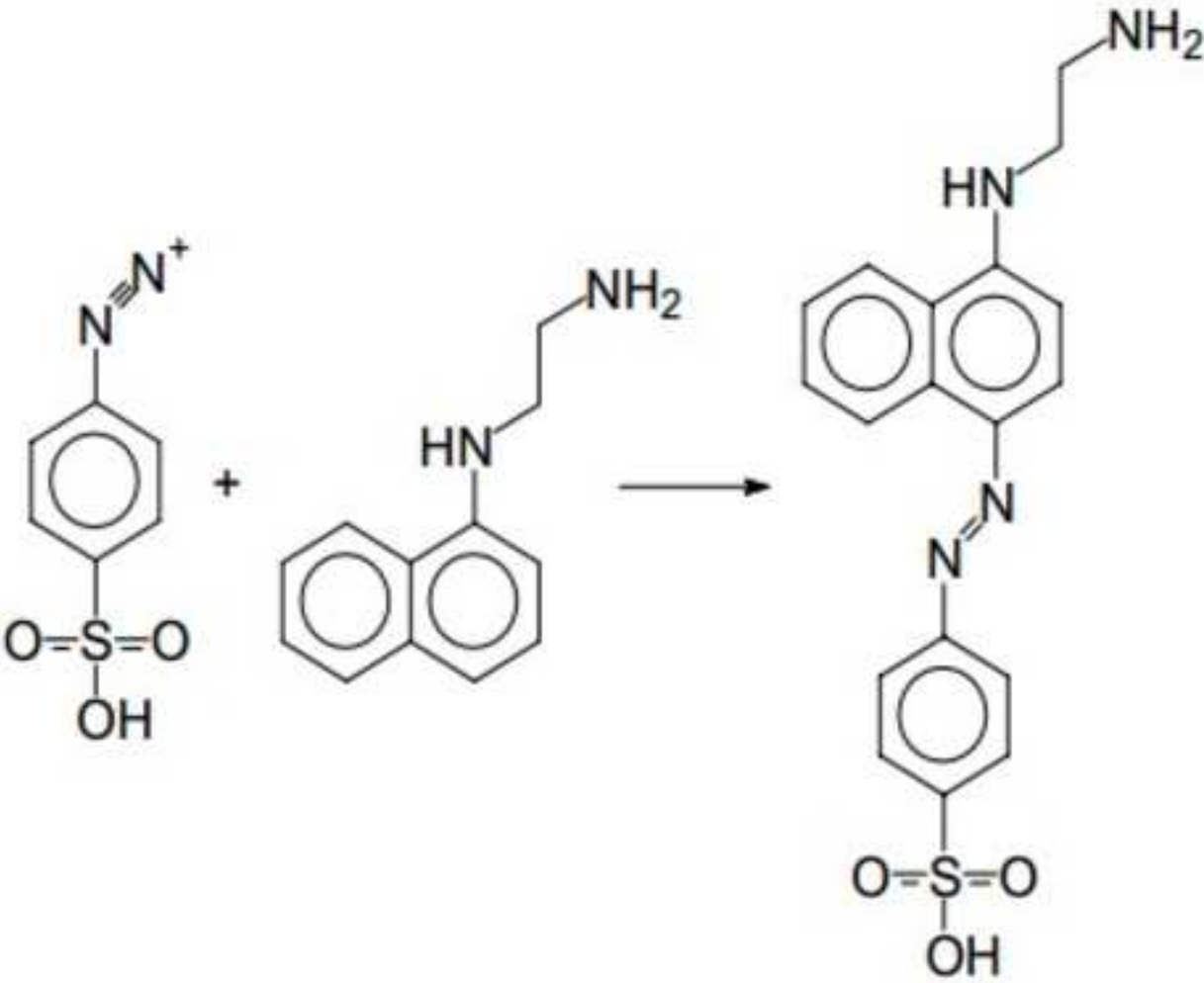
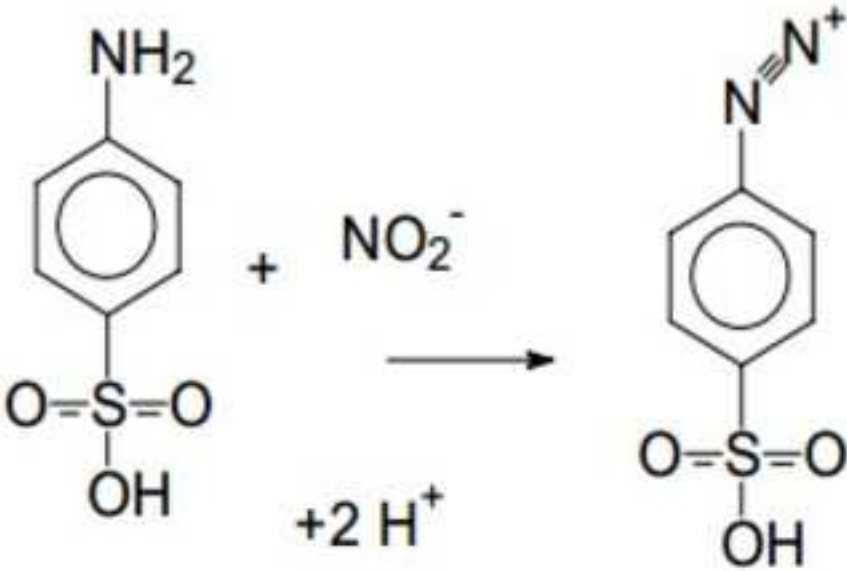


