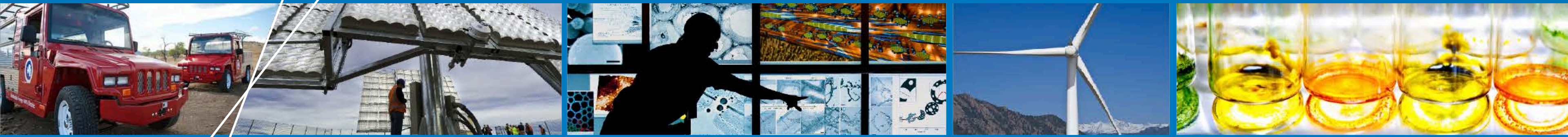
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Hydrogen Sorbent Measurement Qualification and Characterization



2013 U.S. DOE HYDROGEN and FUEL CELLS PROGRAM ANNUAL MERIT REVIEW and PEER EVALUATION MEETING

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ST014

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NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Overview

Timeline*

Start: October 2012
End: to be determined
% complete: ~50%

*previously a component of NREL's materials development program and supported annually since 2006

Budget FY 13

Funding 2013: **$300,000**

Barriers addressed

General: A. Cost, B. Weight and Volume,
C. Efficiency, E. Refueling Time

Reversible Solid-State Material:
M. Hydrogen Capacity and Reversibility
N. Understanding of Hydrogen Physi- and Chemisorption
O. Test Protocols and Evaluation Facilities

Collaborators

H2Technology Consulting, USA – Karl Gross

University of Missouri, USA– Peter Pfeifer group

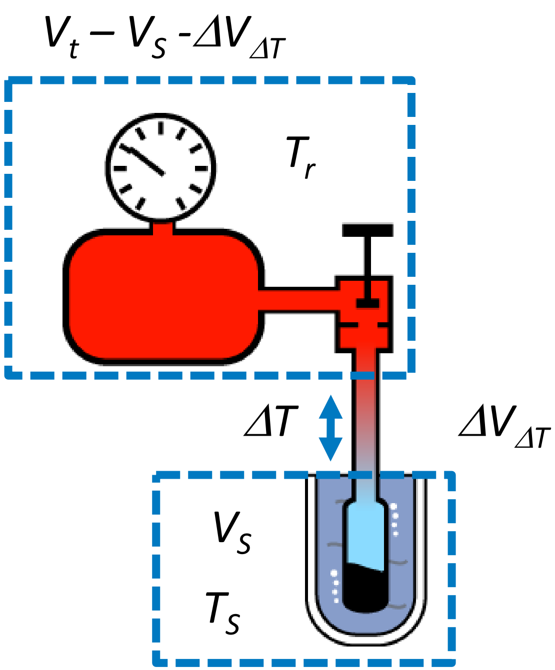
NIST, Facility for Adsorbent Characterization and Testing (FACT) – ARPA-E Project

NIST, USA – Laura Espinal group

Relevance: Measurement Validation

DOE Objective:

Capacity measurements for hydrogen-storage materials must be based on valid and accurate results to ensure proper identification of promising materials for DOE support.



