Science Education Collection

Determination Of NO_x in Automobile Exhaust Using UV-VIS Spectroscopy

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Overview

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In the troposphere, ozone is naturally formed when sunlight splits nitrogen dioxide (NO_2):

NO_2 + sunlight → NO + O

O + O_2 → O_3

Ozone (O_3) can go on to react with nitric oxide (NO) to form nitrogen dioxide (NO_2) and oxygen:

NO + O_3 → NO_2 + O_2

This results in no net gain of ozone (O_3). However, with the anthropogenic production of ozone forming precursors (NO, NO_2, 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_2, and volatile organic compounds (VOCs). For example, mobile sources make up nearly 60% of NO + NO_2 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_2):

$N_{2(g)}$ + $O_{2\ (g)}$→ 2 $NO_{(g)}$

2 $NO_{(g)}$ + $O_{2(g)}$→ 2 $NO_{2(g)}$

The nitric oxide (NO) emitted in the car exhaust is gradually oxidized to nitrogen dioxide (NO_2) in ambient air. This mixture of NO and NO_2 is often referred to as NO_x. When NO_x reacts with volatile organic compounds in the atmosphere in the presence of sunlight, tropospheric ozone forms, as seen in this simplified chemical reaction:

NO_x + VOCs + sunlight → O_3 + other products

This noxious mixture of air pollution, which can include aldehydes, peroxyacetyl nitrates, ozone, VOCs, and NO_x, 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_2 exposure (30 min to 1 day) leads to adverse respiratory effects in healthy people and increased respiratory symptoms in people with asthma. NO_x 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_2.

Due to the impact it has on human health and the environment, the U.S. Environmental Protection Agency (EPA) has classified NO_2 as a criteria pollutant and has set the primary standard at 100 ppb (98th percentile of 1-h daily maximum concentrations, averaged over 3 years) and 53 ppb (annual mean). Considering that on-road vehicles account for approximately 1/3 of NO_x 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_x 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_x concentration in the exhaust. When an NO or NO_2 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_2. The nitrogen atom on the catalyst binds with another nitrogen atom held on the catalyst to form N_2.

Catalytic converters have greatly reduced the emissions of NO_x 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_x. It isn't until the catalytic converter reaches higher temperatures that it effectively removes the NO_x 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_x 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_x than gasoline cars.

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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 NO_x in the photochemical smog.

Principles

In this experiment, the concentration of NO_x 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_x 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_x in the exhaust without the catalytic converter working. The measurement of the exhaust after 10 min represents the amount of NO_x in the exhaust after the catalytic converter is in effect.

The NO_x 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_2 undergo the following reactions to form NO_2^-:

$$2\ NO_{2(g)} + H_2O_{(l)} \rightarrow 2H^+_{(aq)} + NO_2^-{}_{(aq)} + NO_3^-{}_{(aq)}$$

$$4NO_{(g)} + O_{2(g)} + 2\ H_2O_{(l)} \rightarrow 4\ NO_2^-{}_{(aq)} + 4\ H^+_{(aq)}$$

Although the expected ratio between NO_2 and NO_2^- is 2:1 based on the first equation listed previously, it has been determine 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_x 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 ϵ 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_o is aimed at the solution in a cuvette (**Figure 3**). The intensity of the entering beam (I_o) and the emerging beam (I) are measured, and the absorbance is calculated by:

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

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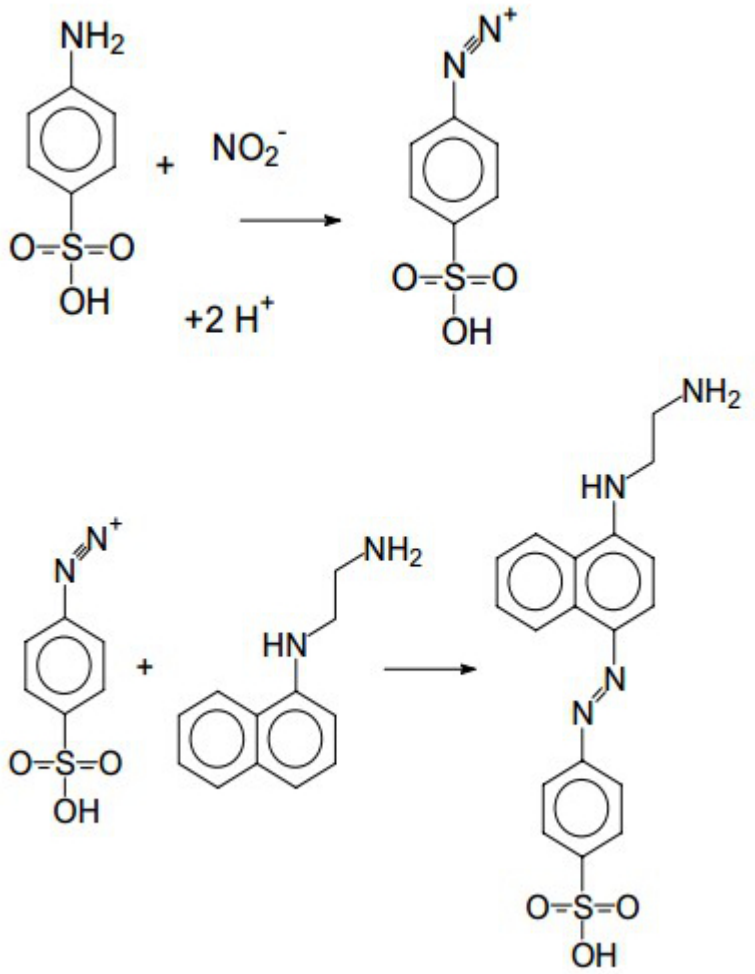

