Accuracy of the Model 280 NOA™ Calibration

The Model 280 NOA's two-point calibration using "zero air" and a part per million (ppm) level standard is accurate over the entire linear range.

One of the challenges in the measurement of low, part per billion (ppb) concentrations of nitric oxide (NO) is accurate calibration of the analyzer. Gas standards of nitric oxide in nitrogen or air at the part per million (ppm) concentrations are commercially available and remain stable for many months Gas standards of NO at high ppb levels (>100 ppb) are not stable for long periods, and are expensive. Stable gas standards at low ppb levels (<100 ppb) are not available. The NOA's 2-point calibration does not require ppb level standards, and can be used to accurately calibrate the instrument over the entire linear range (Ippb-500ppm). To determine the accuracy of our calibration in the low ppb range, we compared the instrument's calculated calibration curve in this ppb range with a calibration curve created using known ppb level gas standards.

Because low level ppb NO standards are not available, we prepared these ppb level gas standards by diluting a known ppm level standard. There are two dilution methods: dynamic dilution and exponential dilution. We have chosen the exponential method to dilute our gases. This technique utilizes a flask of known volume, equipped with gas inlet and outlet ports and a mixing system. The flask is filled with a gas of known NO concentration and the gas inlet is connected to a supply of NO-free gas that is maintained at a constant flow rate into the flask. As the NO-free gas is added to the flask, the concentration of NO flowing out of the flask will decrease exponentially.

For this test, a home-made dilution flask of -1000 mL volume with two pieces of 1/4" OD glass tubing connected on opposite sides of the flask was used. A magnetic stir bar was placed in the flask and the top sealed by melting the glass. To remove any NO, the gas in the flask was evacuated with a vacuum pump for 1 hour before the flask was filled. To facilitate injection of NO into the flask, a septum was installed on the gas inlet and a three-way valve and pressure transducer were installed on the gas outlet tubing. After the flask was evacuated, the three-way valve was closed to maintain the flask at reduced pressure. A small volume (1 cc) of an NO standard was injected into the evacuated flask. A supply of NO-free gas was connected to the three-way valve and the position of the valve was changed to slowly add gas into the flask until the flask was at atmospheric pressure. The gas flow was then stopped and the threeway valve/pressure transducer and septum were removed. A short length of 1/8" OD Teflon® tubing was connected to the outlet gas tubing and the other end of the tubing was connected to a tee fitting installed at the inlet of the NOA . The three-way valve (without the pressure transducer) was connected to the gas inlet of the flask and the flow rate of gas measured with the valve in the divert position (no gas into flask). After the flow rate was measured and shown to be constant, the valve was switched to start the gas flow into the flask and the timer started.

An example of the measured NO concentration versus time for an exponential dilution is shown in Figure 1. For this experiment, the data was collected from the RS-232 port of the NOA at a sampling rate of 1 sample per second. The analyzer had been calibrated with "zero air" and a 99 ppm NO in nitrogen standard before the exponential dilution experiment was performed. In this example, a I cc sample of 99 ppm NO was injected into the flask and zero air used as the dilution gas at a flow rate of 200 mL/min. The concentration of NO in the outlet of the flask at time, t, is $C_t=C_o$*exp(-FtfV) where F = flow rate of dilution gas (mL/sec), V=volume of dilution flask and C_o=initial concentration of NO in flask.