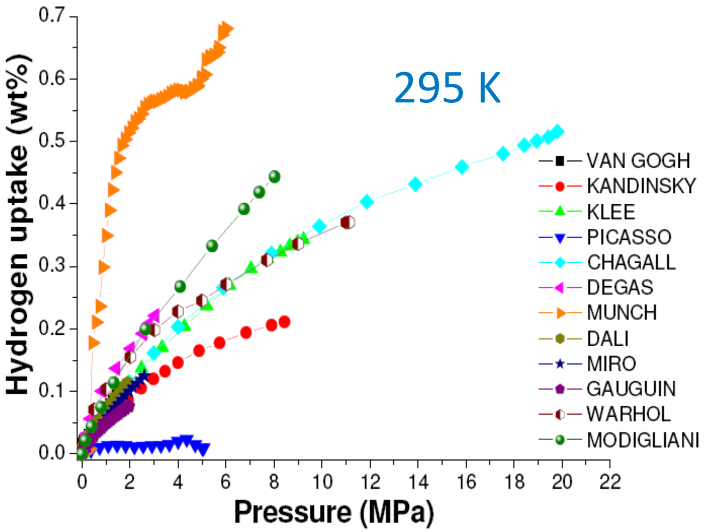
Manometric (aka Volumetric) System

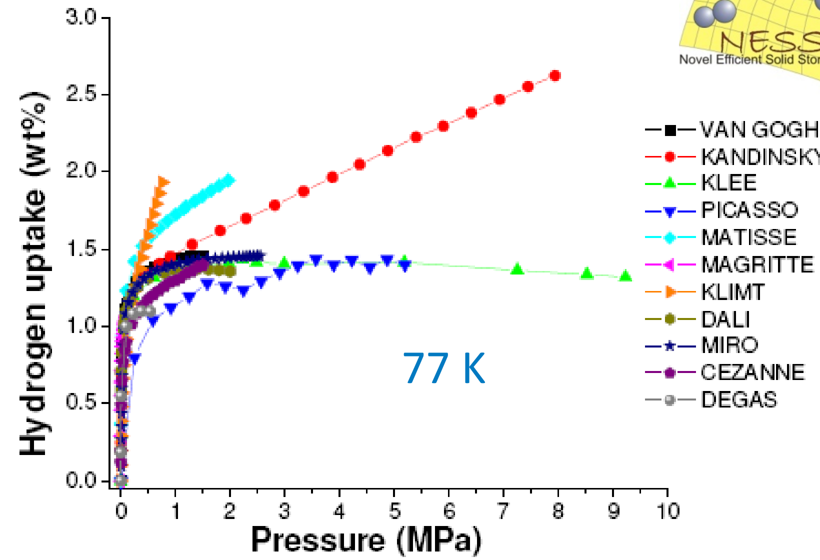
Project Goal:

- Assist materials-research groups to characterize and validate their samples sorption capacities for hydrogen-storage.
  - -Measure external samples at NREL to compare results with source group's and/or third-party's results.
  - -Discover sources of measurement discrepancies and advise on corrective actions, if needed, for source group.
- Analyze for, identify, and recommend corrective actions for major sources of measurement error in volumetric systems.
  - -Analyze ***realistic*** models for random and systematic errors.
  - -Identify the major error sources that will dominate the measurement
  - -Recommend improved instrumentation and experimental procedures to minimize such errors.
  - -Analyze materials for chemical reaction by-products

Relevance: Previous International Round-Robin Testing Directly Illustrated Issues with Sorption Measurements Accuracy

NESSHY Round-Robin Testing Results for High Surface Area Material





Remarkable scatter among participating laboratories, emphasizing the need to review methods and internal calibration or operability of analytical equipment

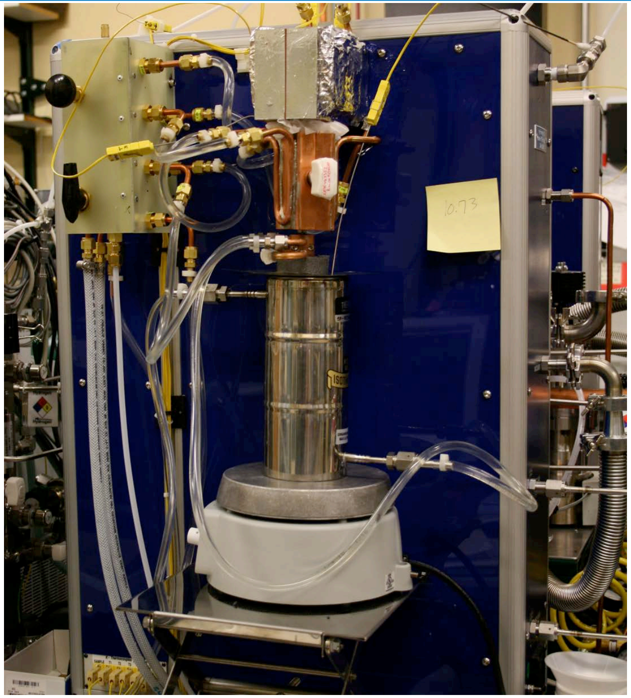
What is going on? Systematic Error!

Researchers do not realize how large the systematic error can be for capacity measurements.

Zlotea et. al., International Journal of hydrogen energy 34 (2009) 3044 – 3057; Miller, SWRI

Approach: Excel At H_2 Capacity Measurements

- **NREL continues with a multiyear intensive effort to:**
  - Improve measurement quality and accuracy
  - Understand the sources of and correct for measurement error
  - Over 1200 high-pressure Sieverts measurements since 2006*
  - Work with external groups to provide measurements and verify results
  - Collaborate with the hydrogen community to improve measurements
  - Manage & coordinate with the "Best Practices" Project (ST052 - Karl Gross) to disseminate recommended practices and procedures



NREL's Sieverts has been extensively customized to improve accuracy

- **Prior to FY12, this effort was folded into the main materials-development program and was not separately reviewed.**
- **This effort has its roots even before the Hydrogen Sorption Center of Excellence (HSCoE), but the effort accelerated during the HSCoE as NREL was the main measurement resource for the HSCoE.**

*Measurements include H_2 capacity, life-cycle, He calibrations at room and LN_2 temperatures, instrument calibration and testing, methodology development and testing. We also measure for side reaction products.

