In Situ Optical Characterization of Solid Precursor Delivery for ALD Processes

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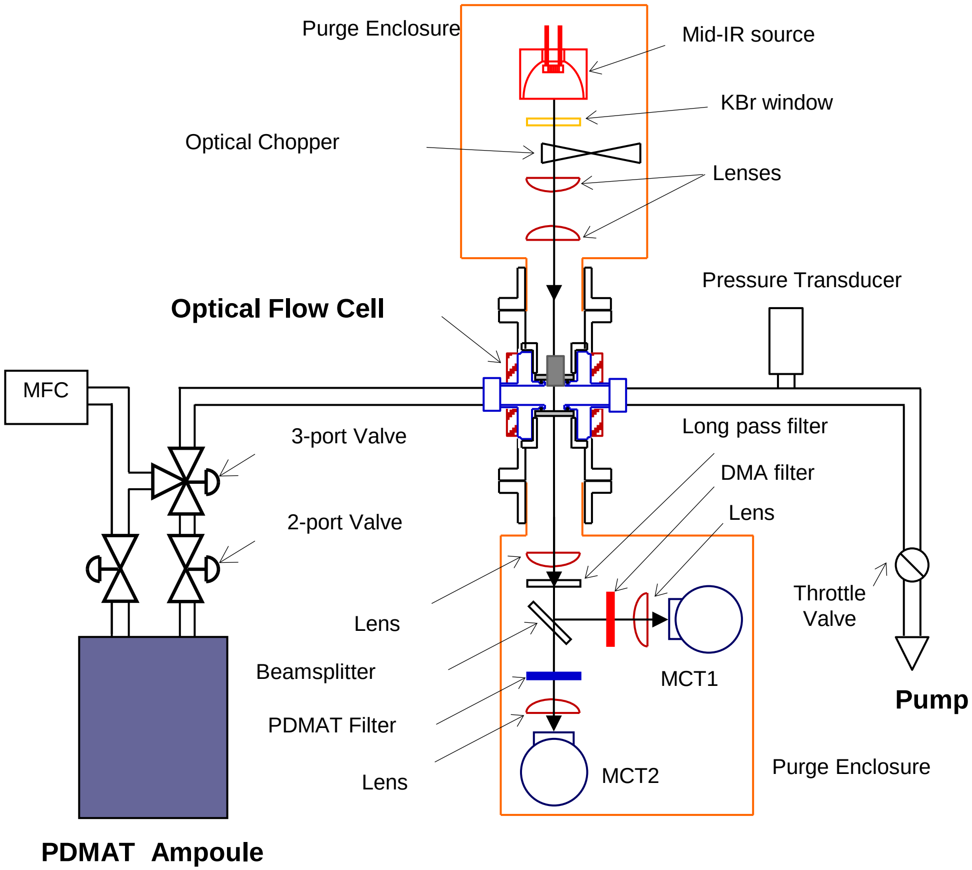
Goals

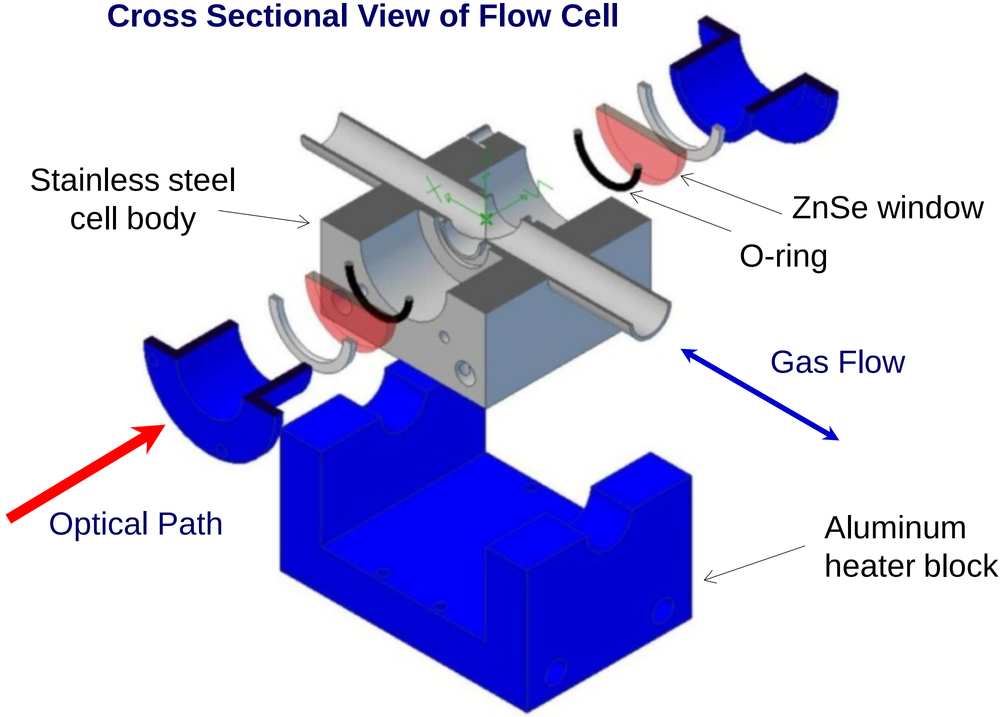
- **To demonstrate the utility of an optical measurement for use as a metalorganic precursor mass flow meter**
- **To use this technique to better understand the factors impacting the delivery of a representative ALD solid precursor, pentakis dimethyamido tantalum (PDMAT)**