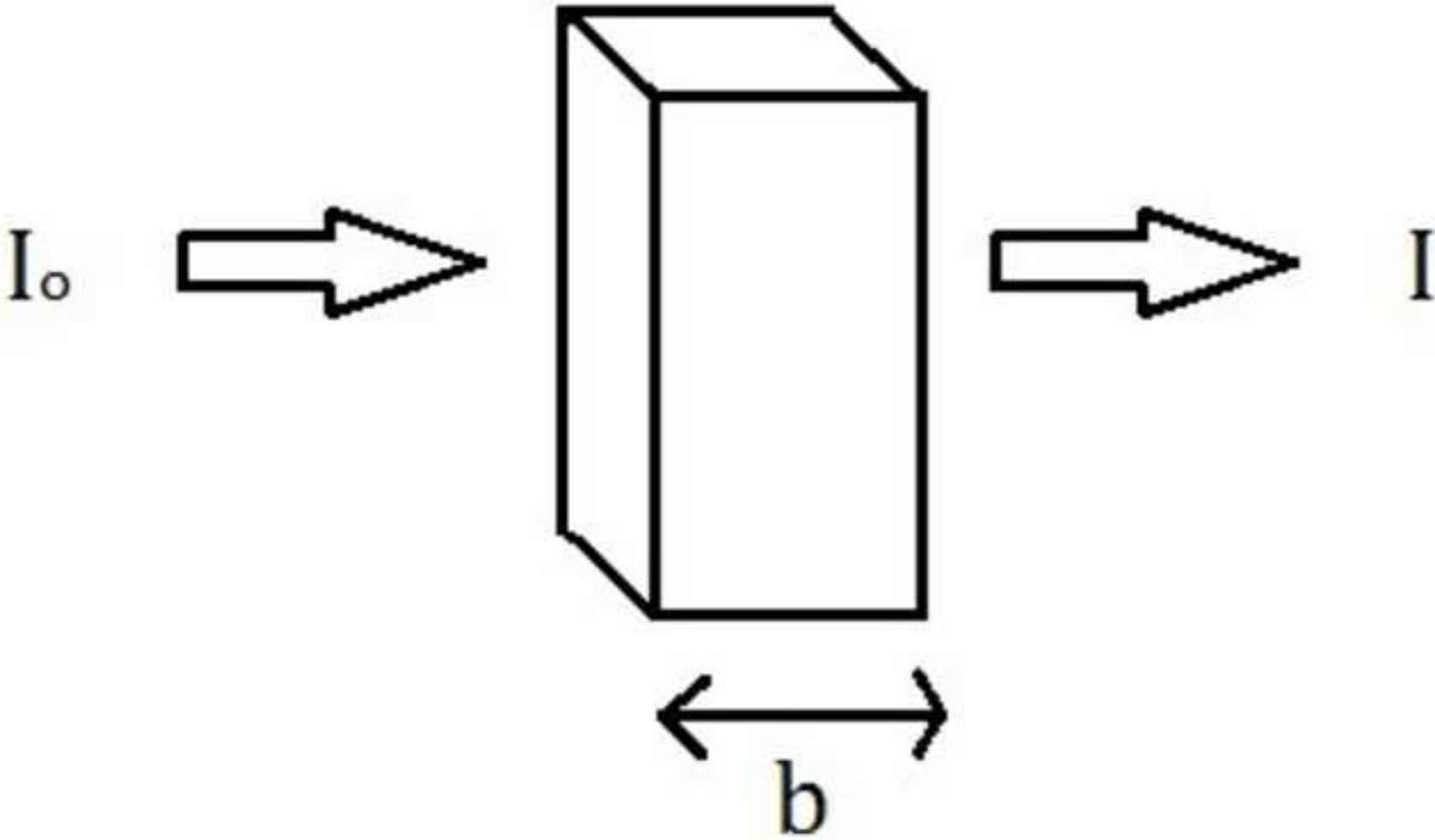
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