

Facilitating analysis of trace impurities in high pressure hydrogen through enrichment

D. Papadias, S.H.D. Lee, S. Ahmed
Argonne National Laboratory

2011 Fuel Cell Seminar & Exposition
Orlando FL, Oct 31 – Nov 3, 2011

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Hydrogen for fuel cell vehicles must meet strict fuel quality standards

Need

- Fuel quality certification requires analysis for all listed species
- Fuel suppliers can monitor canary species to control production process

Challenges

- Allowable limits for some species are very low
 - $\text{H}_2\text{S} < 4 \text{ ppb}$, $\text{NH}_3 < 0.1 \text{ ppm}$, $\text{CO} < 0.2 \text{ ppm}$
- Analysis of trace species requires sophisticated, expensive, and time-consuming analytical tools
- Gas analysis can add 10 cents/kg or more to the cost of H_2





Objective

Facilitate analysis of trace species using impurity enrichment strategies

- Reduce cost and time required for gas analysis
- Develop sampling devices capable of enriching the impurities in H₂
 - Allow use of simple, inexpensive analytical equipment
 - Allow fast, frequent analysis
- Potential users
 - Gas suppliers/producers for quality assurance
 - State regulators to certify the quality of the fuel
 - Providers of gas analysis services

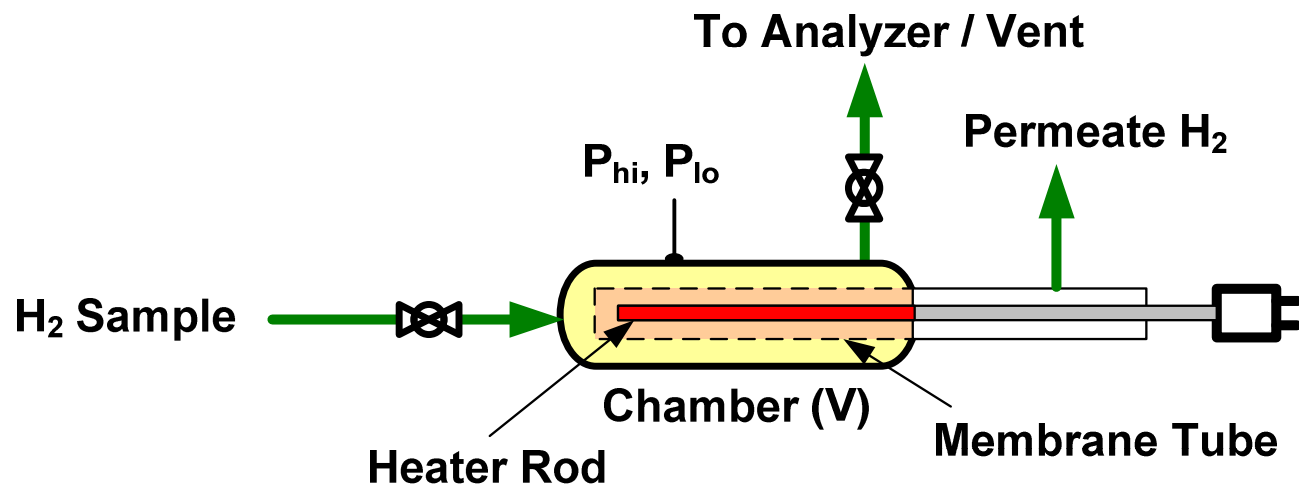
Approaches

1. Enrich impurities by removing H₂, and only H₂, from the gas sample by permeation
2. Enrich select impurities by trapping them on sorbents



Method 1 - Remove H₂ by Permeation, Retain the impurities

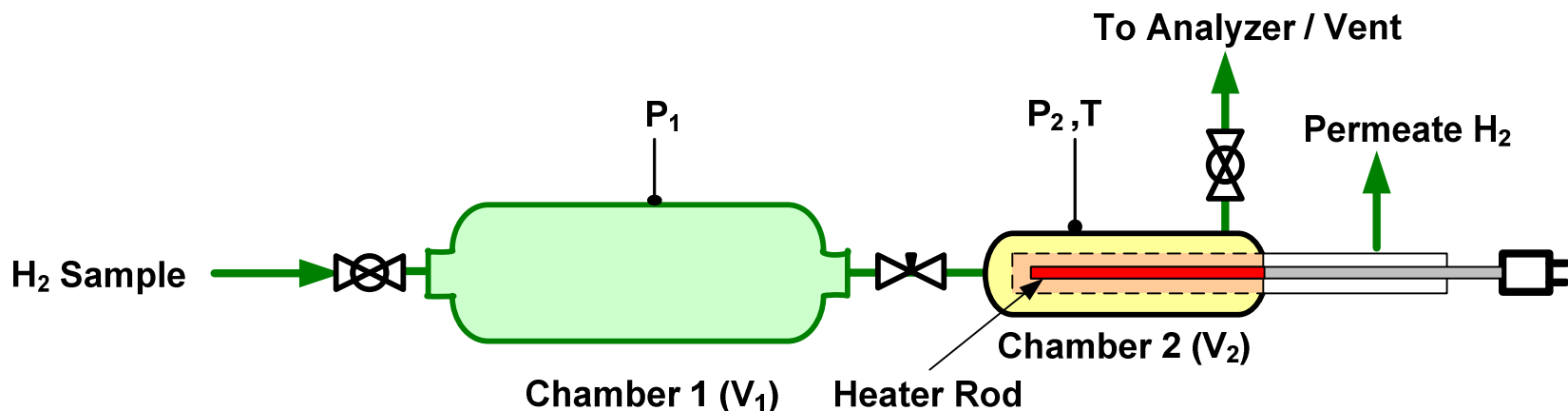
- Collect the sample at a high pressure, P_{hi} (e.g., 1,000 psia)
- Remove H₂ through a heated Pd-alloy membrane
 - H₂ permeation lowers the pressure to P_{lo} (e.g., 25 psia)
- The impurity concentrations are increased
 - Enrichment factor $E \approx P_{hi}/P_{lo}$ (E=40)