Approach: Work with external groups to measure samples and to examine measurement techniques and procedures

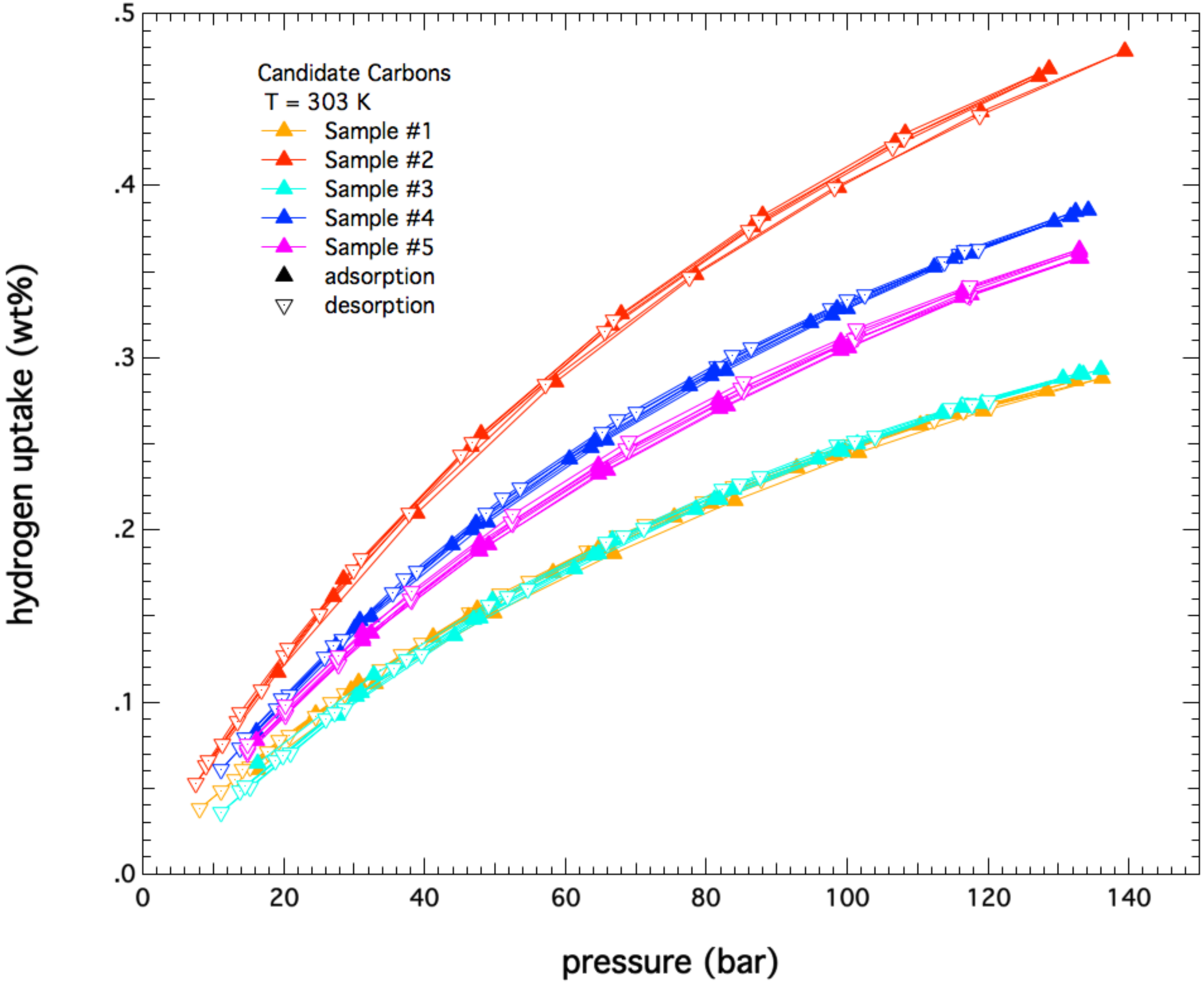
- **Evaluate and establish hydrogen sorption standards for instrument & protocol verification up to 200 bar.**
  - Room temperature
  - Liquid nitrogen temperature
- **Measure external samples at NREL to compare results with source group's and/or third-party's results**
  - Actively seek out collaborations for comparison studies
  - Assist with DOE projects to ensure robust measurements
  - Test and validate promising results for verification
- **Discover sources of measurement discrepancies and advise on corrective actions, if needed, for source group**
  - Send standardized samples to external labs to test instrumentation and experimental procedures
  - Examine data and data analysis protocols to discover possible avenues to improve measurement techniques
  - Make recommendations to labs for improvement