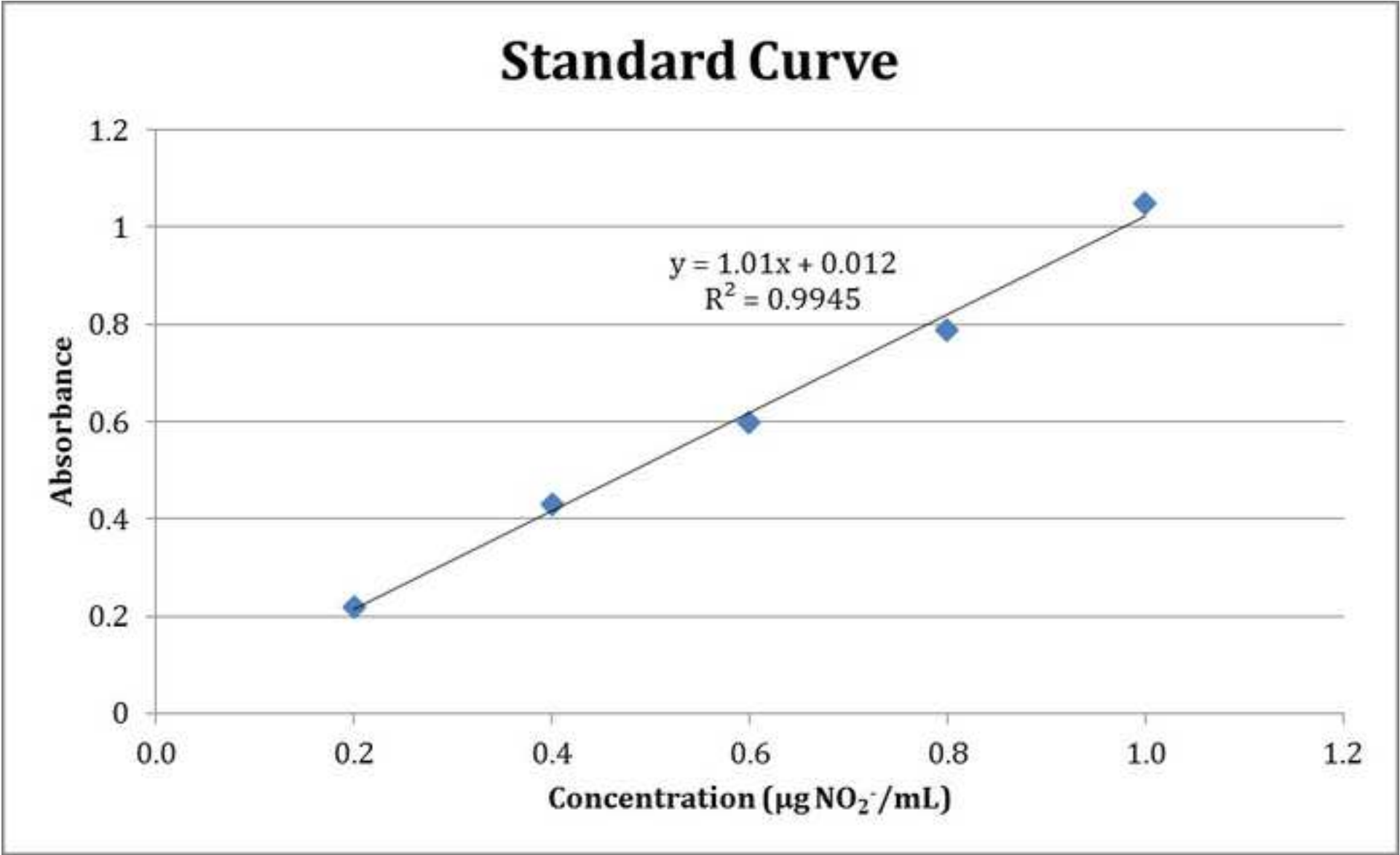
## Determination of NO<sub>x</sub> in Automobile Exhaust Using UV-VIS Spectroscopy