A 2-chamber system offers higher enrichments

- Larger, high pressure chamber for gas collection
- Smaller, lower pressure chamber for permeation/enrichment
 - Thinner membrane, faster permeation
- Elevated T, P combinations are avoided
- Enrichment factor is proportional to pressure and volume ratio

$$CEF \approx \left(\frac{P_{hi}}{P_{lo}} \times \frac{V_1}{V_2} \right)$$

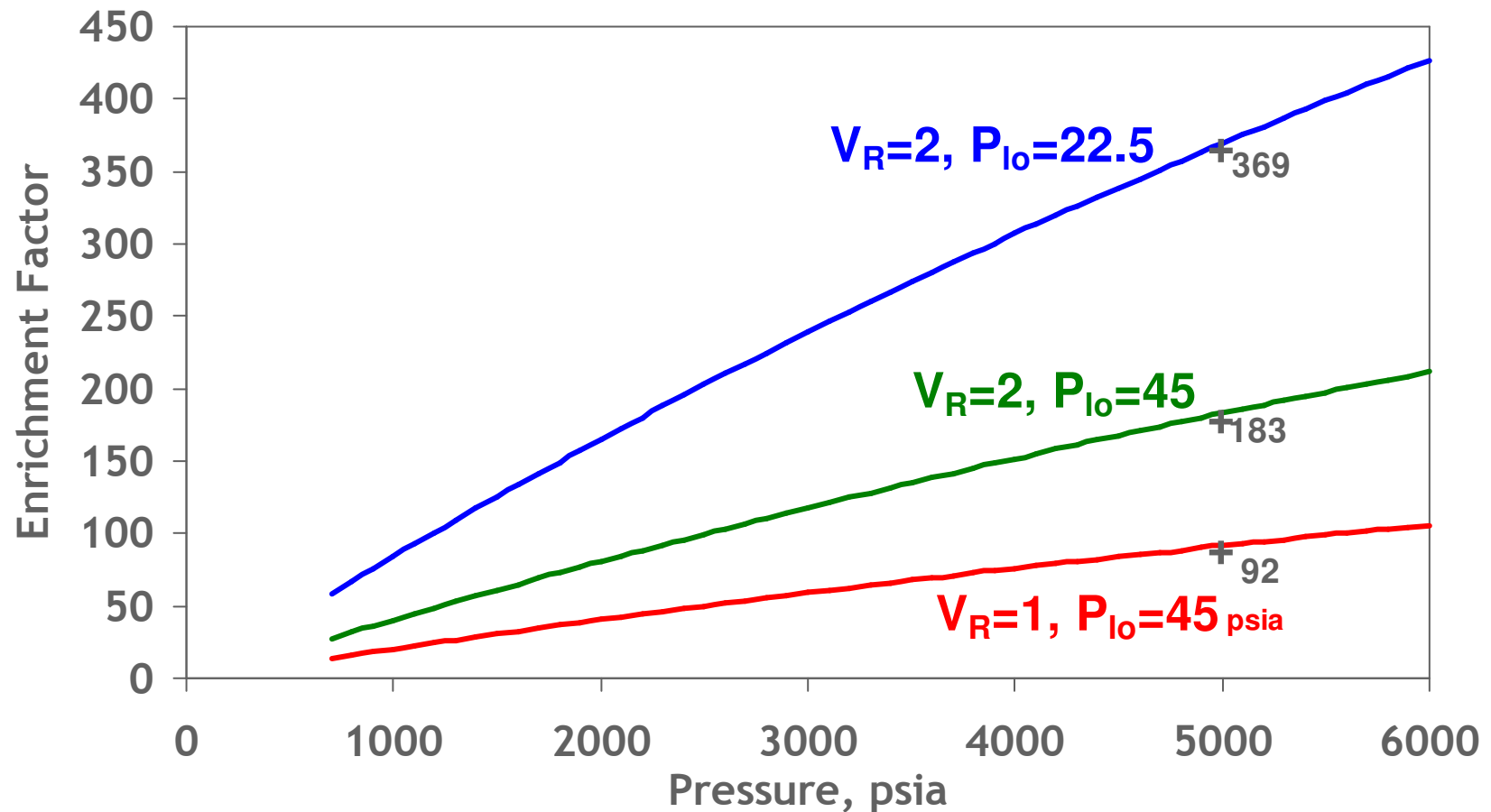


The enrichment factor is affected by the pressures and the chamber volumes

Sampling Vessel Volume = V_1 ;