Accomplishments & Progress: Develop A Room-Temperature Hydrogen Adsorption Standard For Instrument Verification

- **Target Characteristics For Standard Materials**
  - Commercially available
  - Easily handled
  - Non-hazardous
  - No or little contaminants
  - Reasonable capacity but not too easy a measurement
  - Reproducible results
  - Air stable, long shelf life
  - Degassing protocol should be reasonable and not extreme

- **Candidate Materials**
  - 5 different commercial carbons received and evaluated to date:
    - Alfa-Aesar (3)
    - Sigma Aldrich (2)
  - Investigating 2 other materials
  - Initial characterization includes:
    - Degassing conditions
      - Presence of contaminants
    - BET
      - Surface area and effect of degas conditions
    - PCT
      - Sorption capacities

Sample #2 is the best material



Sample #2:

- BET: 1234 m^2/g
- No impurities detected
- Pelletized form
- Currently undergoing rigorous analysis for degassing and/or aging effects.

Next Steps: Develop Hydrogen Adsorption Standard For Instrument And Protocol Verification

- **Additional Studies**
  - Gas Characterization
    - Additional degassing studies (high T)
    - PCT with different masses (50 mg to >1 g)
    - BET reproducibility
    - Aging studies
  - Materials Characterization
    - XRF
    - XRD
    - TGA (ash)
    - ICP-MS
- **Liquid Nitrogen Adsorption Standard**
  - Protocol Development
  - PCT with different masses
  - Temperature error sensitivity

Approach: Work with external groups to measure samples and to examine measurement techniques and procedures

- **Develop informal hydrogen adsorption standards for instrument & protocol verification**
  - Room temperature
  - Liquid nitrogen temperature
- **Measure external samples at NREL to compare results with source group's and/or third-party's results**
  - Actively seek out collaborations for comparison studies
  - Help out with DOE projects to ensure robust measurements
  - Test very promising results for verification
- **Discover sources of measurement discrepancies and advise on corrective actions, if needed, for source group**
  - Send standardized samples to external labs to test instrumentation and experimental procedures
  - Examine data and data analysis protocols to discover possible avenues to improve measurement techniques
  - Make recommendations to labs for improvement

Accomplishments & Progress: Work with external groups to verify samples and to examine measurement techniques and procedures

- **Performed measurements to verify performance of materials**
  - As part of a Go/No-Go DOE milestone for 3rd-parties
  - Multiple temperatures (data is proprietary)
  - Some discrepancies found

- **Any discrepancies had follow-on efforts**
  - To determine cause of discrepancy
  - Extensive evaluation of equipment, protocols and data analysis
  - Reports sent to DOE and 3rd parties
  - (see example in Reviewer-only slides)

Accomplishments & Progress: Milestones

- **4.2.3.1 Provide summary of measurements on at least 2 external samples and...**
  - 2 samples already measured and reports submitted (100% completed).
- **Analyze non-isothermal volumetric measurements for mass balance, error analysis and recommended tests and procedures. These results are to be compiled into a manuscript for publication either on the DOE Hydrogen and Fuel Cells' website or in a peer reviewed journal by 9/30/13 (CPS Milestone #57342).**
  - Manuscript in progress (40% completed).
- **4.2.3.2 Determine a viable room temperature hydrogen storage sorbent standard and protocol (March 2013)**
  - Material identified; finishing up study (95% completed).
- **4.2.3.3 Determine a cryogenic temperature (77K) hydrogen storage sorbent standard and protocol (August 2013)**
  - Work in progress (30% completed).

