

# Commodity-Free Calibration

## 2006 Center Director's Discretionary Fund Project



Propellant Loading/  
Servicing/Storage

Commodity-free calibration is a reaction rate calibration technique that does not require the addition of any commodities. This technique is a specific form of the reaction rate technique, where all of the necessary reactants, other than the sample being analyzed, are either inherent in the analyzing system or specifically added or provided to the system for a reason other than calibration.

After introduction, the component of interest is exposed to other reactants or flow paths already present in the system. The instrument detector records one of the following to determine the rate of reaction: the increase in the response of the reaction product, a decrease in the signal of the analyte response, or a decrease in the signal from the inherent reactant. With this data, the initial concentration of the analyte is calculated.

This type of system can analyze and calibrate simultaneously, reduce the risk of false positives and exposure to toxic vapors, and improve accuracy. Moreover, having an excess of the reactant already present in the system eliminates the need to add commodities, which further reduces cost, logistic problems, and potential contamination. Also, the calculations involved can be simplified by comparison to those of the reaction rate technique.

We conducted tests with hypergols as an initial investigation into the feasibility of the technique. Hypergols are prime candidates for commodity-free calibration because they are highly toxic and exceptionally reactive. Consequently, these vapors present considerable challenges in handling and quantification. After characterization, nitrogen tetroxide (NTO) vapors were collected at low concentrations (about 10 ppm) in a fixed-volume gas collection tube. At  $t = 0$ , immediately after vapor collection, an acidic N-(1-naphthyl)ethylenediamine dihydrochloride (“diamine”) solution was injected through a septum into the collection tube containing the trapped vapors. The NTO vapors were allowed to react with the absorbing solution for a reaction time,  $t$ . At the given  $t$ , the contents of the collection tube were emptied into a cuvette and absorbance was measured with a UV-Vis spectrophotometer. We conducted separate experiments with  $t$  ranging from 1 to 15 min and plotted the resulting data to generate a reaction profile of instrument response versus time for this reaction (Figure 1). The resultant curve merely approximates the actual reaction profile because

its data reflects a series of reactions rather than a single reaction monitored over time. However, these results do look promising in that the reaction proceeds at a rate reasonable for use in analysis.

To monitor the kinetics of a single reaction, we designed a custom UV-Vis cuvette (Figure 2) that could be placed in the spectrophotometer, with a gas sample being introduced at  $t = 0$ . Time-based absorbance measurements would monitor the formation of the product, and from the resulting data, the concentration of the NTO vapors could be calculated. Reaction reversibility is crucial in order for this procedure to fit the commodity-free requirement. If the reaction were not reversible, the commodity expended during operation would need to be replenished. For demonstration, NTO vapors were reacted with a diamine solution. Time-based absorbance measurements were taken during the process, and the results are plotted in Figure 3. The spherical bubble

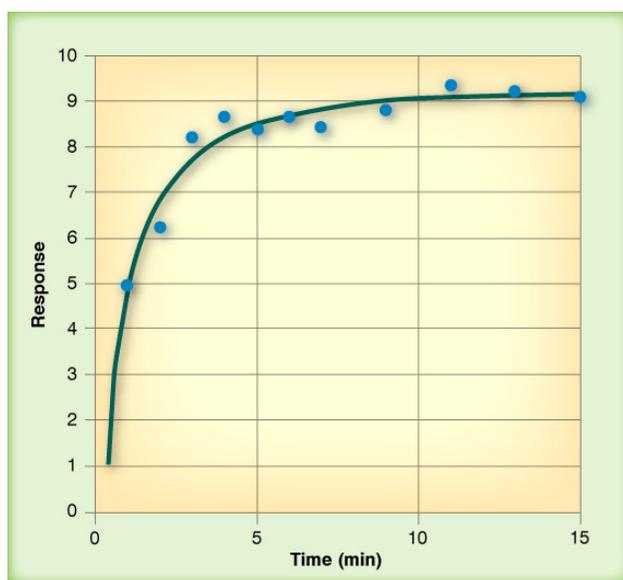


Figure 1. Reaction rate profile.

on top of the cuvette contains the NTO vapors and maximizes the solution-vapor interaction under these restricted reaction conditions. Upon delivery of the cuvette, reaction profiles from singular reactions over time can be generated. The plot of the log of the absorbance intensity (which is proportional to the product concentration) versus reaction time should be linear, with a slope that represents the reaction rate constant,  $k$ .