--Manuscript Draft--

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Sample	Absorbance
0.2 µg NO <sub>2</sub> <sup>-</sup> /ml standard	
0.4 µg NO <sub>2</sub> <sup>-</sup> /ml standard	
0.6 µg NO <sub>2</sub> <sup>-</sup> /ml standard	
0.8 µg NO <sub>2</sub> <sup>-</sup> /ml standard	
1.0 µg NO <sub>2</sub> <sup>-</sup> /ml standard	
Diesel Car Exhaust (upon startup)	
Diesel Car Exhaust (after running 10 min)	
Gasoline Car Exhaust (upon startup)	
Gasoline Car Exhaust (after running 10 minutes)	

Sample	Absorbance
0.2 µg NO <sub>2</sub> <sup>-</sup> /ml standard	0.22
0.4 µg NO <sub>2</sub> <sup>-</sup> /ml standard	0.43
0.6 µg NO <sub>2</sub> <sup>-</sup> /ml standard	0.60
0.8 µg NO <sub>2</sub> <sup>-</sup> /ml standard	0.79
1.0 µg NO <sub>2</sub> <sup>-</sup> /ml standard	1.05
Diesel Car Exhaust (upon startup)	1.03
Diesel Car Exhaust (after running 10 minutes)	1.03
Gasoline Car Exhaust (upon startup)	0.10
Gasoline Car Exhaust (after running 10 minutes)	0.04

Vehicle	NO <sub>x</sub> Concentration (ppm)
Diesel Car (upon startup)	500
Diesel Car (after running 10 minutes)	500
Gasoline Car (upon startup)	48
Gasoline Car (after running 10 minutes)	21



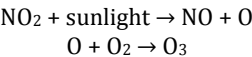
[Click here to download Photo or Graphic File: Frye\\_Workman\\_NOx\\_Car\\_exhaust\\_fig1.jpg](#)



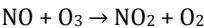
**PI Name:** Margaret Workman and Kimberly Frye, DePaul University  
**Science Education Title:** Determination of NO<sub>x</sub> in Automobile Exhaust Using UV-VIS Spectroscopy

**Overview**

In the troposphere, ozone is naturally formed when sunlight splits nitrogen dioxide (NO<sub>2</sub>):



Ozone (O<sub>3</sub>) can go on to react with nitric oxide (NO) to form nitrogen dioxide (NO<sub>2</sub>) and oxygen:



This results in no net gain of ozone (O<sub>3</sub>). However, with the anthropogenic production of ozone forming precursors (NO, NO<sub>2</sub>, and volatile organic compounds) through the combustion of fossil fuels, elevated levels of ozone in the troposphere have been found. Motor vehicle exhaust is a significant source of these ozone forming precursors: NO, NO<sub>2</sub>, and volatile organic compounds (VOCs). For example, mobile sources make up nearly 60% of NO + NO<sub>2</sub> emissions.

