RESEARCH SUMMARY

Using Oscillations to Determine Capillary Condensation in MCM-41

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Outline

- Motivation
- Objective
- Material
- Calibration Methodology
- Procedure
- Results:
    - Effective Spring Constant
    - Sensitivity Analysis
    - Added Mass coefficient
- Need to account for change in mass due to pore gas
- Pore Volume and Porosity calculation using He gas
- Calculation of change in mass due to adsorption and condensation

Motivation

- Condensation of hydrocarbon fluids in micropores and mesopores in unconventional resources is important as nanopores contribute to a significant amount of porosity in the unconventional resources
- Ordered nanoporous materials are used because of their well-defined pore sizes, high surface area and high pore volume
- Helpful to verify our methodology

Objective

- Measure capillary condensation in artificially created MCM-41 nanosilica material with specific pore size using a new oscillation based-gravimetric method
- Perform the measurement at high-pressure and high-temperature conditions

Principle of measurement:

Determine change in mass of a sample using object's inertia during harmonic oscillations

Spring mass system

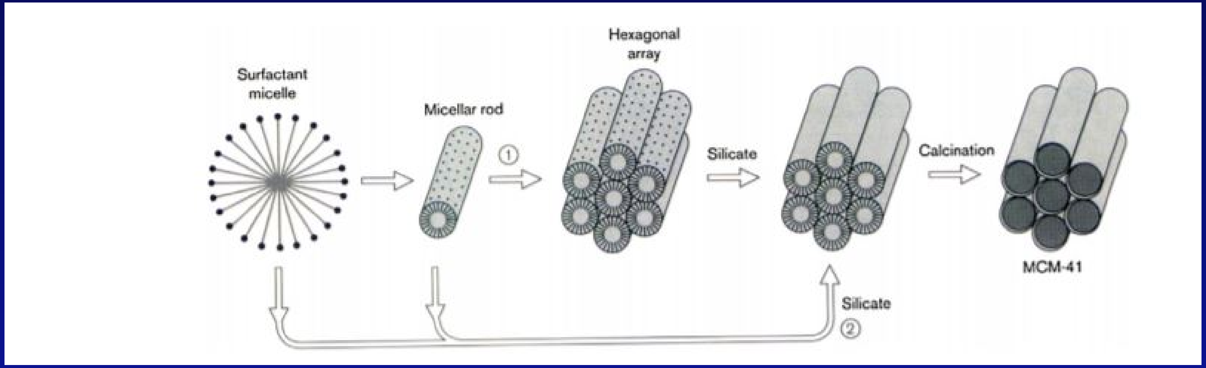
- Using the oscillating frequency of a spring-mass system to measure the mass of an object placed in the pressurized gas environment
- Account for the effect of mass of surrounding dense gas on the object's oscillating frequency (Adapted from Larson et al, 2015)
- Account for the effect of mass gas occupied in pores on the object's oscillating frequency

Advantages:

- Easy to set up
- Easy to operate
- Simple

Material: Mobile Crystalline Material(MCM-41)

- Contains Mesopores
- Typically synthesized by silica-surfactants mixtures
- Porosity can be as high as 80%
- Pore diameter typically tuned to: 2-10nm
- High pore volume, high BET surface area and high hydrocarbon sorption capacity



MCM-41 Synthesis Procedure adapted from Raji et al., 2013

MCM-41: Characterization using Nitrogen

Adsorption average pore diameter	2.4-2.6 nm

BJH adsorption (between 1.7 nm and 300 nm diameter)	0.82 ± 0.075 cm^3/g
BJH desorption (between 1.7 nm and 300nm diameter)	0.95 ± 0.067 cm^3/g

BET Surface area	1032.92 m^2/g

Calibration Methodology

Change in Frequency of a Porous Solid

- Change in the mass of co-accelerated gas outside porous solid

  M_a

  a = added mass

- Change in the mass of co-accelerated gas inside porous solid

  M_p

  p = pore gas

- Change in the mass due to adsorption and condensation

  $M_{Adsorption\ and\ Condensation}$

Calibration Methodology

Change in frequency is related to change in mass

$$f = \frac{1}{2\pi} * \sqrt{\left(\frac{k}{M_{Total}}\right)}$$

$$\Delta f \alpha \, \Delta M_{Total}$$

Where, $M_{Total} = M_a + M_p + M_{Adsorption+Condensation}$

Calibration is done following the 3 steps below:

Step 1:

Calibration for added mass

$$M_a = \alpha P$$

Where, $\alpha = added\ mass\ coefficient$ (unit: g/psi)

using a non porous mass of the same shape as the porous solid weighing 15g, 20g and 25g.