Experimental Method: Measurement Configuration



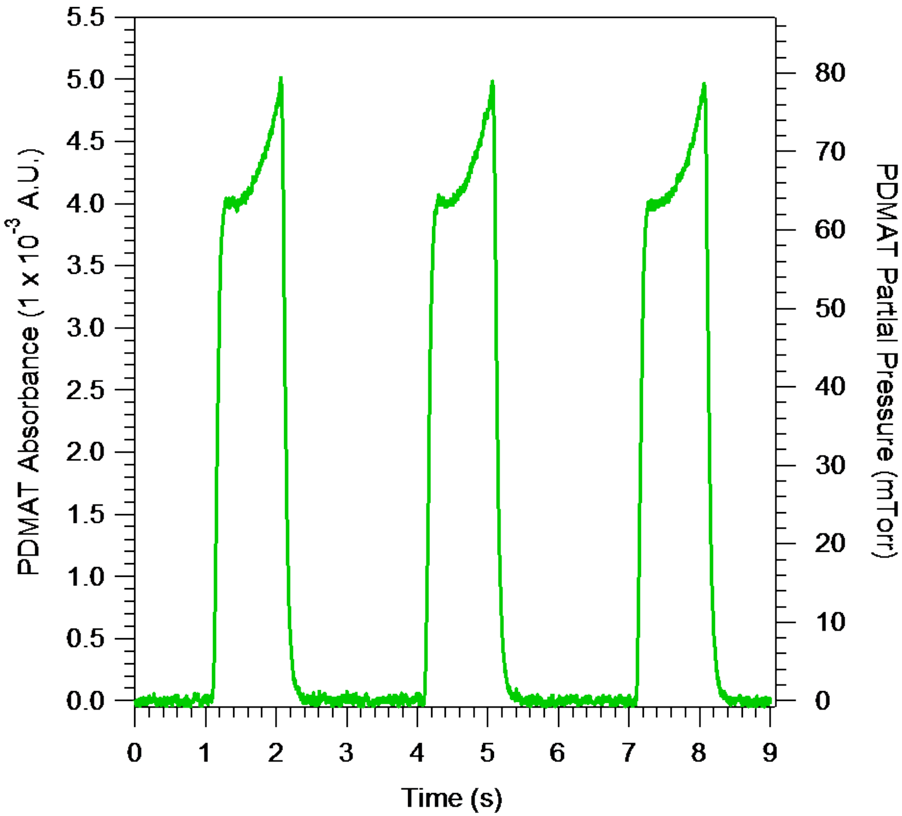
- **50 g PDMAT was loaded into a 1.2 L-volume industrial ampoule**
  - Ampoule was a direct vapor draw design
  - Ampoule is jacketed in aluminum
  - All lines and valves are wrapped with heating tape and maintained ~90 °C
- **PDMAT Injection Conditions**
  - Nitrogen carrier gas with mass flow rates from 100 sccm to 1500 sccm
  - 1 sec PDMAT injection followed by 2 sec purge
- **PDMAT channel signal, DMA channel signal, system pressure, and ampoule jacket temperature were measured as a function of time during PDMAT delivery for 12 days**
  - Optical measurements were performed using a 2-channel mid-infrared bandpass filter-based infrared absorption technique

Experimental Method: Optical Flow Cell Design



- **Optical access to the gas stream was achieved with a custom-designed optical flow cell that was mounted in the delivery line just downstream of the ampoule**
  - **Optical access was designed around a ½" OD stainless steel tube**
    - Single pass configuration
    - Optical pathlength of ~10 mm
  - **The window design was such that (coupled with heating of the cell) perturbations to gas flow and temperature in the gas stream were minimized**
  - **The flow cell was incased in an aluminum block to provide uniform heating and minimize PDMAT condensation**