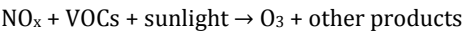
At the high temperatures found in a car’s combustion chamber, nitrogen and oxygen from the air react to form nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>):



~~The nitric oxide (NO) can react further with oxygen (O<sub>2</sub>) to form nitrogen dioxide (NO<sub>2</sub>):~~



The nitric oxide (NO) emitted in the car exhaust is gradually oxidized to nitrogen dioxide (NO<sub>2</sub>) in ambient air.-This mixture of NO and NO<sub>2</sub> is often referred to as NO<sub>x</sub>. When NO<sub>x</sub> reacts with volatile organic compounds in the atmosphere in the presence of sunlight, tropospheric ozone forms, as seen in this simplified chemical reaction:



This noxious mixture of air pollution, which can include aldehydes, peroxyacetyl nitrates, ozone, VOCs, and NO<sub>x</sub>, is called photochemical smog. Ozone is the largest component of photochemical smog. This smog is found in all modern cities, but it’s found especially in cities with sunny, warm, dry climates and large numbers of motor vehicles. The yellow-brown color of smog in the air is due in part to the nitrogen dioxide present, since this gas absorbs visible light near 400 nm (**Figure 1**).

Short-term NO<sub>2</sub> exposure ([30 min to 1 day](#)) leads to adverse respiratory effects in healthy people and increased respiratory symptoms in people with asthma. NO<sub>x</sub> reacts with ammonia and other compounds to form particulates. These small particles can penetrate the lungs and cause respiratory problems, including emphysema and bronchitis. Individuals who spend a lot of time on the road or who live near a roadway experience considerably higher exposure to NO<sub>2</sub>.

Due to the impact it has on human health and the environment, [the U.S. Environmental Protection Agency \(EPA\) has classified NO<sub>2</sub> as a criteria pollutant and has set the primary standard at 100 ppb \(98th percentile of 1-hour daily maximum concentrations, averaged over 3 years\) and 53 ppb \(annual mean\)](#). Considering that on-road vehicles account for approximately 1/3 of NO<sub>x</sub> emissions in the U.S., automobile emissions are [therefore](#) regulated through the Clean Air Act. The U.S. EPA established emission standards that automobile manufacturers must follow when producing cars. Currently, Tier 2 emission standards set that manufacturers must have fleet average NO<sub>x</sub> emissions of no more than 0.07 g/mile.

One way manufacturers meet this standard is by using catalytic converters on their cars. This device is placed between the engine and the tailpipe. The exhaust stream passes through the catalytic converter and is exposed to a catalyst. A reduction catalyst of platinum and rhodium is used to reduce the NO<sub>x</sub> concentration in the exhaust. When an NO or NO<sub>2</sub> molecule in the exhaust contacts the catalyst, the nitrogen atom is grabbed off the molecule and held onto by the catalyst. The oxygen is freed and forms O<sub>2</sub>. The nitrogen atom on the catalyst binds with another nitrogen atom held on the catalyst to form N<sub>2</sub>.

Catalytic converters have greatly reduced the emissions of NO<sub>x</sub> from car exhaust – [up to 80% reduction, when performing properly](#). However, they only work when they have reached a fairly high temperature. Therefore, when doing a cold start of a car, the catalytic converter is removing virtually no NO<sub>x</sub>. It isn't until the catalytic converter reaches higher temperatures that it effectively removes the NO<sub>x</sub> from the exhaust stream. [Catalytic converters do not work on diesel passenger cars due to the lean conditions under which they operate. -In addition, the sulfur in diesel fuel also deactivates the catalyst. The NO<sub>x</sub> in diesel engines are reduced mainly through the exhaust gas recirculation \(EGR\) valve, which cools the temperature of the combustion gases. As a result, diesel cars generally emit more NO<sub>x</sub> than gasoline cars.](#)

## Principles

In this experiment, the concentration of NO<sub>x</sub> in the exhaust stream of various brands of automobiles are measured twice (upon start-up and after 10 min) to study the ability of the car's catalytic converter to remove NO<sub>x</sub> from the exhaust. [The catalytic converter requires a high temperature to be effective. -Therefore, the measurement of the exhaust upon start-up of the car represents the amount of NO<sub>x</sub> in the exhaust without the catalytic converter working. -The measurement of the exhaust after 10 min represents the amount of NO<sub>x</sub> in the exhaust after the catalytic converter is in effect.](#)

The NO<sub>x</sub> concentration is determined colorimetrically by diazotization of sulfanilic acid and subsequent reacting with N-(1-naphthyl)-ethylenediamine and measuring the color intensity of the resulting azo dye molecule using a UV-VIS spectrophotometer set at 550 nm.

