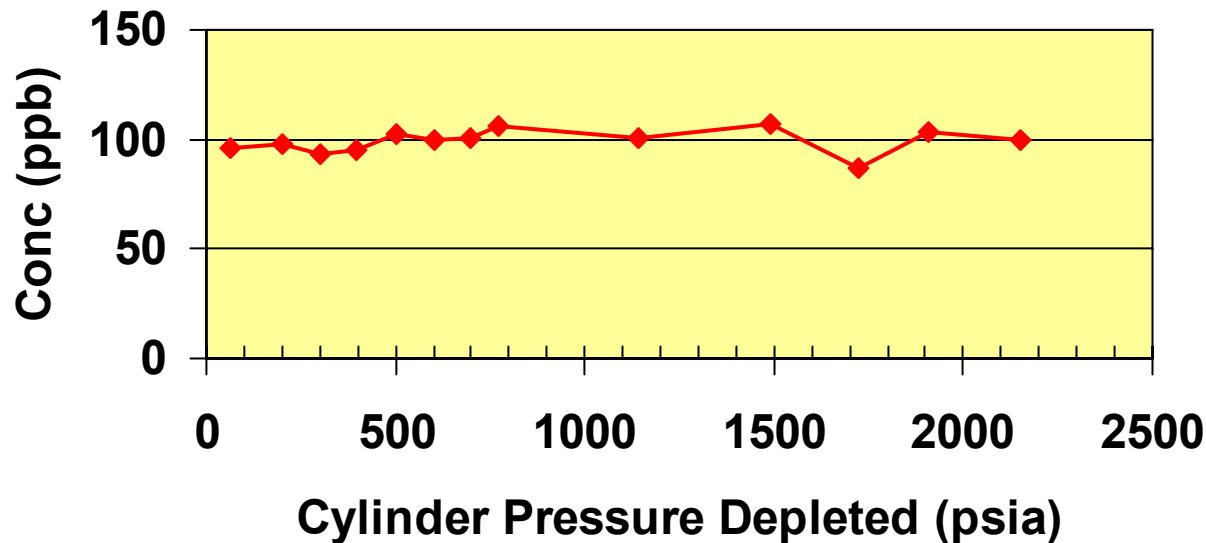
Operation development

- **Currently undergoing a production test with our specialty gas fill plant**
  - Alphatech™ cylinders prepared at specialty gas manufacturing facility
  - Cylinders filled and analyzed at facility

    - Different size cylinders (16 & 30)
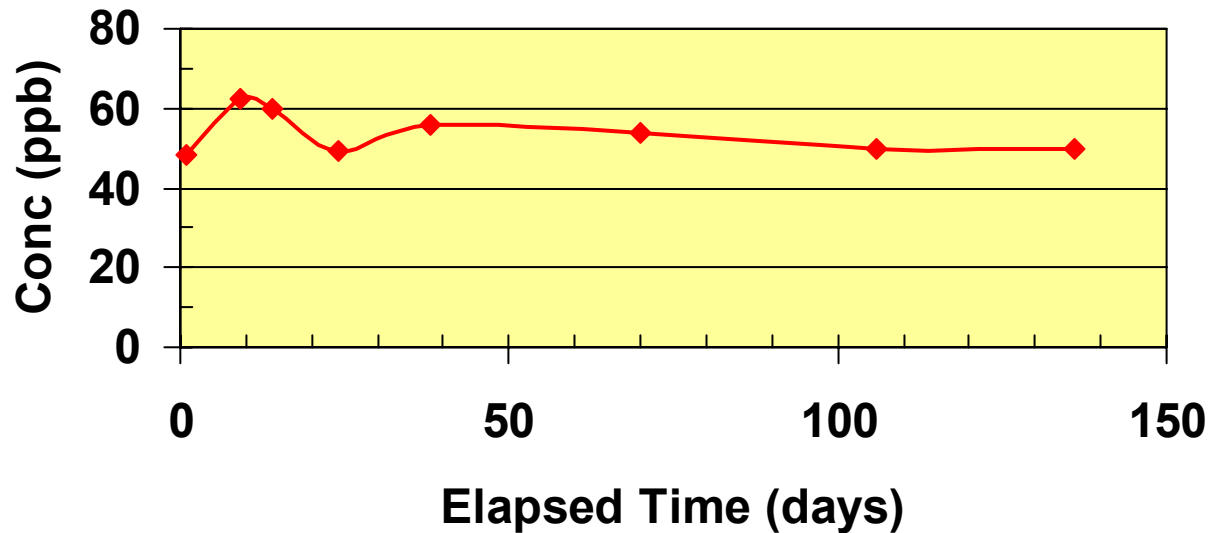   - Different concentrations (nominal 50 and 100 ppb)

Other Testing

- Application of *Alphatech^{TM}* to other analytes and balance gases

**Alphatech^{TM} Stability Test
100 ppb COS in Nitrogen**
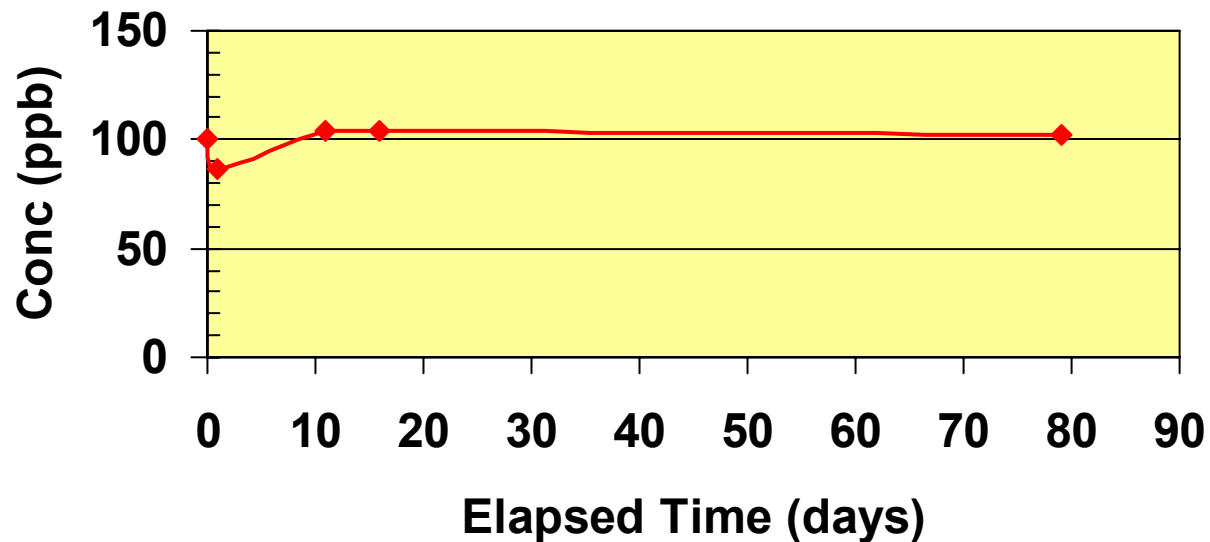
Other Testing

Alphatech™ Stability Test
50 ppb H₂S in Gaseous Ethylene

Conclusions

- **Developed a cylinder treatment / process suitable for storage of low level H_2S compounds**
  - ✓ Provide stability for at least 9 months
  - ✓ Currently in operational development phase for production scale up
    - Reliable - Easily repeatable
  - ✓ *Alphatech^{TM}* application to other sulfur analytes and balance gases underway

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AIR LIQUIDE ™

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  ✔ Product Specialists

  • Technical Experts