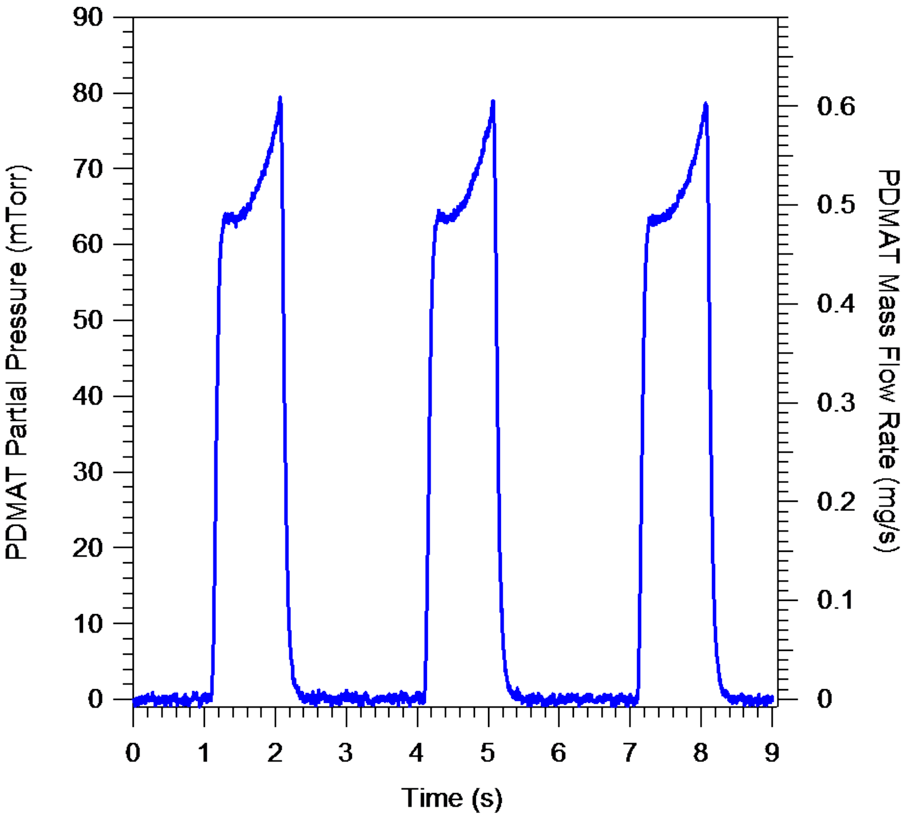
Experimental Method: Determination of Partial Pressure



- **Convert measured detector signal to Absorbance**
- **Convert Absorbance to partial pressure for both PDMAT and DMA**
  - Employ a calibration curve constructed by measuring Absorbance as a function of pressure for a series of pressures (for both PDMAT and DMA)
  - Calibration measurements were performed in a static UHV optical cell and assume ideal gas behavior
- **This optical technique provides a measurement of partial pressure**

Carrier Gas Flow Rate:	**1 slm**
System Pressure:	**~39 Torr**
Ampoule Jacket Temperature:	**74-75 °C**

Experimental Method: Calculation of Mass Flow Rate



Carrier Gas Flow Rate: 1 slm
System Pressure: ~39 Torr
Ampoule Jacket Temperature: 74-75 °C

- **Convert partial pressure to mass flow rate (STP) assuming that**

$$\frac{F_{\mathrm{PDMAT}}}{F_{\mathrm{N_2}}} = \frac{P_{\mathrm{PDMAT}}}{P_{\mathrm{N_2}}}$$

$$P_{\mathrm{sys}} = P_{\mathrm{N_2}} + P_{\mathrm{PDMAT}} \approx P_{\mathrm{N_2}}$$

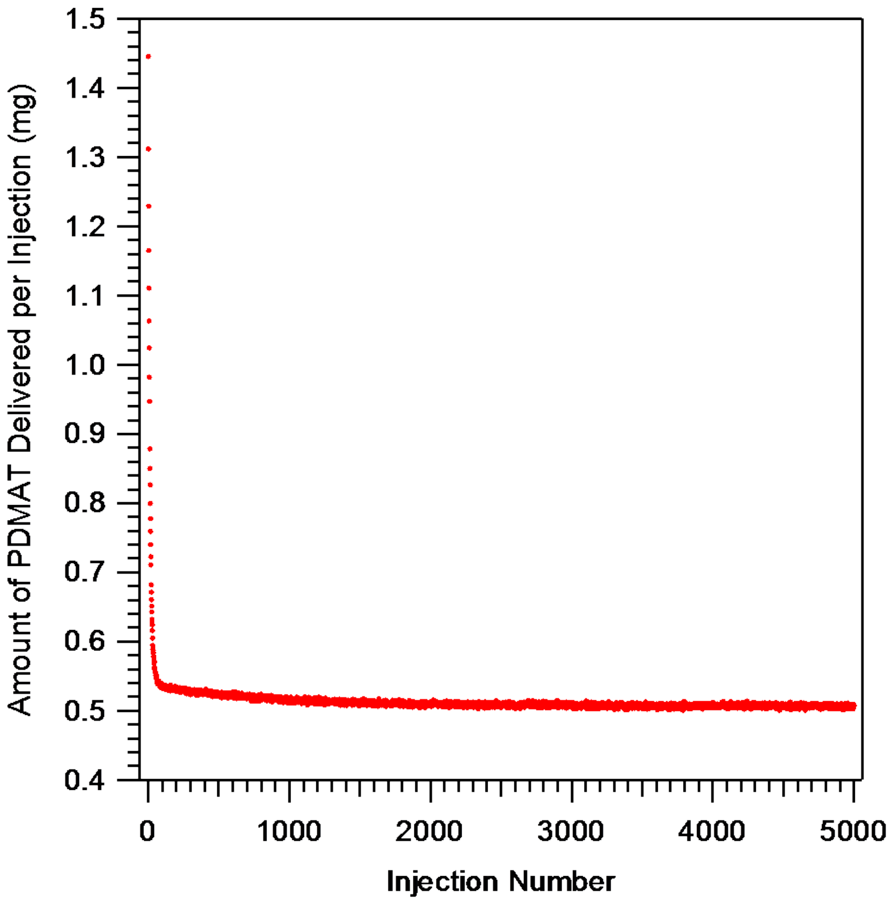
Where F_{PDMAT} is the PDMAT flow rate, $F_{\mathrm{N_2}}$ is the nitrogen carrier gas mass flow rate, P_{PDMAT} is the PDMAT partial pressure, P_{sys} is the total system pressure, and P_{N2} is the nitrogen partial pressure