Step 2: Calibration for pore gas

- For porous samples, the mass of gas inside the pores, mpG, should also be determined, because this mass also adds to the total inertial mass sensed by the oscillation
- Ultra high purity Helium Gas is used on the MCM-41 sample to determine the pore volume

$$m_{pG} = (Pore\,Volume) * \frac{P}{zRT} * MW$$

- m_{pG} is then calculated for propane, using the determined pore volume (using Helium) and molecular weight of Propane (44.01g/mol)

Step 3: Mass change due to Adsorption and Condensation

- Using High purity Propane Gas (99.9999%) to determine the change in mass after determining the change in mass due to pore gas
- Any additional mass other than m_a and m_{PG} will be associated to mass due to adsorption and condensation

$$\boldsymbol{m_T - m_a - m_{PG} = m_C}$$

m_T is the total change in mass

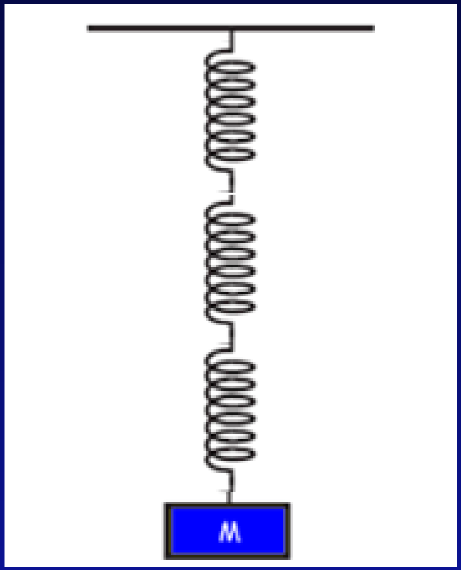
m_a is the change in mass due to added mass

m_{PG} is the change in mass due to pore gas

m_C is the change in mass due to adsorption and condensation

Procedure

To account for small mass of sample, springs had to be connected in series and the total weight (test object, weight holder and magnet) had to be reduced



Weight Holder

- To reduce the deadweight from the weight holder, an aluminum sample container (1.45” diameter) is used to hold the sample. Holes are drilled on the top of the cap to suspend it from the top of the pressure vessel
- The new sample holder is attached to the top of the PVT cell using a cotton thread (to avoid deadweight addition and wearing)
- Holes are drilled on the cap of the sample holder to let the gas in

Determination of Effective Spring Constant

Mass	Spring Constant (N/mm)
Using 1 Spring	
16.016	0.153
32.079	0.152
48.189	0.153
71.216	0.152
Using 2 Springs	
16.016	0.076
32.171	0.077
48.189	0.077
63.875	0.077

Determination of Spring Constant

Mass	Spring Constant Effective (N/mm)
Using 3 Springs	
6.645	0.051
10.340	0.051
16.985	0.051
26.448	0.051
16.106	0.051
32.171	0.051
48.000	0.051
63.686	0.051

Determination of Spring Constant

Mass	Spring Constant Effective (N/mm)
Using 4 Springs	
14.660	0.038
17.090	0.038
19.280	0.038
23.440	0.038
25.580	0.038
30.280	0.038