Figure 2. A pink-colored molecule that develops when sulfanilic acid and N-(1-naphthyl)-ethylenediamine are added to the solution.

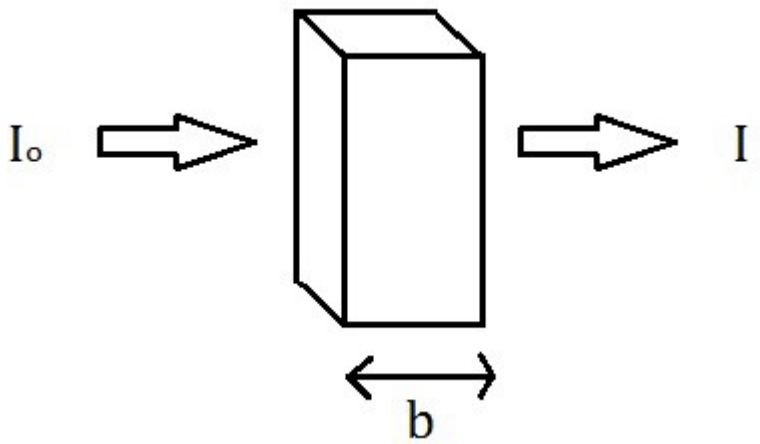

Figure 3. A beam of light with intensity Io aimed at the solution in a cuvette.

Procedure

1. Preparation of Nitrite (NO_2^-) Stock Solution

1. Weigh out 1.500 g $NaNO_2$ and add to a 1-L volumetric flask.
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 1,000 µg NO_2^-/mL stock solution.

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3. To make a 5.0 µg NO_2^-/mL solution, take 1 mL of the 1,000 µg NO_2^-/mL solution and dilute to 200 mL in a volumetric flask.

2. Preparation of NO_x Indicator Solution

1. Weigh out 5.0 g of anhydrous sulfanilic acid and add to a 1-L volumetric flask.
2. Add 500 mL of nanopure water.
3. Add 140 mL of glacial acetic acid.
4. Using a stir bar, stir the solution until the sulfanilic acid dissolves. This takes approximately 30 min.
5. Weigh out 0.020 g of N-(1-naphthyl)-ethylenediamine dihydrochloride and add to the volumetric flask.
6. Dilute to the mark using nanopure water.
7. Transfer to a dark bottle (to prevent photodecomposition) and stopper tightly (to prevent reaction with air).

3. Preparation of Calibration Standards

1. Put 1.0 mL of the 5.0 µg NO_2^-/mL solution in a 25 mL volumetric flask and dilute with the NO_x indicator solution to the mark. This makes a 0.2 µg NO_2^-/mL standard solution.
2. Put 2.0 mL of the 5.0 µg NO_2^-/mL solution in a 25 mL volumetric flask and dilute with the NO_x indicator solution to the mark. This makes a 0.4 µg NO_2^-/mL standard solution.
3. Put 3.0 mL of the 5.0 µg NO_2^-/mL solution in a 25 mL volumetric flask and dilute with the NO_x indicator solution to the mark. This makes a 0.6 µg NO_2^-/mL standard solution.
4. Put 4.0 mL of the 5.0 µg NO_2^-/mL solution in a 25 mL volumetric flask and dilute with the NO_x indicator solution to the mark. This makes a 0.8 µg NO_2^-/mL standard solution.
5. Put 5.0 mL of the 5.0 µg NO_2^-/mL solution in a 25 mL volumetric flask and dilute with the NO_x indicator solution to the mark. This makes a 1.0 µg NO_2^-/mL standard solution.

4. Creation of the Standard Curve

1. Using a UV-VIS spectrophotometer, set the instrument to read Absorbance.
2. Set the wavelength to 550 nm on the spectrophotometer.
3. Using the NO_x indicator solution, zero the spectrophotometer.
4. Measure the absorbance of the 5 standard solutions. Record values on the data table (**Table 1**).