In solution, NO and NO<sub>2</sub> undergo the following reactions to form NO<sub>2</sub><sup>-</sup>: is converted to nitrous acid (HNO<sub>2</sub>) through the following reactions:



Although the expected ratio between NO<sub>2</sub> and NO<sub>2</sub><sup>-</sup> is 2:1 based on the first equation listed previously, it has been determined empirically to be 1.39:1.

When sulfanilic acid and N-(1-naphthyl)-ethylenediamine are added to the solution, a pink-colored molecule develops (**Figure 2**).

The concentration of this pink-colored molecule is directly proportional to the concentration of the NO<sub>x</sub> in the solution. The concentration of the azo dye molecule is measured using a UV-VIS spectrophotometer set at 550 nm.

UV-VIS spectroscopy is based on the measurement of the absorbance (A) of solutions held in a transparent container of width b (in cm). The concentration of the absorbing species is directly proportional to the absorbance, as seen in the following equation:

$$A = \epsilon b c$$

where  $\epsilon$  is the molar absorptivity. This equation is known as Beer's Law. The molar absorptivity is a measure of how strongly a substance absorbs light at a given wavelength and is a constant for a given substance.

To measure the absorbance of a solution, a beam of light with intensity  $I_0$  is aimed at the solution in a cuvette (**Figure 3**). The intensity of the entering beam ( $I_0$ ) and the emerging beam ( $I$ ) are measured, and the absorbance is calculated by:

$$A = -\log T = -\log \frac{I}{I_0}$$

## Procedure

### 1. Preparation of Nitrite (NO<sub>2</sub><sup>-</sup>) Stock Solution

1.1. Weigh out 1.500 g NaNO<sub>2</sub> and add to a 1 L volumetric flask.

1.2. Dilute to the mark using nanopure water. (Check the distilled water from the tap – it may contain enough nitrite to interfere with the measurements.) This produces a 1000  $\mu\text{g NO}_2^-/\text{ml}$  stock solution.

1.3. To make a 5.0  $\mu\text{g NO}_2^-/\text{ml}$  solution, take 1 ml of the 1,000  $\mu\text{g NO}_2^-/\text{ml}$  solution and dilute to 200 ml in a volumetric flask.

## 2. Preparation of $\text{NO}_x$ Indicator Solution

2.1. Weigh out 5.0 g of anhydrous sulfanilic acid and add to a 1 L volumetric flask.

2.2. Add 500 ml of nanopure water.

2.3. Add 140 ml of glacial acetic acid.

2.4. Using a stir bar, stir the solution until the sulfanilic acid dissolves. This takes approximately 30 min.

2.5. Weigh out 0.020 g of N-(1-naphthyl)-ethylenediamine dihydrochloride and add to the volumetric flask.

2.6. Dilute to the mark using nanopure water.

2.7. Transfer to a dark bottle (to prevent photodecomposition) and stopper tightly (to prevent reaction with air).

## 3. Preparation of Calibration Standards

3.1. Put 1.0 ml of the 5.0  $\mu\text{g NO}_2^-/\text{ml}$  solution in a 25 ml volumetric flask and dilute with the  $\text{NO}_x$  indicator solution to the mark. This makes a 0.2  $\mu\text{g NO}_2^-/\text{ml}$  standard solution.

3.2. Put 2.0 ml of the 5.0  $\mu\text{g NO}_2^-/\text{ml}$  solution in a 25 ml volumetric flask and dilute with the  $\text{NO}_x$  indicator solution to the mark. This makes a 0.4  $\mu\text{g NO}_2^-/\text{ml}$  standard solution.