- **Rearranging and solving for F_{PDMAT}**

$$F_{\mathrm{PDMAT}} = F_{\mathrm{N_2}} \frac{P_{\mathrm{PDMAT}}}{P_{\mathrm{sys}}}$$

- **Convert from PDMAT flow rate (STP) to flow rate in g/s**
- **Integrate PDMAT flow rate (g/s) over time to obtain grams delivered per injection**

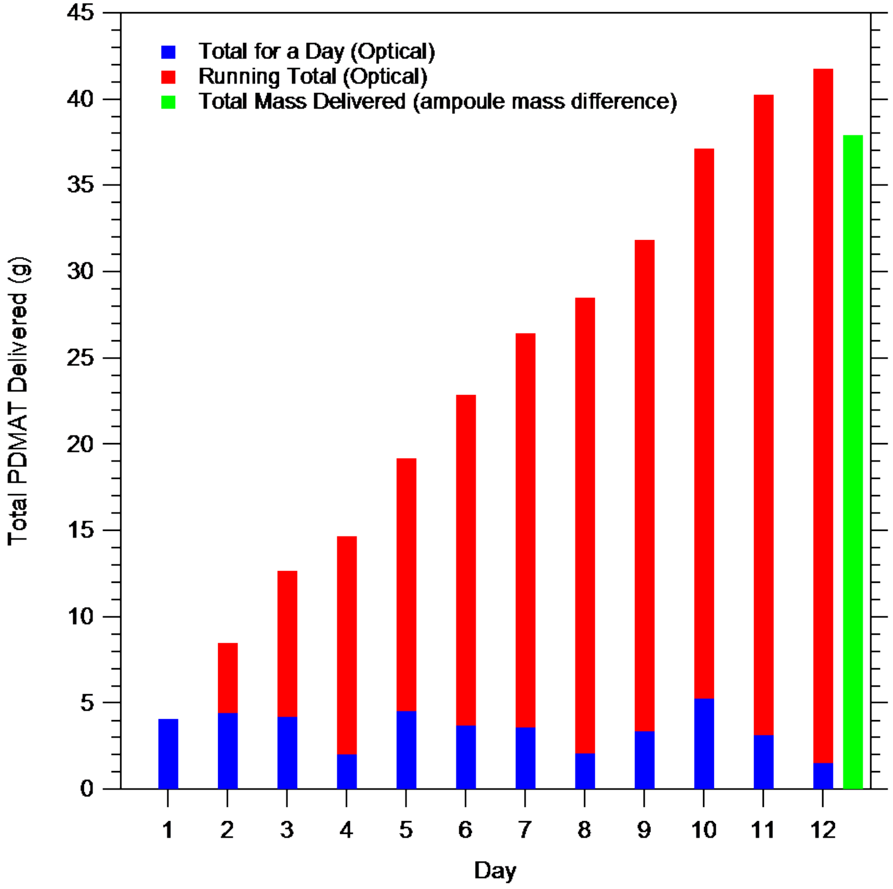
PDMAT Mass Delivered Per PDMAT Injection During One Run on Day 3



Carrier Gas Flow Rate:	**1 slm**
System Pressure:	**~39 Torr**
Ampoule Jacket Temperature:	**74-75 °C**

