The Measurement of Gaseous Atmospheric Pollutants

**Background**

The process of changing the mixture of gases in the atmosphere of the Earth is as old as life itself. Plants absorb carbon dioxide and return oxygen. Animals thrive on the oxygen and return carbon dioxide. The planet itself has "outgassed" large amounts of various substances over geologic time and these have taken their place in the atmosphere--at least on a temporary basis--and sometimes on the surface in condensed form, e.g., water.

The atmosphere of the planet is a very large system and it takes a long time and/or a lot of material to make significant changes locally, even longer globally. It is convenient to point to the beginning of industrialization as a period in human history during which the <u>rate</u> of alteration to the atmosphere (at least the lower part or *troposphere*) increased substantially. The need for energy to drive machinery quickly outstripped the availability of convenient water-power sources and with the development of the steam engine suddenly large amounts of heat energy were needed to keep the engines of industrialization moving. That heat came from the combustion of carbon-based fuel of one kind or another: wood, coal, oil, gas, etc. The combustion of carbon-based fuels rapidly releases sequestered CO_2 which has been stored by plant organisms over time (sometimes many thousands of years) and returns much of it to the atmosphere. Many scientists interpret current climate models and the "rapid" increase in atmospheric levels of carbon dioxide and conclude that the balance is shifting in favor of an atmosphere which will hold more of the radiant infra-red from the planet (resulting from solar warming) rather than allow it to return to space. The result is a gradual rise in average terrestrial temperatures, what we today call "global warming".

The combustion of carbon-based or "fossil" fuels generates other gases, however, which have more immediate and obvious effects. Anyone who lives in an urban area is very familiar with some of those effects. Burning eyes, shortness of breath, hazy and often discolored skies are just some of the more familiar consequences of what we collectively call *air pollution*. Some of that pollution is particulate in nature: tiny particles of carbon soot and other solids which are released into the atmosphere during combustion and other processes. It is the gaseous matter that is of interest in this experiment, and two gases in particular: **nitrogen dioxide** and **ozone**.

When combustion occurs in our atmosphere oxygen combines with the fuel material chemically to form a variety of compounds. But the air also contains about 80% nitrogen and while nitrogen is relatively inert, it *will* combine with oxygen at elevated temperatures. Nitrogen forms a number of oxides. They include N_2O ("laughing gas"), NO, N_2O_3, NO_2, N_2O_4 and N_2O_5. Most of these compounds are interconvertible but during more or less uncontrolled combustion the principal compounds formed are NO and NO_2. In fact, any time NO forms in our atmosphere, NO_2 is produced:

$$NO_{(g)} + \tfrac{1}{2}\ O_{2(g)} \rightarrow NO_{2(g)}$$
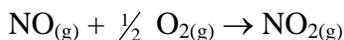
This reaction is rapid but that only tells part of the story. NO_2 will photodissociate upon exposure to ultraviolet light of fairly low energy (readily available in sunny cities):

$$NO_{2(g)} \xrightarrow{392\ nm} NO_{(g)} + O_{(g)}$$
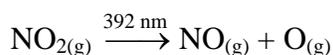
Adapted from: <u>Colorimetric Microdetermination of Nitrogen Dioxide in the Atmosphere</u>, Bernard E. Saltzman, *Analytical Chemistry*, vol. 26, No. 12, p. 1949
<u>A Simple Method for Measuring Ground-Level Ozone in the Atmosphere</u>, John V. Seeley et. al., *JChemEd*, vol. 82, No. 2, p. 282-285
<u>Chemistry of Gases, a Microscale Approach</u>, Bruce Mattson, Michael Anderson, Cece Schwennsen

The NO produced simply makes more NO_2 and the whole cycle repeats, but the atomic oxygen reacts with molecular oxygen:

$$O_{(g)} + O_{2(g)} \rightarrow O_{3(g)}$$
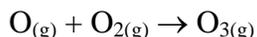
The product is <u>tropospheric ozone</u> and the mix of NO, NO_2 and O_3 are among the substances collectively known as *photochemical smog*. The process does not end there since ozone is extremely reactive and attacks other molecules in the lower atmosphere such as volatile hydrocarbons (octane escaping from gas tanks, solvents evaporating from paints, etc.) creating even more obnoxious compounds which are irritants and often quite dangerous in high concentrations.

Before describing some of the properties of the two gases of interest here it is a good idea to clearly draw the distinction between tropospheric ozone and <u>stratospheric ozone</u>. For lack of a tidier description we might think of these as "bad" ozone and "good" ozone.