3.3. Put 3.0 ml of the 5.0  $\mu\text{g NO}_2^-/\text{ml}$  solution in a 25 ml volumetric flask and dilute with the  $\text{NO}_x$  indicator solution to the mark. This makes a 0.6  $\mu\text{g NO}_2^-/\text{ml}$  standard solution.

3.4. Put 4.0 ml of the 5.0  $\mu\text{g NO}_2^-/\text{ml}$  solution in a 25 ml volumetric flask and dilute with the  $\text{NO}_x$  indicator solution to the mark. This makes a 0.8  $\mu\text{g NO}_2^-/\text{ml}$  standard solution.

3.5. Put 5.0 ml of the 5.0  $\mu\text{g NO}_2^-/\text{ml}$  solution in a 25 ml volumetric flask and dilute with the  $\text{NO}_x$  indicator solution to the mark. This makes a 1.0  $\mu\text{g NO}_2^-/\text{ml}$  standard solution.

#### 4. Creation of the Standard Curve

4.1. Using a UV-VIS spectrophotometer, set the instrument to read Absorbance.

4.2. Set the wavelength to 550 nm on the spectrophotometer.

4.3. Using the  $\text{NO}_x$  indicator solution, zero the spectrophotometer.

4.4. Measure the absorbance of the 5 standard solutions. Record values on the data table (**Table 1**).

#### 5. Automobile Exhaust Sample Measurement

5.1. Start the diesel powered automobile.

5.2. Using a 60 ml gas-tight syringe, insert it a few inches into the tailpipe. Avoid burns and don't breathe in fumes. Draw in and expel the exhaust twice to condition the syringe.

5.3. Draw 25 ml of the  $\text{NO}_x$  indicator solution into the syringe. Expel any air from the syringe without spilling the indicator solution.

5.4. Draw 35 ml of exhaust into the syringe, pulling the plunger to the 60 ml mark.

5.5. Cap the syringe. Shake the solution in the syringe for 2 min. Cover the syringe with aluminum foil.

**Commented [AW3]:** Do you do this by hand, or on a shaker?

**Commented [maw4]:** By hand

5.6. Measure the air temperature at the tailpipe when collecting the samples.

5.7. Repeat steps 5.1 – 5.6 using a gasoline powered automobile. These steps can be repeated as many times as desired, using various models of automobiles.

5.8. Repeat steps 5.1 – 5.6 after the automobiles have been running at least 10 min.

5.9. Wait 45 min to allow the color to develop, before measuring the absorbance of the solution.

5.10. After the 45 min are up, expel the gas from the syringe, put the solution into a cuvette, and measure the absorbance using the spectrophotometer set at 550 nm. Record values on the data table (**Table 1**).

## Representative Results

Table 2 provides an example of proper results. Using the absorbance measurements of the standard solutions, a plot of Absorbance vs. Concentration of  $\text{NO}_2^-$  can be made (Figure 4). Then, the best fit line of the data can be determined. Using the best fit line of the standard curve, the concentration of  $\text{NO}_2^-$  in each unknown solution ( $\mu\text{g}/\text{ml}$ ) can be calculated. This value can be converted to the concentration of  $\text{NO}_2$  in the exhaust gaseous sample using the following equation:

$$\frac{\mu\text{g NO}_2}{\text{— L}} = \frac{\mu\text{g NO}_2^-}{\text{ml}} \times \frac{1.39 \text{ mol NO}_2}{1 \text{ mol NO}_2^-} \times \frac{V_{\text{sol}}}{V_{\text{gas}}} \times \frac{1000 \text{ ml}}{1 \text{ L}}$$