5. Automobile Exhaust Sample Measurement

1. Start the diesel-powered automobile.
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.
3. Draw 25 mL of the NO_x indicator solution into the syringe. Expel any air from the syringe without spilling the indicator solution.
4. Draw 35 mL of exhaust into the syringe, pulling the plunger to the 60 mL mark.
5. Cap the syringe. Shake the solution in the syringe for 2 min. Cover the syringe with aluminum foil.
6. Measure the air temperature at the tailpipe when collecting the samples.
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.
8. Repeat steps 5.1 – 5.6 after the automobiles have been running at least 10 min.
9. Wait 45 min to allow the color to develop, before measuring the absorbance of the solution.
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**).

Sample	Absorbance
0.2 µg NO_2^-/mL standard	
0.4 µg NO_2^-/mL standard	
0.6 µg NO_2^-/mL standard	
0.8 µg NO_2^-/mL standard	
1.0 µg NO_2^-/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 min)	

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

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Results

Table 2 provides an example of proper results. Using the absorbance measurements of the standard solutions, a plot of Absorbance vs. Concentration of 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 NO_2^- in each unknown solution (µg/mL) can be calculated. This value can be converted to the concentration of NO_2 in the exhaust gaseous sample using the following equation:

$$\frac{\mu g\ NO_2}{L} = \frac{\mu g\ NO_2^-}{mL} \times \frac{1.39\ mol\ NO_2}{1\ mol\ NO_2^-} \times \frac{V_{sol}}{V_{gas}} \times \frac{1000\ mL}{1\ L}$$

Based on the balanced equation of NO_2 in H_2O seen previously, a 2 mol NO_2/1 mol NO_2^- ratio is expected. In empirical experiments, it has been found to be nearer a 1.39:1 ratio. The volume of solution used was 25 mL. The volume of the gas sample was 35 mL.

The concentration of NO_2 calculated actually represents all of the NO_X in the exhaust sample (**Table 3**). The equation for conversion between ppmV and µg/L depends on the temperature and pressure at which the samples were collected. The conversion equation is:

$$ppmV\ NO_x = \frac{\mu L\ NO_x}{L} = \frac{\mu g\ NO_x}{L} \times \frac{R \cdot T}{P \cdot MW}$$

Where R = universal gas constant = 0.08206 atm·L/mol·K, P = atmospheric pressure in atm, T = temperature in K, and MW = molecular weight of NO_x (as NO_2) = 46.01 g/mol. Therefore,

$$ppmV\ NOx = \frac{\mu g\ NO_x}{L} \times \frac{(0.08206\ atm \cdot L/mol \cdot K) \cdot (T)}{(P) \cdot 46.01\ g/mol}$$

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

Sample	Absorbance
0.2 µg NO_2^-/mL standard	0.22
0.4 µg NO_2^-/mL standard	0.43
0.6 µg NO_2^-/mL standard	0.60
0.8 µg NO_2^-/mL standard	0.79
1.0 µg NO_2^-/mL standard	1.05
Diesel Car Exhaust (upon startup)	1.03
Diesel Car Exhaust (after running 10 min)	1.03
Gasoline Car Exhaust (upon startup)	0.10
Gasoline Car Exhaust (after running 10 min)	0.04

Table 2. Data table with representative results of absorption.

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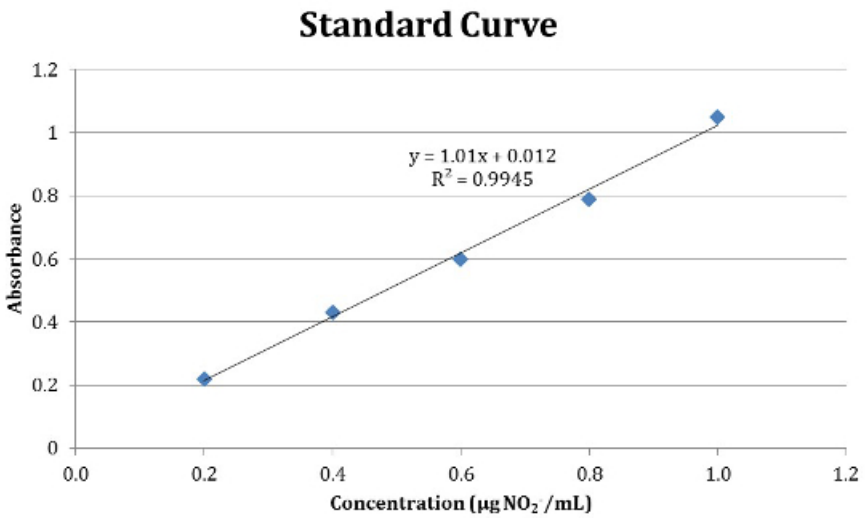

Figure 4. A standard curve plot of Absorbance vs. Concentration of NO_2^-.

Vehicle	NO_x 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

Table 3. NO_x concentration (ppm) per vehicle.

Applications and Summary

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 NO_x concentrations in air samples – car exhaust, laboratory rooms, air quality of cities, etc. In addition, this method can be used to monitor NO_x in cigarette smoke. 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 NO_x in cigarette smoke than coming out of the tailpipe of automobiles, which tends to be surprising to many. Typical values for 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 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 µg/mL.

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