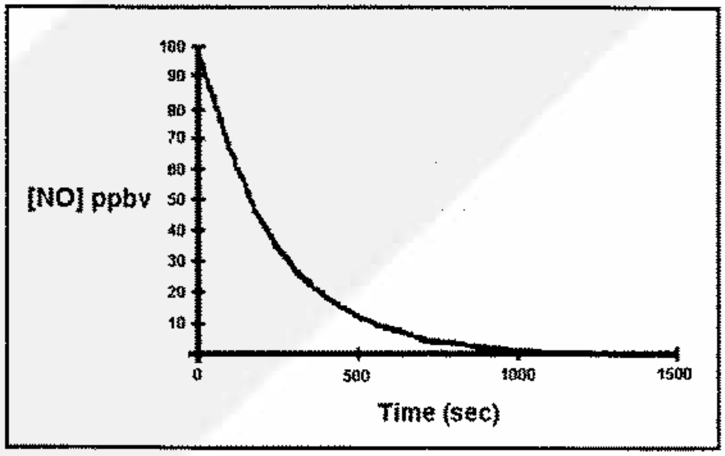

Figure 1: Measured Concentration of NO in Exponential Dilution

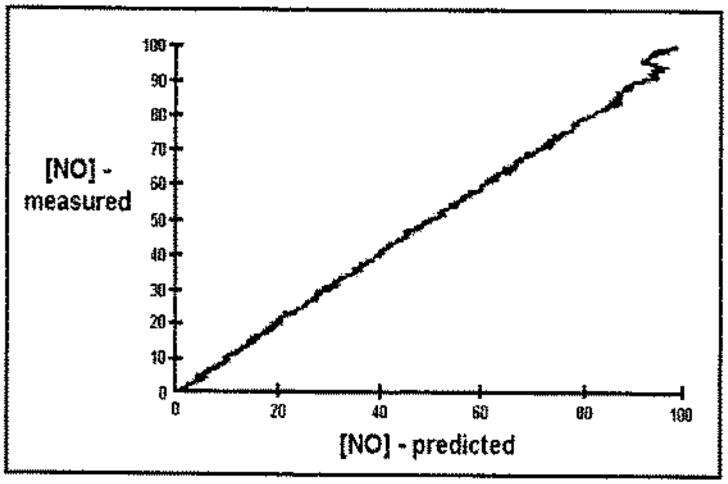

Figure 2. Measured [NO] versus Predicted [NO]

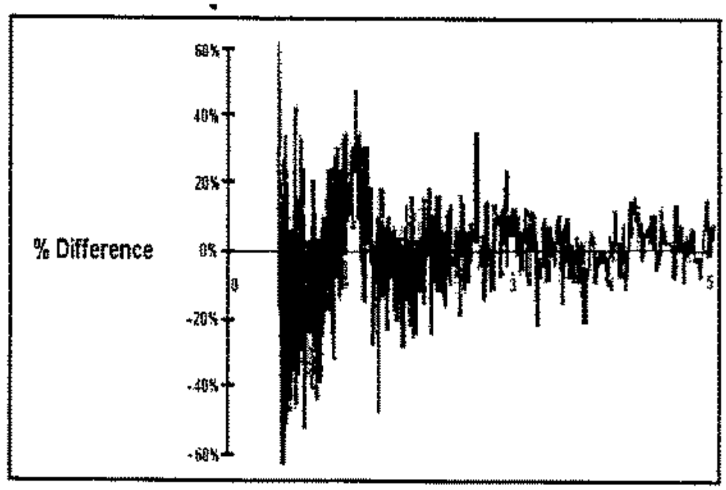

Figure 3. Percent Difference between Measured and Calculated [NO] from 5 to 0.5 ppb.

Figure 2 shows a plot of the measured NO concentration versus the calculated concentration. After some initial variations as the flow was established in the system, the measured value is in excellent agreement with the calculated value down to 1 ppb.

Another way to view the data is to plot the % difference between the measured and calculated NO concentrations versus the calculated NO concentration. This is shown in Figure 3 for the range from 5 ppb to 0.5 ppb and indicates that the deviation of the measured value from the calculated value increases at the lower concentrations. With the exception of a positive deviation around 1.5 ppb, the percent difference versus the calculated concentration is symmetrically distributed around zero indicating that there is no systematic error in the measurement of these low NO concentrations.

Figure 4 shows the average absolute % difference for 0.5 ppb intervals. Over the range of 5- 10 ppb, the average % difference was 3% (range was 2% to 5%). Over the range 2-5 ppb, the average % difference was 7% (range 4.5 - 10%). Below 2 ppb, the average % difference increases to 16% for 1 to 1.5 ppb up to 43% over the range 0.2 to 0.4 ppb. It should be noted that 0.2 ppb is the resolution of the 12 bit Analog to Digital Converter used in the NOA .