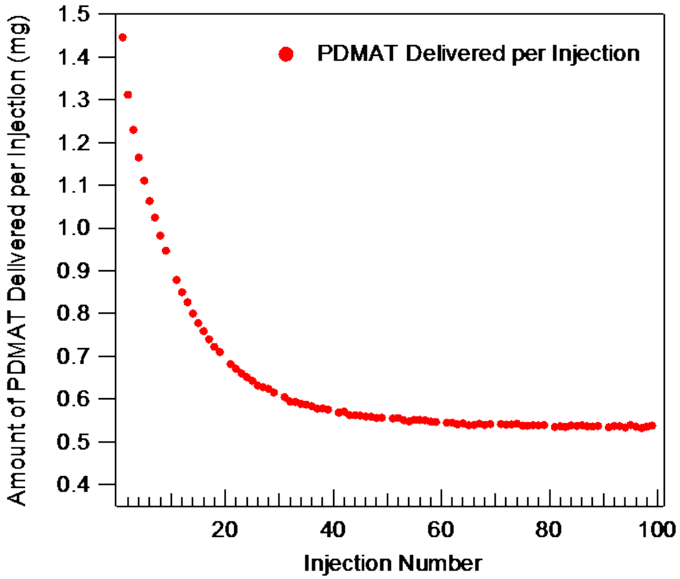
- **The amount of PDMAT delivered per injection can be calculated for all injections with a measurement of PDMAT partial pressure (optically measured), system pressure (from pressure transducer), and carrier gas mass flow rate (from mas flow controller)**
- **The dependence on time of the amount of PDMAT delivered typically appears as shown, for an uninterrupted run at a given set of conditions**
  - An initial sharp decrease in mass of PDMAT delivered
  - A steady-state value eventually is reached
    - The time needed to reach a steady-state value depends on injection conditions and the amount of time since PDMAT ampoule was used
- **The origin of these features will be discussed subsequently**

Total PDMAT Mass Delivered During All Runs



- **Measurements were made on 12 different days over a period of ~2 weeks**
  - Total number of injections ~83750
  - Between 1 g and 6 g delivered per day
  - Flow rates between 100 sccm and 1500 sccm
  - Ampoule jacket temperature at ~74-75 °C or ~79-80 °C
- **Mass Delivered Comparison**
  - **Ampoule mass difference: ~37.9 g**
  - **Optically-determined mass: ~41.8 g**
  - **~10 % difference**

Origin of Initial Decrease of PDMAT Delivered

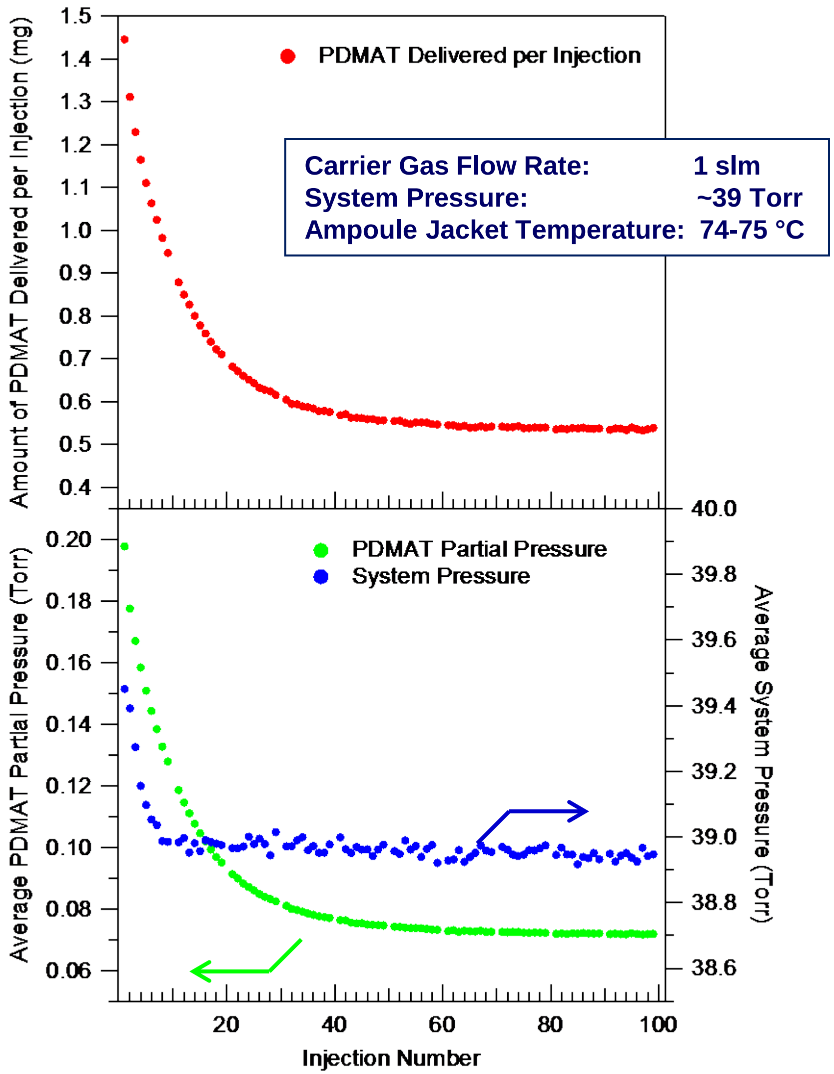


Carrier Gas Flow Rate:	**1 slm**
System Pressure:	**~39 Torr**
Ampoule Jacket Temperature:	**74-75 °C**