Sensitivity Results

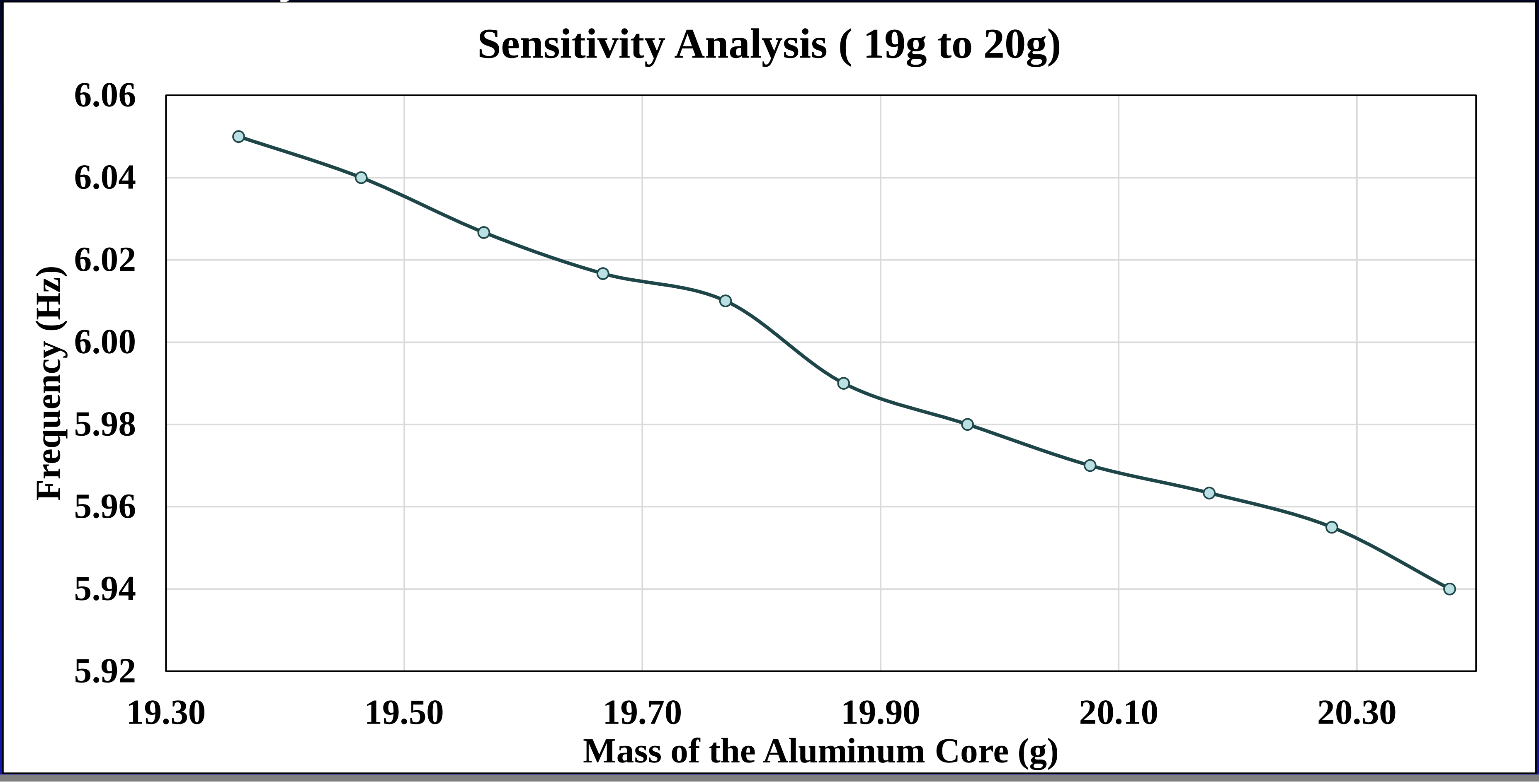
Mass	Spring Constant Effective (N/mm)
4 Springs	
16.108	0.038
17.111	0.038
18.114	0.038
19.117	0.038
19.362	0.038
20.365	0.038
20.620	0.038
21.368	0.038
22.371	0.038
23.874	0.038

Sensitivity Results

Mass	Spring Constant Effective (N/mm)
4 Springs	
19.361	0.038
19.464	0.038
19.667	0.038
19.770	0.038
19.869	0.038
19.973	0.038
20.076	0.038
20.176	0.038
20.279	0.038
20.378	0.038

Sensitivity Results

- The smallest mass change that could be detected: 0.1g out of 20g
- Sensitivity: 0.5%