Collaborations

Activities include: technical discussions on equipment and procedures, sample exchange, & data analysis

- **H2Technology Consulting, USA – Karl Gross**
  - "Best Practices" document & error analysis
- **University of Missouri, USA– Peter Pfeifer group**
  - Sample verification & protocol discussion
- **NIST, Facility for Adsorbent Characterization and Testing (FACT) – ARPA-E Project**
  - Instrumentation & protocol discussion
- **NIST, USA – Laura Espinal group**
  - Error analysis & protocol discussion

Proposed Future Work

- **Continue efforts to measure external samples, assist others in improving measurement procedures, publish error analysis and recommended protocols**
- **Coordinate with new projects and DOE to ascertain new measurement needs and improve NREL's capabilities to meet those needs**
  - Wider temperature ranges
- **Add new capabilities to community efforts**
  - Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)
  - High pressure NMR
  - Low-T thermal conductivity (including powders)

Summary

- **Relevance: Measurement Validation**
  - Determining which materials are promising for hydrogen storage is crucial
  - Implement proper measurement techniques and procedures
- **Approach**
  - Develop a H_2 adsorption *ad hoc* “standard” for room temperature and LN_2
  - Verify measurements on external samples
  - Identify, implement and disseminate corrective measures for sources of error in volumetric systems
- **Accomplishments & Progress**
  - Developed a H_2 adsorption “standard” for room temperature; working toward LN_2 standard
  - Verified measurements and investigated discrepancies
  - Developed realistic models, identified major sources of errors, disseminated improvement through talks and publications
- **Collaborations**
  - Interacted with 4 groups on measurement techniques and procedures
- **Proposed Future Work**
  - Develop new capabilities to meet future measurement requirements such as PCT over wider temperature ranges and DRIFTS *in-situ* measurements

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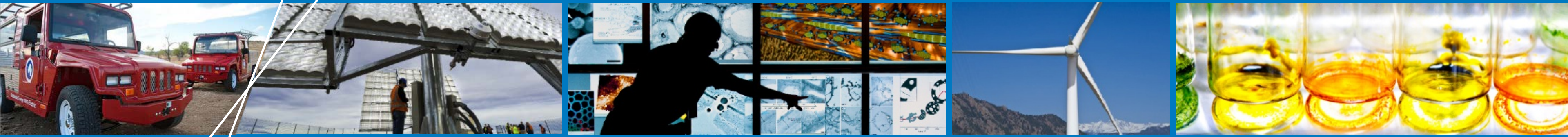
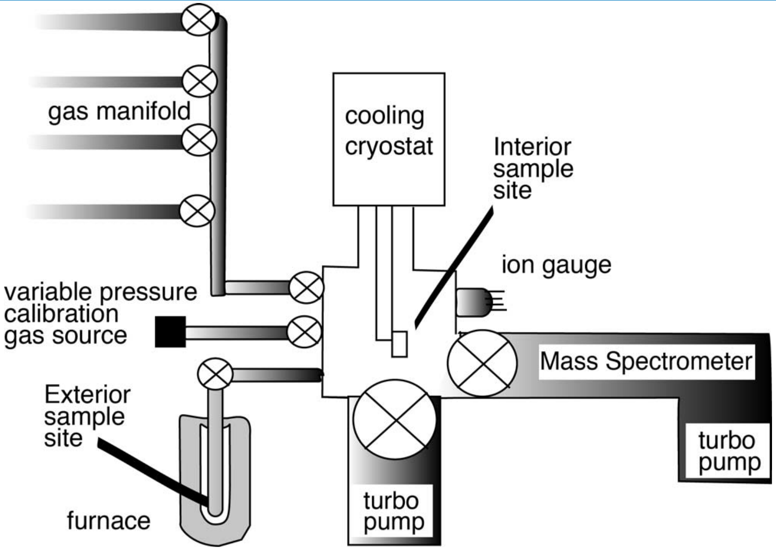


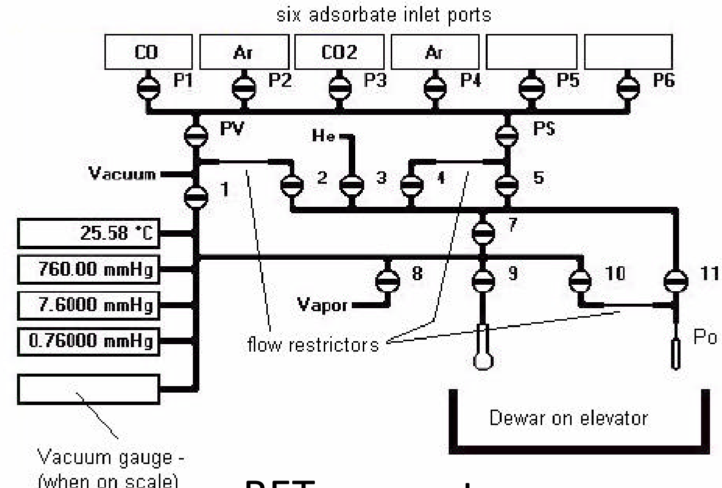
Technical Back-Up Slides

Develop A Room-Temperature Hydrogen Adsorption Standard For Instrument Verification: Degassing & BET