- **The amount of PDMAT delivered per injection depends on the PDMAT partial pressure, system pressure, and carrier gas mass flow rate**

$$F_{\mathrm{PDMAT}} = F_{\mathrm{N_2}} \frac{P_{\mathrm{PDMAT}}}{P_{\mathrm{sys}}}$$

Origin of Initial Decrease of PDMAT Delivered



- **The amount of PDMAT delivered per injection depends on the PDMAT partial pressure, system pressure, and carrier gas mass flow rate**
  - **Carrier gas mass flow rate is stable (not shown)**
  - **System pressure stabilizes relatively quickly**
  - **Both the PDMAT delivered and the PDMAT partial pressure exhibit a sharp initial decrease**
- **The decrease in the amount of PDMAT delivered per injection is attributed to the decrease in PDMAT partial pressure**
  - **A maximum PDMAT partial pressure of ~0.2 Torr is observed only during the first injection**
    - The reported PDMAT vapor pressure at 74 °C is ~0.24 Torr (72 °C is ~0.2 Torr)
- **Origin of the decrease in PDMAT partial pressure?**
  - **Lower PDMAT vapor pressure resulting from cooling of the PDMAT powder due to sublimation and/or**
  - **Incomplete saturation of the carrier gas due to insufficient residence time/sublimation rate**

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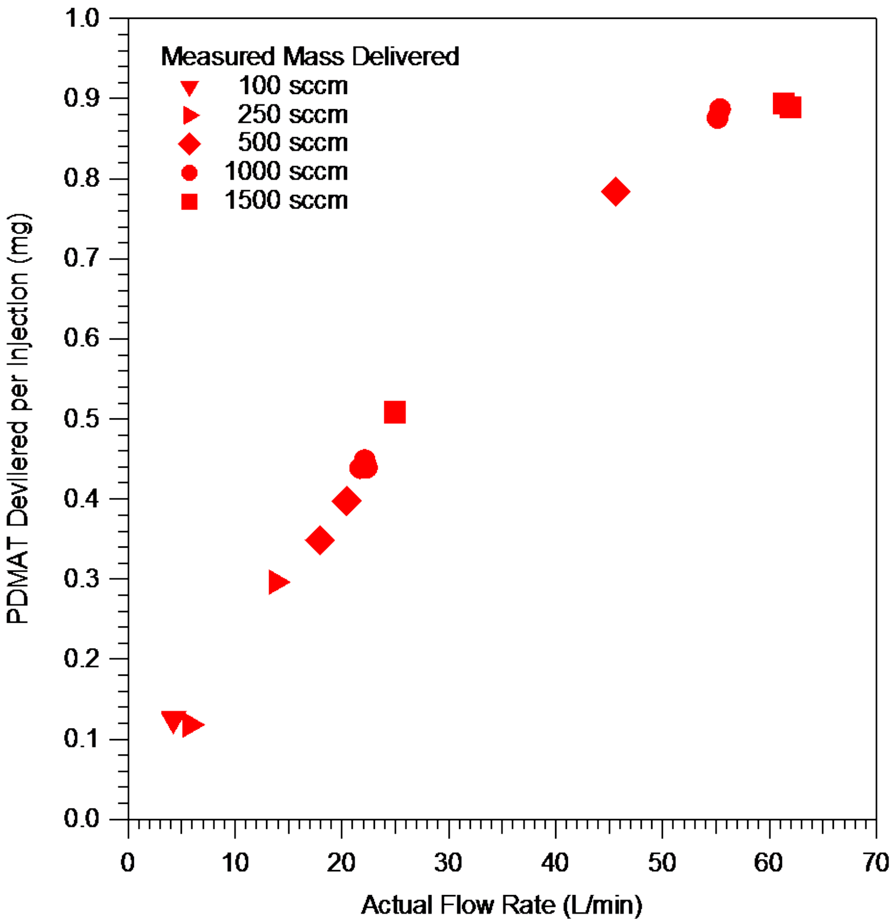
Dependence of PDMAT Mass Delivered on Flow Rate