The data shown in Figure 4 can be used to estimate the uncertainty expected in the measurement of low ppb NO concentrations when the NOA is calibrated with ppm level standards. Since the average % difference for 5 ppb is about 4.5%, measurements of a gas stream containing 5 ppb should average between 4.8 and 5.2 ppb, although individual measurements may show larger variations.

This data demonstrates that the Model 280 NOA calibrated with a ppm-level standard will provide accurate measurements across the entire linear range of 1 ppb-500ppm.

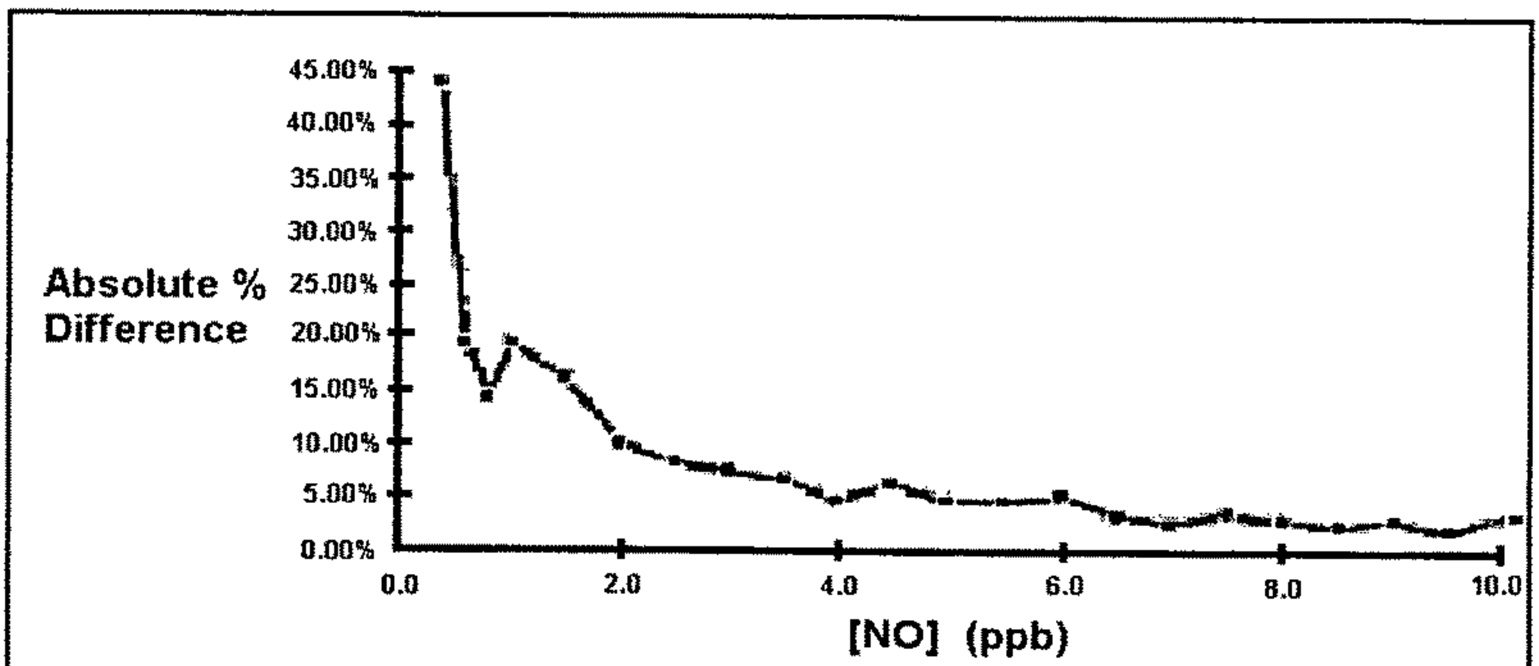

Figure 4. Absolute % Difference in 0.5 ppb Intervals from 0.5 to 10 ppb