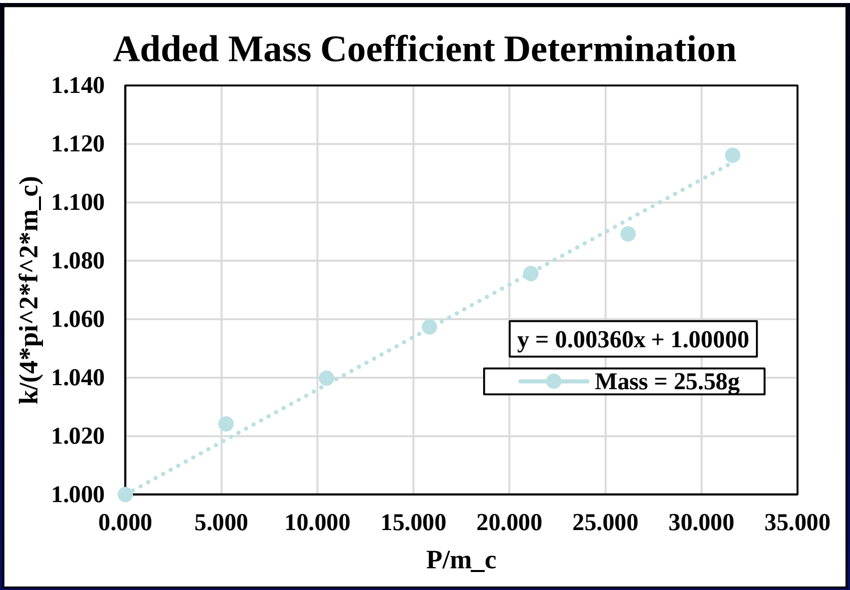


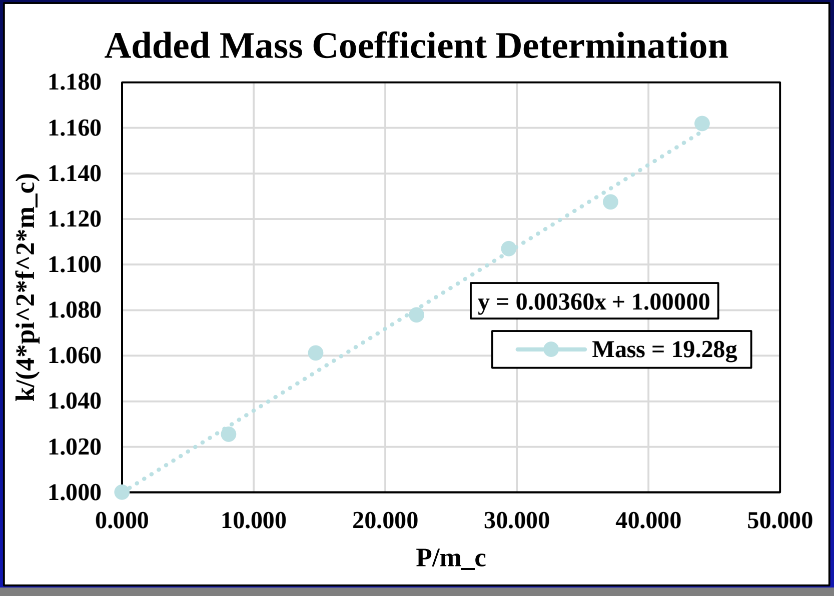
Added Mass Coefficient Results

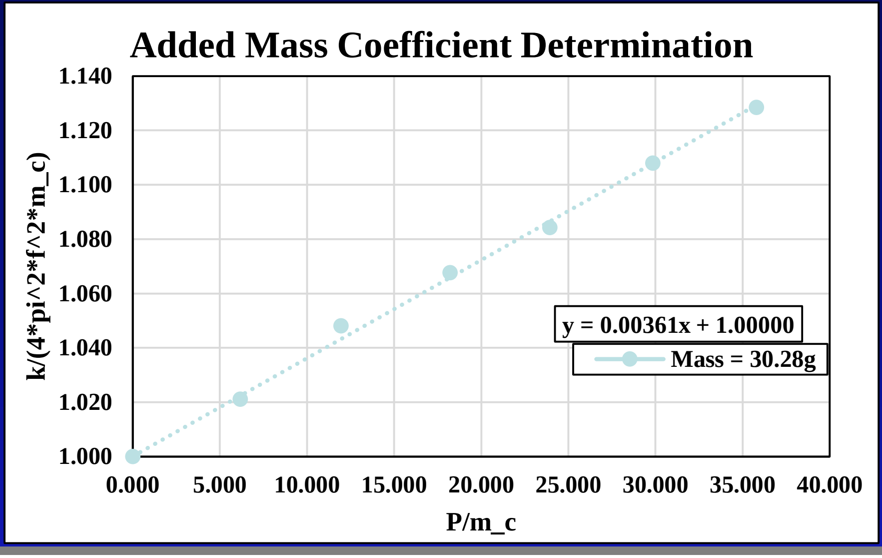
$$f = \frac{1}{2\pi} * \sqrt{\left(\frac{k}{M_{Total}}\right)}$$