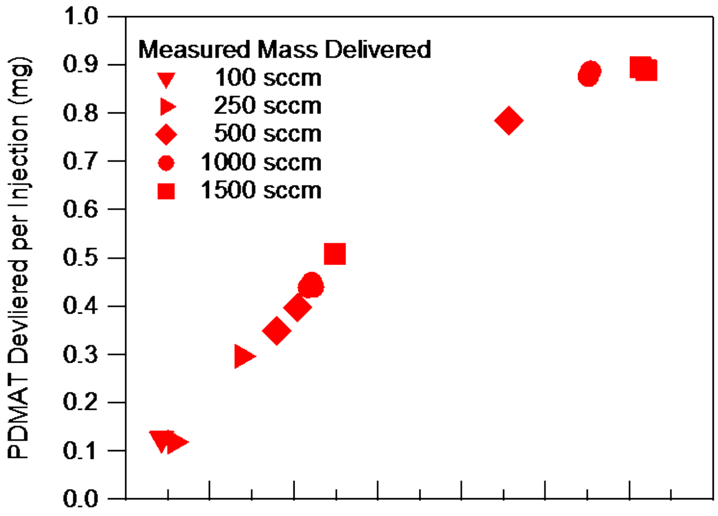
- **The amount of PDMAT delivered per injection (at steady-state) exhibits a strong dependence on actual flow rate except at high mass flow rate**

$$F_{\mathrm{PDMAT}}^{\mathrm{act}} = F_{\mathrm{PDMAT}}^{\mathrm{STP}} \left(\frac{P_{\mathrm{STP}}}{P_{\mathrm{sys}}}\right)\left(\frac{T_{\mathrm{cell}}}{T_{\mathrm{STP}}}\right)$$

Where $F_{\mathrm{PDMAT}}^{\mathrm{act}}$ is the actual PDMAT flow rate, $F_{\mathrm{PDMAT}}^{\mathrm{STP}}$ is the PDMAT flow at STP, P_{STP} is pressure at STP, P_{sys} is the total system pressure, T_{cell} is the temperature of the optical cell, and T_{STP} is the temperature at STP

- **For a given mass flow rate (STP), lower system pressure (higher actual flow rate) results in higher PDMAT flow rates, as expected**
- **There is little difference in mass of PDMAT delivered at flow rates of 1000 sccm and 1500 sccm under these conditions (actual flow rates above ~50 L/min)**

Origin of PDMAT Mass Flow Rate Saturation at High Carrier Gas Flow Rate



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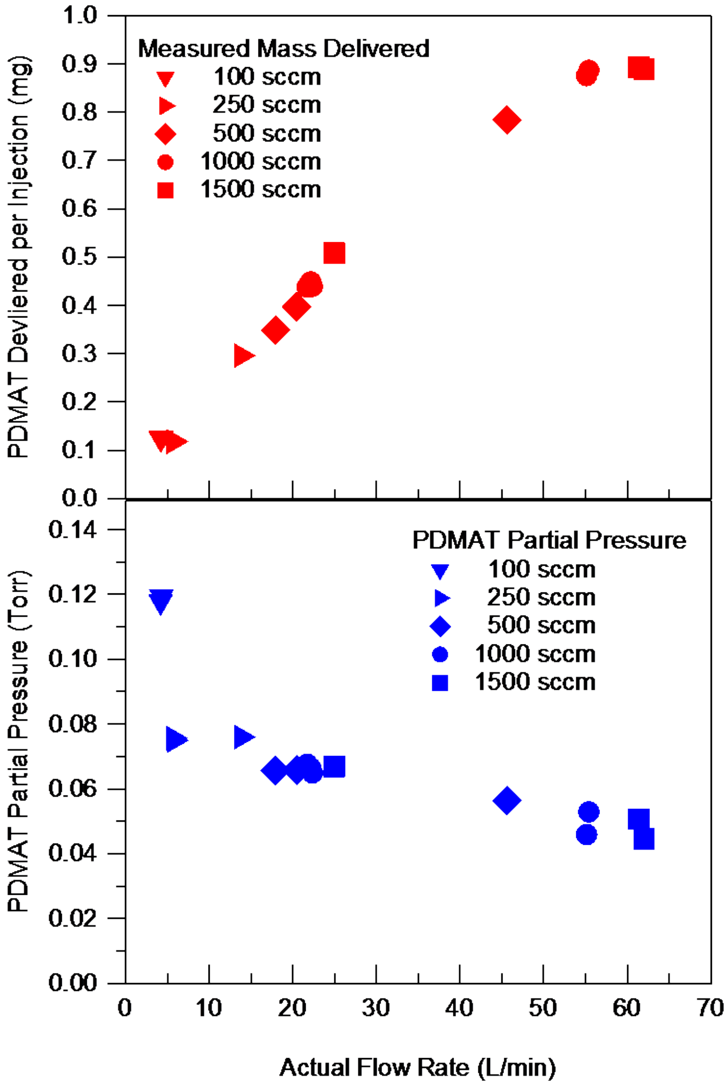
Origin of PDMAT Mass Flow Rate Saturation at High Carrier Gas Flow Rate



- **PDMAT partial pressure generally decreases with increasing actual flow rate**
  - Steady-state partial pressure does not approach reported PDMAT vapor pressure of ~0.24 Torr at 74 °C
  - A partial pressure of 0.2 Torr would result in between ~2x the amount of PDMAT delivered at low flow rates to ~4X at high flow rates
- **The saturation of the amount of PDMAT delivered per injection is attributed to the decrease in PDMAT partial pressure**
- **Origin of the decrease in PDMAT partial pressure?**
  - Lower PDMAT vapor pressure resulting from cooling of the PDMAT powder due to sublimation

    and/or

  - Incomplete saturation of the carrier gas due to insufficient residence time/ insufficient sublimation rate