Enrichment Vessel Volume = V_2 ;

Volume Ratio = $V_R = V_1/V_2$;



Concept demonstrated by enriching impurities by ~30X

- Tested for N₂, CO, CO₂, CH₄ (initial concentration: 0.2% each)

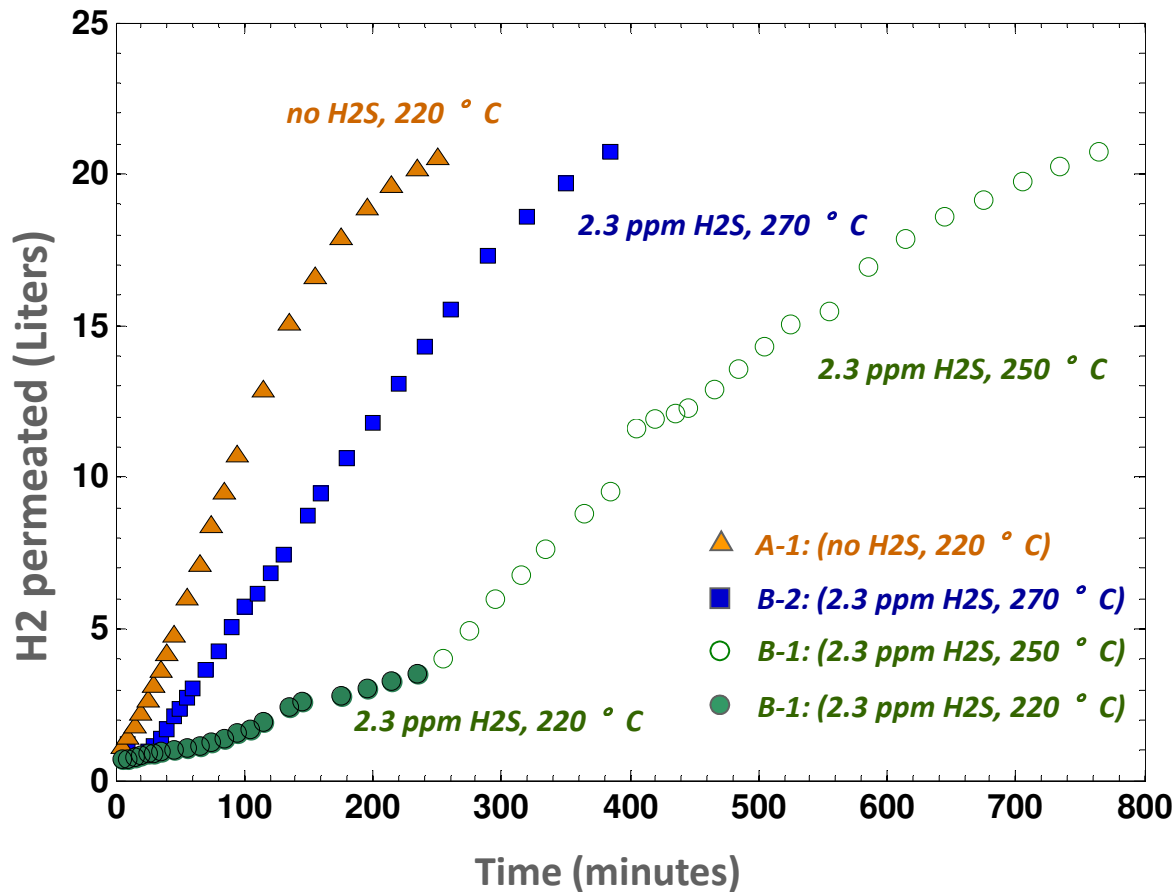
Test (M1)	Mem-A	Mem-B
Pressure (Initial / Final), psig	700 / 19.2	700 / 19.8
Calculated Enrichment Factor	32.3	31.8
Membrane Temperature, °C	250	250
Measured Enrichment : N ₂	33.4	32.9
Measured Enrichment : CH ₄	31.4	31.3
Measured Enrichment: CO	32.5	32.4
Measured Enrichment : CO ₂	31.5	31.1