The troposphere is the lowest level of the atmosphere which extends from the surface of the planet up to about 10 miles out. Much of the air pollution chemistry involving oxides of nitrogen and ozone occurs there [in geographic regions where coal and fuel oil are heavily used, sulfur dioxide is also an important gaseous pollutant, produced by the combustion of sulfur impurities in some types of these fuels]. Ozone in this region of the atmosphere is "out of place". Electrical discharges, such as lightening strikes, form ozone naturally but in limited quantities over time. Photochemical processes such as those described earlier, on the other hand, create a steady supply of ozone which causes considerable damage in the tropospheric environment to plants and animals alike. This is the "bad" ozone.

Higher in the atmosphere is the *stratosphere*. It extends roughly from 10 miles to 30 miles above the ground. Ozone occurs naturally in that level of the atmosphere, a product of the action of ultraviolet radiation on molecular oxygen. Some molecules of oxygen split and the free atomic oxygen then combines with other molecules to form O_3. But ozone itself is susceptible to ultraviolet radiation and also breaks down into O_2 and atomic oxygen. This cycle occurs endlessly in the stratosphere and the significance of the process is that each transformation <u>absorbs</u> some ultraviolet radiation which would otherwise reach the surface. Ultraviolet radiation is damaging to both plants and animals so the ozone in the stratosphere acts as a protective layer--this is the "good" ozone.

There are chemicals--such as halocarbons--humans have produced in considerable quantities and released into the atmosphere which gradually work their way up to the stratosphere (sometimes taking many years to get there) and react preferentially with ozone, breaking the cycle which should result in ozone being regenerated from the action of ultraviolet radiation on molecular oxygen. This allows more ultraviolet radiation to reach the surface of the planet and the story goes on and on.

The irony, of course, is that we have ozone near the ground which we can't seem to get rid of while we are depleting ozone in the stratosphere which, taken to the extreme case, could eventually eliminate the major cause of the unwanted ozone in the troposphere: <u>us</u>!

Back to the experiment. Both nitrogen monoxide and nitrogen dioxide are reactive molecules and perhaps the most familiar odd-electron species (try drawing the Lewis structures). During combustion only about 10% of the nitrogen oxides produced directly are NO_2 but since NO reacts rapidly with the oxygen in the air, the end result is more or less as if only NO_2 were produced. Ordinary atmospheric concentrations of NO_x (NO and NO_2) are about 0.5 to 1 ppbv [ppbv = "<u>p</u>arts <u>p</u>er <u>b</u>illion by <u>v</u>olume", meaning the upper limit is equivalent to 1 Litre of NO_x per 10^9 Litres of air].

In urban areas the concentrations of these gases may climb to as much a 1-2 ppmv [parts per million] for NO and 0.5 ppmv for NO_2 for a one-hour average. 500 ppmv is considered fatal but a lot of damage is done by much smaller amounts over prolonged periods.

All oxides of nitrogen are *acid anhydrides*. That means they will form acidic solutions in water. NO_x is responsible for part of the acid rain problem since NO_2 reacts with water to form nitric acid:

$$3\ NO_{2(g)} + H_2O_{(l)} \rightarrow 2\ H^+_{(aq)} + NO_3^-_{(aq)} + NO_{(g)}$$

The NO reacts with more oxygen to produce more NO_2, which in turn……

The concentration of ozone in the stratosphere ranges from 1 to 10 ppmv. This is about 90% of the atmospheric ozone. Near the surface concentrations from photochemical reactions generally fall between 0.02 to 0.3 ppmv (or 20 to 300 ppbv). The reactions of ozone with other chemicals in the troposphere are too varied to even begin to list but the molecule is a strong oxidizing agent (not unlike NO_2) and unstable.

The laboratory preparation of NO_2 is fairly straightforward. Any reaction which produces NO will also produce NO_2 if given access to additional oxygen. The oxidation of copper metal by nitric acid is a classic method for producing NO [see quotation by Ira Remsen facing the title page in this text]:

$$3\ Cu_{(s)} + 8\ H^+_{(aq)} + 5\ NO_3^-_{(aq)} \rightarrow 3\ Cu^{2+}_{(aq)} + 2\ NO_{(g)} + 4\ H_2O_{(l)}$$
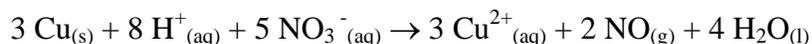
In practice what is produced is NO_2 for the reasons mentioned earlier unless some precautions are taken.