Based on the balanced equation of  $\text{NO}_2$  in  $\text{H}_2\text{O}$  seen previously, a 2 mol  $\text{NO}_2$ /1 mol  $\text{NO}_2^-$  ratio is expected. In empirical experiments, it has been found to be nearer a 1.39:1 ratio. Keep it at the 2:1 ratio for simplicity. The volume of solution used was 25 ml. The volume of the gas sample was 35 ml. The concentration of  $\text{NO}_2$  calculated actually represents all of the  $\text{NO}_x$  in the exhaust sample (Table 3). The equation for conversion between ppmV and  $\mu\text{g}/\text{L}$  depends on the temperature and pressure at which the samples were collected. The conversion equation is:

$$\text{ppmV NO}_x = \frac{\mu\text{L NO}_x}{\text{L}} = \frac{\mu\text{g NO}_x}{\text{L}} \times \frac{R \cdot T}{P \cdot \text{MW}}$$

Where  $R$  = universal gas constant = 0.08206 atmL/molK,  $P$  = atmospheric pressure in atm,  $T$  = temperature in K, and  $\text{MW}$  = molecular weight of  $\text{NO}_x$  (as  $\text{NO}_2$ ) = 46.01 g/mol. Therefore,

$$\text{ppmV NO}_x = \frac{\mu\text{g NO}_x}{\text{L}} \times \frac{(0.08206 \text{ atmL/mol K}) \cdot (T)}{(P) \cdot 46.01 \text{ g/mol}}$$

It's important to input  $T$  in K and  $P$  in atm.

## Applications

The measurement of nitrite using the modified Saltzman reaction is very common and useful in many different fields. As described, the method can be used to measure  $\text{NO}_x$  concentrations in air samples – car exhaust, laboratory rooms, air quality of cities, etc. In addition, this method can be used to monitor  $\text{NO}_x$  in cigarette smoke (Figure 5). The procedure would be very similar to this experiment, except instead of drawing car exhaust into the syringe, cigarette smoke would be drawn in. There is often a higher concentration of  $\text{NO}_x$  in cigarette smoke than coming out of the tailpipe of automobiles, which tends to be surprising to many. Typical values for  $\text{NO}_x$  in cigarette smoke range from 500 – 800 ppm.

This method can also be used to test the levels of nitrate produced in the presence of nitrification bacteria. Nitrification bacteria are found in soil and water and play an important role in the nitrogen cycle – oxidizing ammonia to nitrite and then nitrate. The nitrate in the sample is first converted to nitrite by the enzyme nitrate reductase. Then the

**Commented [AW5]:** From the reactions above, it's not clear why the 2:1 ratio is used. Because the nitrate doesn't participate?

**Commented [AW6]:** Can we film all three of these applications in your lab? If so, that would make a very strong video.

**Commented [maw7]:** Yes we could, depending on how it is written. I have never personally done these but have the procedures and materials, so could do them.

**Commented [AW8]:** Just to make sure, you can demonstrate this on the shoot date, correct? Are there any other deviation in the procedure that we should point out?

**Commented [maw9]:** We can, although I admit I haven't done this personally. But I know someone else in our department did this so we have the materials.

nitrite is measured using the modified Saltzman reaction. Lastly, this method can be used to determine the concentration of nitrates and nitrites in food products. Nitrites and nitrates are added to food mainly to preserve meats and meat products. A typical value for nitrite in cured meats is approximately 125  $\mu\text{g/mL}$ .

## Legend

Figure 1: Characteristic coloration for smog in California in the beige cloud bank behind the Golden Gate Bridge. The brown coloration is due to the  $\text{NO}_x$  in the photochemical smog.

Figure 2: A pink-colored molecule that develops when sulfanilic acid and N-(1-naphthyl)-ethylenediamine are added to the solution.

Figure 3: A beam of light with intensity  $I_0$  aimed at the solution in a cuvette.

Figure 4: A standard curve plot of Absorbance vs. Concentration of  $\text{NO}_2^-$ .

Figure 5: Cigarette smoke often has a higher concentration of  $\text{NO}_x$  than car exhaust.

Table 1: Blank data table to record values of absorption.

Table 2: Data table with representative results of absorption.

Table 3:  $\text{NO}_x$  concentration (ppm) per vehicle.

**Commented [maw10]:** Not sure if we can film this. I would have to research this more, as we have never done it personally. I have the procedure for it and could test it out before hand.

**Commented [AW11]:** Can you demonstrate this process on the filming date? If so, how is the procedure different?