- Enrichment factor variability was less than $\pm 4\%$
- Analytical repeatability of enriched gas concentrations (%) was very good
 - N₂= 6.90 ± 0.018 , CH₄= 6.68 ± 0.004 , CO= 6.76 ± 0.008 , CO₂= 6.60 ± 0.014
- C, O, and N balances were 97.5-105%

V₁=0.5L
V₂=0.3L



H₂S reduced permeation rate Higher temperature accelerated permeation



- Detectable H₂S is not expected from PSA-based processes
- Device can be adapted for S-containing gas

V₁=0.5L
V₂=0.3L



The device can be designed for higher and faster enrichment

- Higher enrichment factors can be achieved by
 - Higher pressure gas sample
 - Higher ratio of chamber volumes (V_R)
- Faster enrichment is possible by
 - Smaller volume of enriched gas needed for analyses
 - Increased hydrogen permeation rates

Details of this work are reported in:

S. Ahmed, S. Lee, D. Papadimas, "Analysis of trace impurities in hydrogen: Enrichment of impurities using a H₂ selective permeation membrane," *Int. J. of Hydrogen Energy* 35(2010) 12480-12490

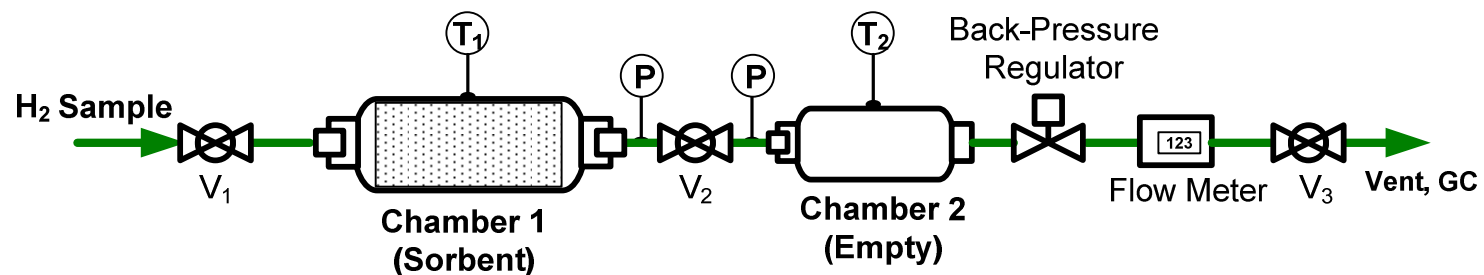


Method 2 - Trap the impurities on a sorbent

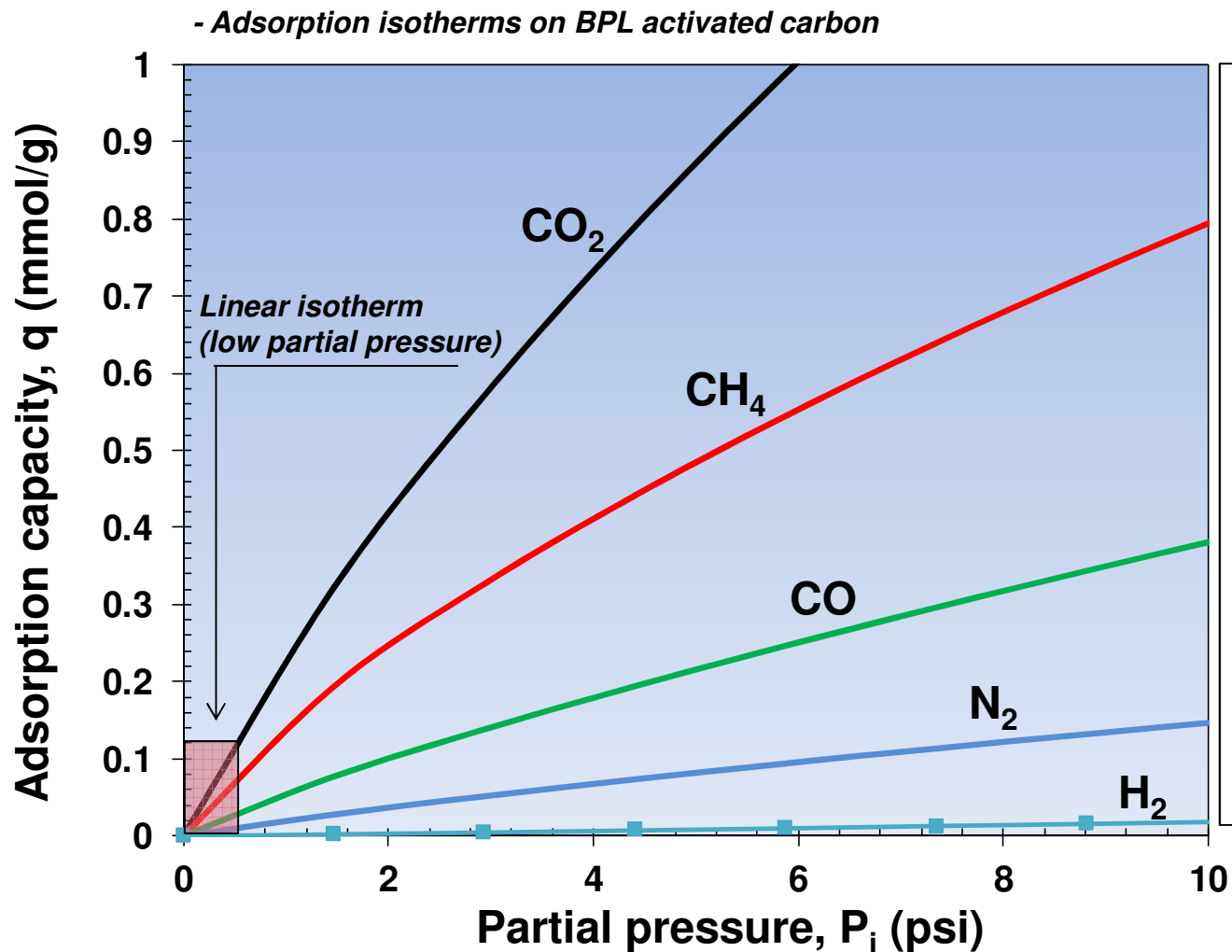
- Flow the analyte gas at high pressure P_1 (e.g., 1,000 psig) over a sorbent bed (e.g. activated carbon) to adsorb the impurities
- Reduce the sorbent chamber pressure to desorb the impurities
- Analyze the released gas, which contains a higher concentration of the impurities