$$\frac{k}{4\pi^2 f^2} = m_c + \alpha P$$

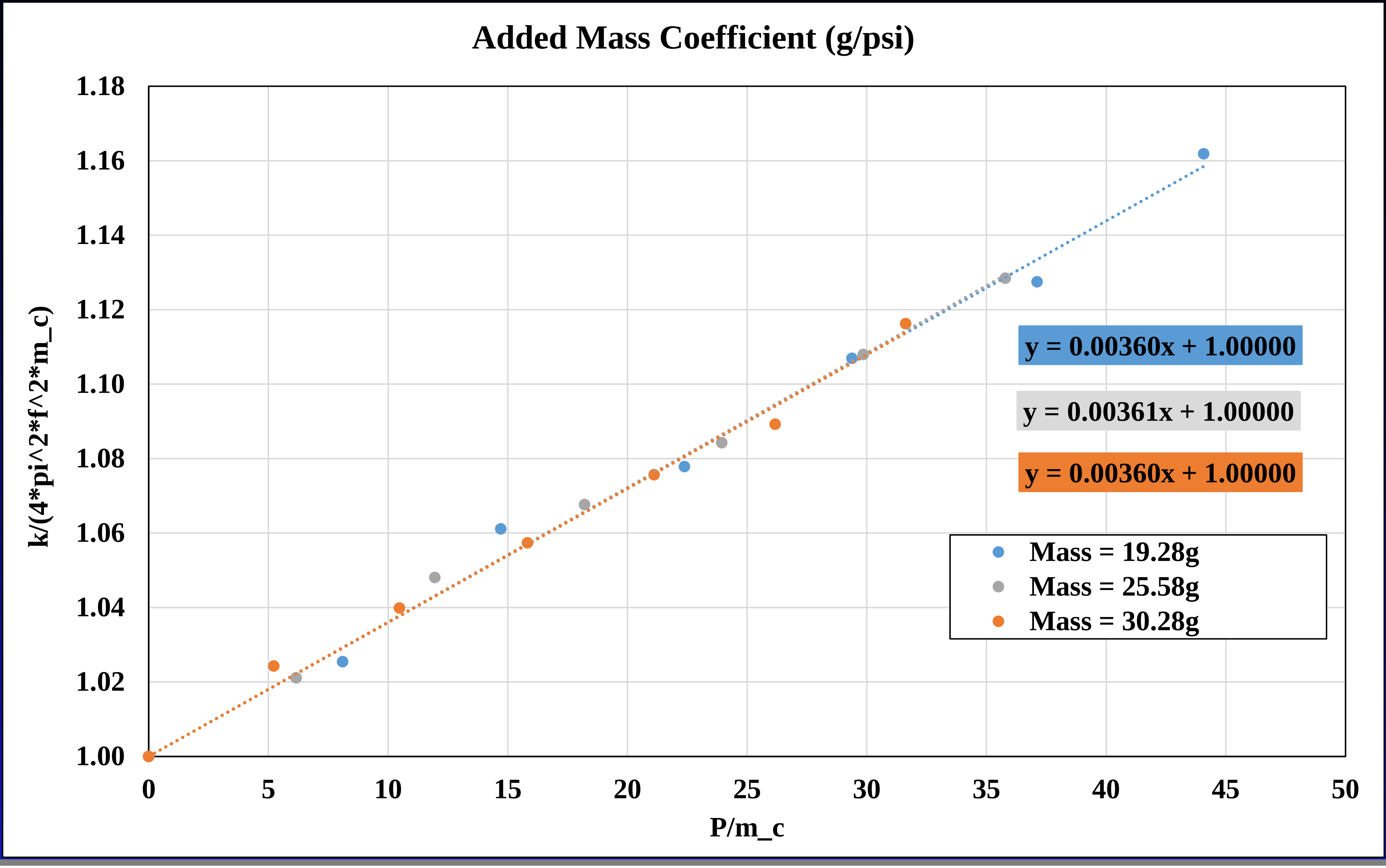
$$\frac{k}{4\pi^2 f^2 m_c} = 1 + \alpha\left(\frac{P}{m_c}\right)$$







Added Mass Coefficient Results



Future Work

- Need to account for change in mass due to pore gas
- Pore Volume and Porosity calculation using He gas
- Calculation of change in mass due to adsorption and condensation

Objective

Thank you