- **Degas Protocol:**
  - Pump out at 30 °C, time as needed
  - Ramp to 100 °C in 10 min.; hold for 2 hours
  - Ramp to 300 °C in 30 min.; hold for 12 hours
- **Degassing**
  - #1: Sulfur detected
  - #2: No significant effluent detected
  - #3: Sulfur detected
  - #4: No significant effluent detected
  - #5: HCl detected
- **BET**
  - #1: 644 m^2/g
  - #2: 1234 m^2/g
  - #3: 654 m^2/g
  - #4: 1017 m^2/g
  - #5: 861 m^2/g



TPD apparatus for degassing studies



BET apparatus

ASAP2020 physisorption plumbing diagram

Approach: Analyze for, identify, and recommend corrective actions for major sources of measurement error in volumetric systems

- **Analyze *realistic* models for random and systematic errors**
  - Volumetric mass-balance models in the scientific literature, although ideally correct, typically do not account for real-world measurement situations
  - Most volumetric systems contain many more moles in the gas phase than the moles sorbed onto the sample thus requiring very accurate mass-balance accounting
  - Examples of real-world issues absent in the models:
    - Valves that change volume with operation and can transport gas between volumes
    - Assumptions of non-measured pressure values
    - Absence of temperature gradients or unrealistic temperature gradients
- **Identify the major error sources that will dominate the measurement**
  - The most dominant errors are systematic errors!
  - Sources of systematic error:
    - Improper “null” calibration
    - Inadequate data analysis models (mass-balance models)
    - Ignorance of the large error associated with non-uniform temperature fluctuations
    - Ignorance of the importance of having adequate sample mass
- **Recommend improved instrumentation, protocols and data analysis to minimize such errors**
  - NREL emphasizes the need for careful procedures and control experiments
  - NREL manages and collaborates on the “Best Practices” project (ST052)

- **Error Analysis on Full Mass-Balance Model:**
  - Null miscalibration
  - Reference volume miscalibration
  - Non-uniform temperature fluctuations
  - Digital error
  - Helium Adsorption during calibration
- **Recommended Procedures:**
  - It is extremely important to measure the null calibration as accurately as possible (~ 1 /1000 to 1/10,000)
  - The system should be tested (& occasionally retested) with no sample to determine its ability to measure ‘zero’ adsorption (isothermal and non-isothermal conditions)
  - The system should be tested with a known material to check the absolute calibration
  - The system’s temperature profile should be controlled and monitored (pressure stability test)
  - Use the highest sample mass as possible for measurements

Non-Isothermal Measurements

Models have been developed to realistically handle non-isothermal measurements.

Equation must reflect the volumes at different temperatures and the temperature gradient

$$n_{ads_i} = \frac{1}{R\,T_r}\left[\left(\frac{P_{Chr_i}}{z_{Chr_i}} - \frac{P_{Clr_i}}{z_{Clr_i}}\right)V_r - \left(\frac{P_{E_i}}{z_{Er_i}} - \frac{P_{E_{i-1}}}{z_{Er_{i-1}}}\right)\left(V_t - V_s - \Delta V_{\Delta T}\right)\right]$$

$$- \frac{V_s}{R\,T_s}\left(\frac{P_{E_i}}{z_{Es_i}} - \frac{P_{E_{i-1}}}{z_{Es_{i-1}}}\right) - \frac{\Delta V_{\Delta T}}{R}\left(\frac{P_{E_i}}{\tau_{E_i}} - \frac{P_{E_{i-1}}}{\tau_{E_{i-1}}}\right)$$

$$\boxed{z_{Xk_i} \equiv z\left(P_{X_i}, T_k\right) \quad ; \quad \frac{1}{\tau_{E_i}} \equiv \frac{1}{L}\int_{x=T_r}^{x=T_s} \frac{dx}{T(x)\,z(P_{E_i}, T(x))}}$$

Why is accuracy so important?

- **Inaccurate measurements create confusion in the research community (false positives & false negatives)**
- **Wastes time & money for all involved**
  - Originating group
  - Funding agency
  - Other research groups who try and replicate the results
  - Misdirects funding to poor materials
  - Prematurely dismisses a promising material
- **Damages reputations**