Same Principle
as
Pressure Swing
Adsorption



Adsorption isotherms determine the enrichment for each individual species



At high concentrations, the adsorption for each species depends on the gas mixture

$$q_{CO} = \frac{K_A P_{CO}}{1 + K_{H_2} P_{H_2} + K_{CO} P_{CO} + K_{CO_2} P_{CO_2} + \dots}$$

- But for trace concentrations ~ 0

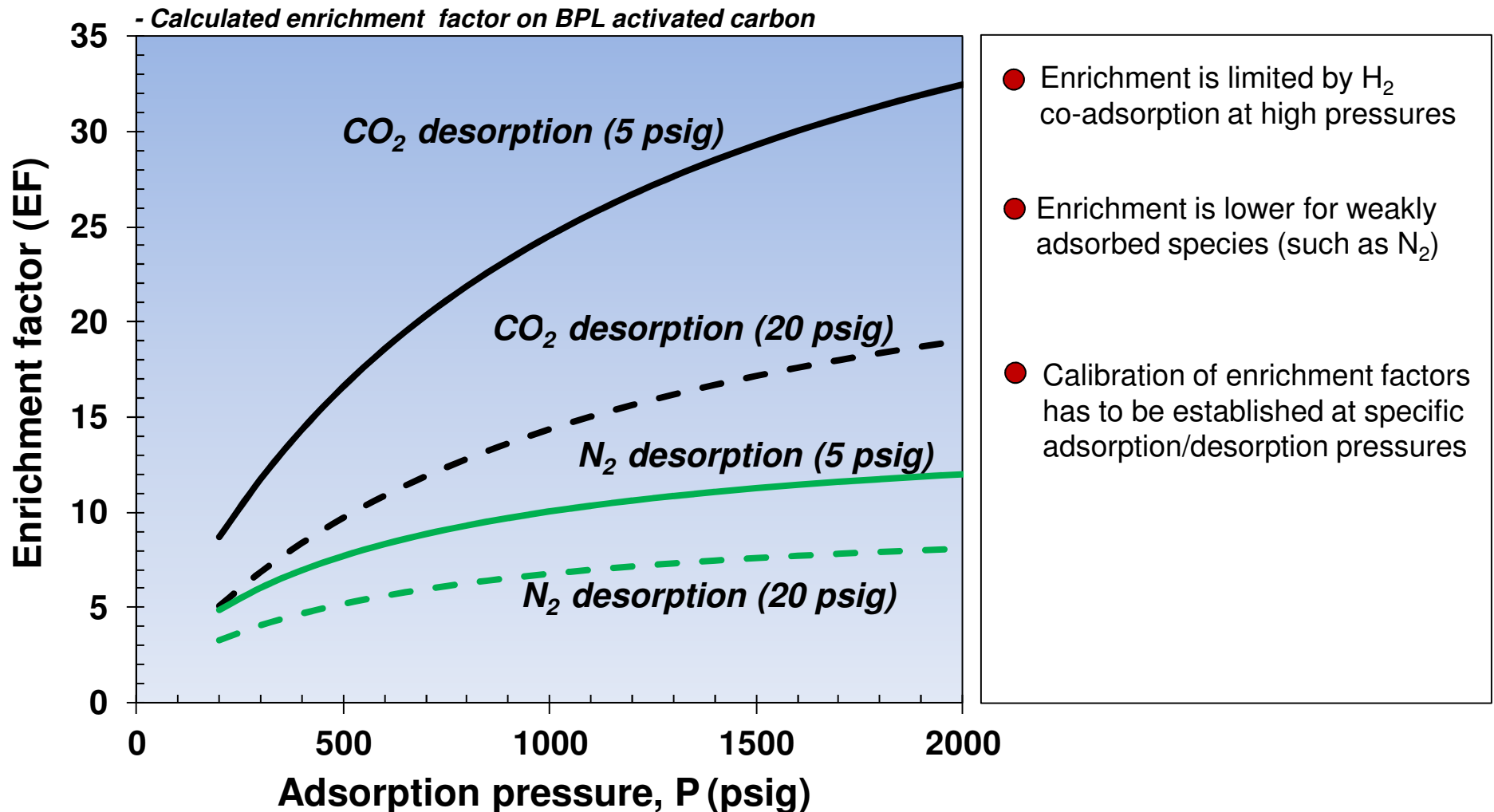