We studied the feasibility of using reaction time to calibrate a wide range of sensors and tested color-indicating chemistry as a way to track the reaction progress. We also developed systems using computer control, rather than color, to ensure the results are consistent. Our tests of these systems are showing promise for refining the technique. Future work includes finishing studies using the thermal desorption system to demonstrate if the technology is feasible for NASA's goals. Other reaction techniques could also be examined to determine the best approach.

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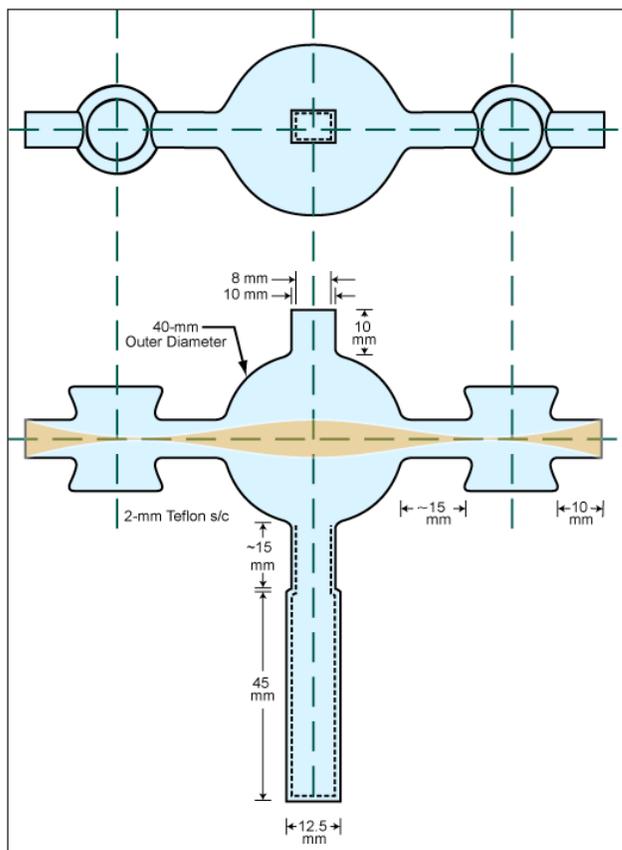


Figure 2. Custom-built UV-Vis cuvette.

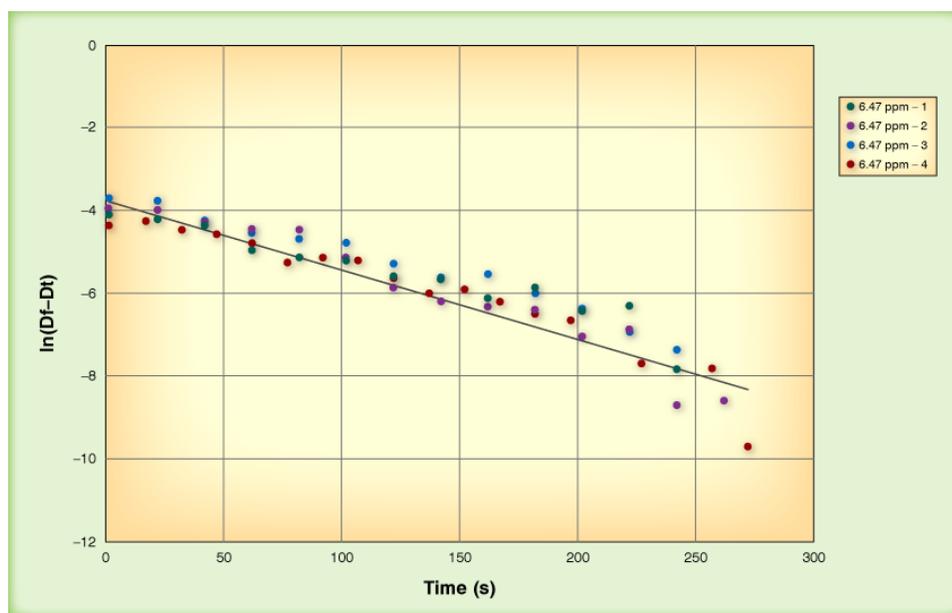


Figure 3. Time-based absorbance of NTO.