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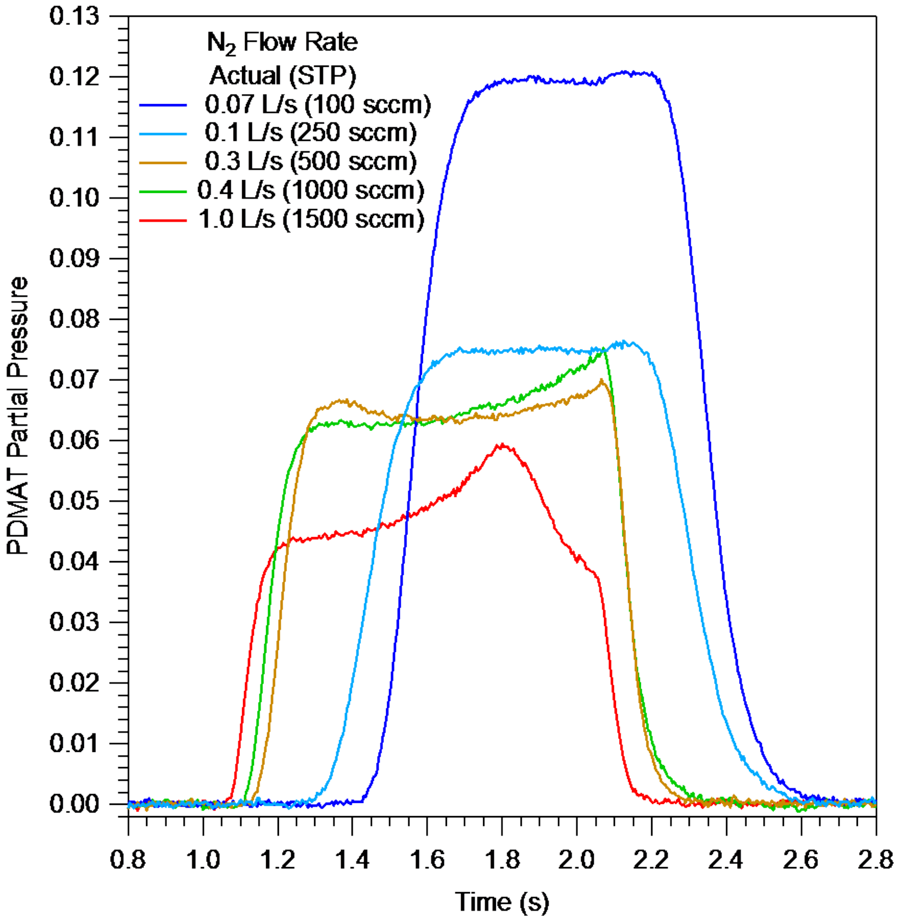
Individual PDMAT Injection Profiles for Different Flow Rates



- **The complexity of the PDMAT partial pressure versus time injection profile suggests a number of competing factors affecting overall partial pressure**
- **These injection profiles are reproducible at steady-state, for a given set of conditions**
- **At the lower flow rates the injection profile is squared off suggesting that the carrier gas is saturated**
- **At higher flow rates the profile is more complicated**
  - **The initial increase in partial pressure is attributed to injection of ~90 °C gas from the upstream valves and lines**
  - **A decrease in partial pressure at the end of the injection is observed at the higher flow rates that correspond to the plateau in the amount of PDMAT mass delivered at high flow rates**

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Summary and Conclusions

- **A direct absorption, optical method has been demonstrated to be suitable for a PDMAT mass flow meter**
  - The optical system is relatively simple, robust, and can provide high temporal resolution
  - This system is applicable to other organometallic compounds with mid-IR active modes by switching bandpass filters
- **This technique was employed to better understand the factors affecting the delivery of PDMAT from a direct vapor draw ampoule**
  - Upon initial PDMAT injection for a given set of conditions, the PDMAT partial pressure decreases rapidly from approximately the vapor pressure at the ampoule temperature
    - The time required to reach steady-state depends on injection conditions
  - The PDMAT partial pressure decreases with increasing actual flow rate
    - Compared to a PDMAT partial pressure of 0.2 Torr, this reduced PDMAT partial pressure corresponds to between ~50% less PDMAT delivered at low flow rates and ~77% less at higher flow rates
  - The lower observed PDMAT partial pressure is attributed to lower PDMAT vapor pressure resulting from cooling of the PDMAT powder due to sublimation and/or incomplete carrier gas saturation due to insufficient residence time/sublimation rate
  - The results demonstrate that higher carrier gas mass flow rates do not necessarily result in a higher mass of precursor delivered per injection