The adsorption depends on pressure only

$$q_{CO} = \frac{K_A P_{CO}}{1 + K_{H_2} P}$$



The enrichment factor depends on the pressure ratio

Lower desorption pressures favor the enrichment of trace contaminants

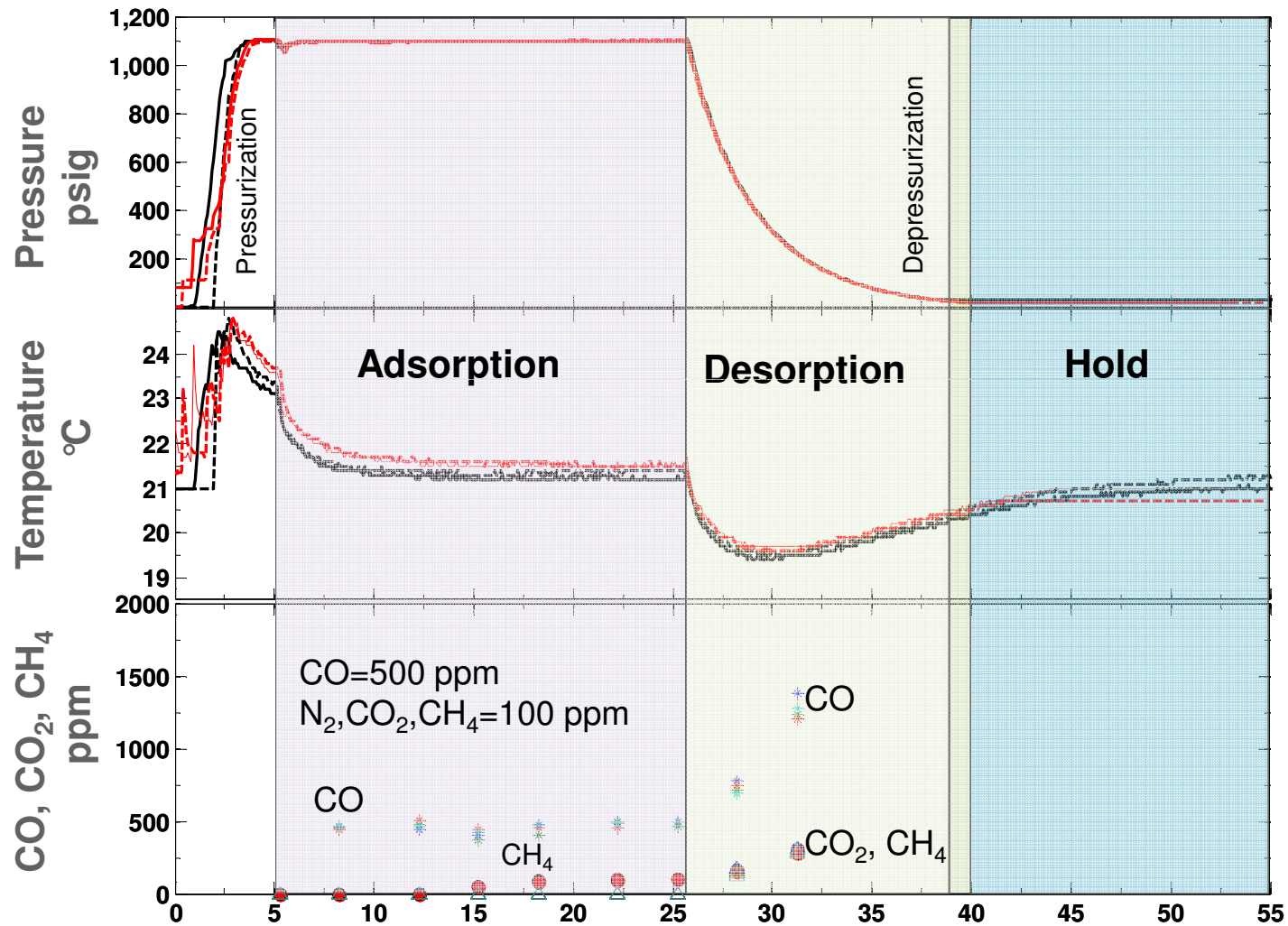


Test hardware was designed to balance size, enrichment factor, enriched gas volume, and cycle time

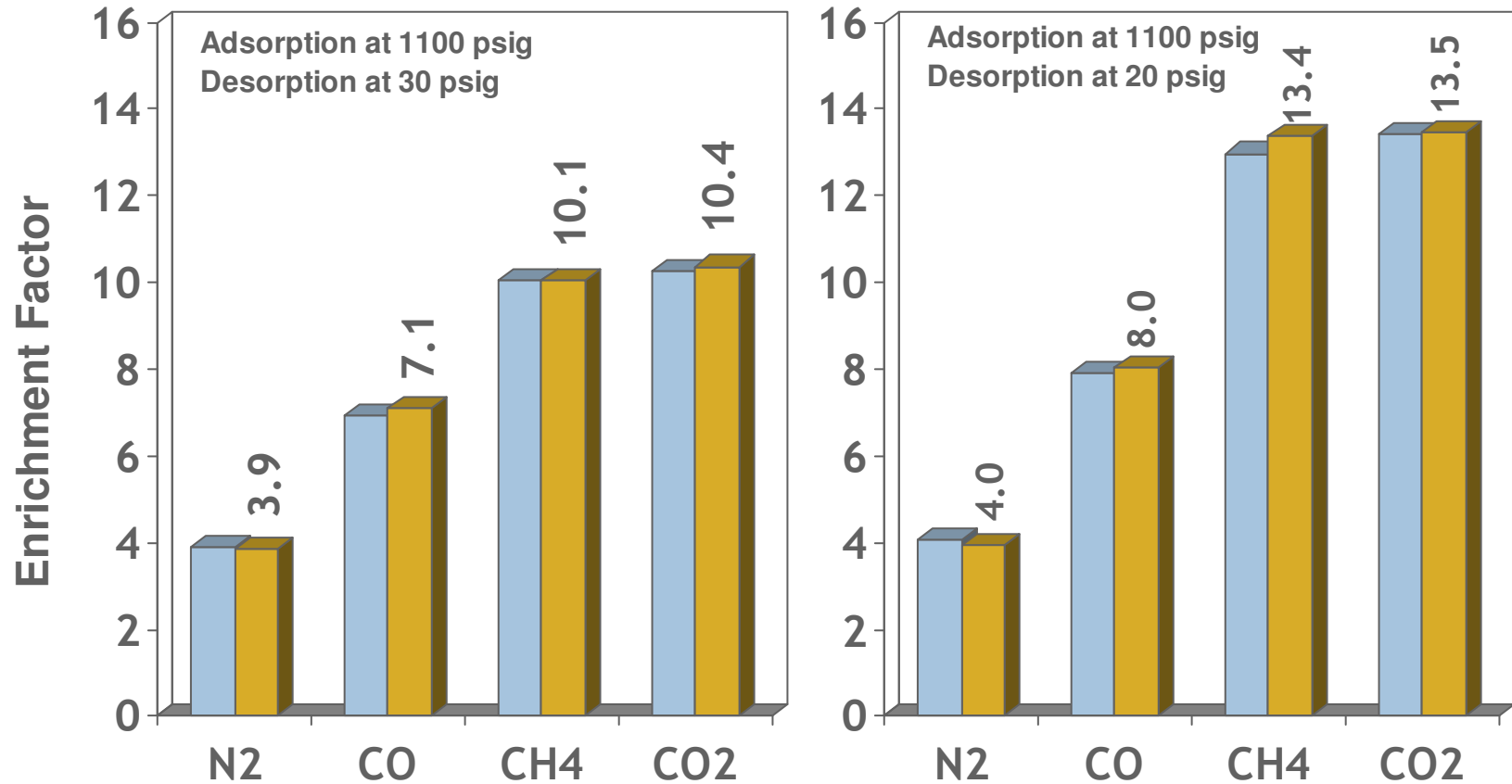
Sample Collection Chamber Volume, C1	150	mL
Adsorbent Chamber Volume, C2	15	mL
Particle (Activated Carbon) Size	1.2-1.7	mm
Sample Loop Volume, C3	4.9	mL
Sample Collection Pressure	5,000	psig
Adsorption Pressure	1,500	psig
Desorption Pressure	6	psig
Enriched Sample Volume	2	mL
Estimated Enrichment Factor for CO (at 5 psig)	19	



Effluent gas composition showed the effect of adsorption and release of the impurities



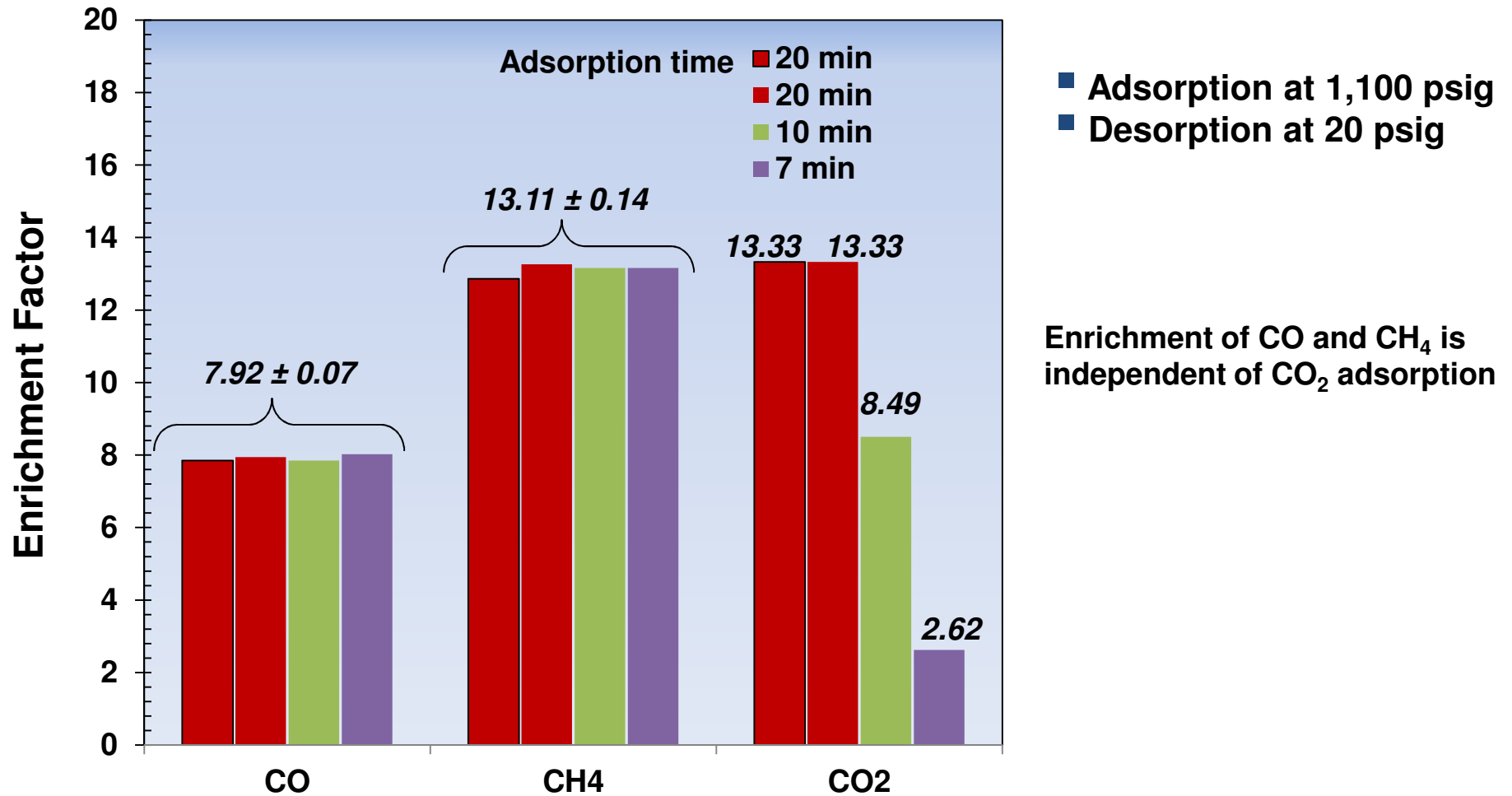
Enrichment factor varied with desorption pressure; CO was enriched by 7-8X



- Lower pressure desorption led to higher enrichment
- The repeatability was excellent



For only CO enrichment, required adsorption time and flow can be reduced



The two enrichment strategies meet slightly differing needs

Need

Gas Supplier

- Process quality assurance through frequent monitoring of 1-2 species
- Pass/Fail may be sufficient

Gas Analysis Companies

- Analysis of key or all species
- Accurate

State Regulator

- Analysis of all species
- Accurate

Technology

Membrane Enrichment

- Enriches all species uniformly
- High enrichment factor (100X)
- Cost of Pd membrane vs. cycle time
- Larger enriched gas volume

Adsorption Enrichment

- Suitable for key species
- Fast enrichment vs. enriched sample volume
- Inexpensive
- Thermal cycling is not essential



Summary

- The two enrichment methods facilitate the analysis and monitoring of trace species
 - Suited for analysis with simple, inexpensive equipment
 - Pre-prototypes for both methods have been developed and tested
- The membrane method was shown to be effective for high and uniform enrichment
- The adsorption method was highly repeatable and fast for weakly adsorbing species
- The membrane enrichment method can be adapted for faster enrichment

Acknowledgment

This work was funded by the U. S. Department of Energy's Vehicle Technology and Fuel Cell Technology Program Offices