The disproportionation of nitrite ion in acid will also produce NO (and therefore NO_2):

$$6\ NaNO_{2(s)} + 4\ H^+_{(aq)} \rightarrow 4\ NO_{(g)} + 2\ NO_3^-_{(aq)} + 2\ H_2O_{(l)} + 6\ Na^+_{(aq)}$$
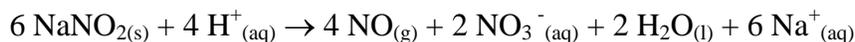
To generate some of both gases to study in this experiment a homogeneous system will be employed in which nitrite ion is reduced by iron(II) ion in acid solution:

$$NO_2^-_{(aq)} + Fe^{2+}_{(aq)} + 2\ H^+_{(aq)} \rightarrow NO_{(g)} + Fe^{3+}_{(aq)} + H_2O_{(l)}$$
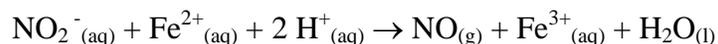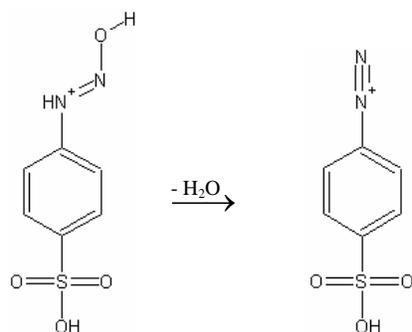
When this reaction is performed in the absence of air the colorless NO will form. After some chemical tests are done with part of the gas, air can be introduced into the remaining gas, forming NO_2, giving a NO_x mixture. Some additional tests can then be done on the NO_2.

The quantitative determination of trace gases in the atmosphere poses some special challenges, not the least of which is their dilution factor. While the detrimental effects of NO_x and O_3 in the troposphere are beyond question it is still true that there is very little of either (thankfully). Analytical methods must therefore be sensitive and generally employ large air samples and/or sampling times. Tropospheric concentrations of both of these gases are generally determined by special instruments but there are chemical methods which can give good results if carefully applied.

Christian Schönbein discovered ozone in 1839 and also developed a simple chemical method for estimating its concentration in the air. Schönbein used a test paper prepared from filter paper soaked in a mixture of cornstarch, water and potassium iodide. The moistened paper is exposed for a fixed period of time and the ozone concentration is determined by the intensity of the purple color which develops as iodide is oxidized to iodine by the ozone and in turn creates the familiar blue/purple complex with the starch. The reactions can be represented as:

$$2 \text{ KI} + O_3 + H_2O \rightarrow 2 \text{ KOH} + O_2 + I_2$$
$$I_2 + \text{starch} \rightarrow \text{blue/purple complex}$$

Objective interpretation of the color on the paper is difficult and humidity is an important factor in the color development as well. The same basic chemical system can be employed in solution by drawing air through a solution containing KI. After a significant air sample has been processed and some I_2 has formed [actually I_3^-] starch is added to the solution to develop the blue color. The sample can then be analyzed with a spectrophotometer, comparing the absorbance with some standard I_3^- solutions. The reaction is represented differently in solution but the stoichiometry between ozone and triiodide is still 1:1.

$$O_{3(g)} + 3 \text{ I}^-_{(aq)} + 2 \text{ H}^+_{(aq)} \rightarrow I_3^-{}_{(aq)} + O_{2(g)} + H_2O_{(l)}$$

A colorimetric system for measuring atmospheric NO_2 (but not NO) was described by Bernard Saltzman in 1954. The process begins with bubbling air through an aqueous solution containing a number of ingredients. When NO_2 is bubbled through water it disproportionates:

$$2 \text{ NO}_{2(g)} + H_2O_{(l)} \rightarrow HNO_{2(aq)} + H^+_{(aq)} + NO_3^-{}_{(aq)}$$

The weak and unstable nitrous acid is an important ingredient in a particular type of reaction in organic chemistry which is used to make dyes.

The synthesis sequence involves a number of steps. First the nitrous acid reacts with an organic base (an *amine*, characterized by the presence of the -NH$_2$ group):

sulfanilic acid   + HNO$_2$ →   a *nitrosamine*   + H$^+$

The reaction mixture also contains acetic acid and sufficient free protons to protonate the oxygen on the nitrosamine compound:

+ H$^+$ →

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Water is then eliminated from the structure resulting in a diazonium ion:

Diazonium ions (characterized by the N≡N) are electrophiles, i.e., they seek out species with electrons which can be shared. Such a species is the compound known as N-(1-naphthyl)ethylenediamine (called N-NED for short) and coupling occurs at the position opposite the amine group on the N-NED;

N-NED
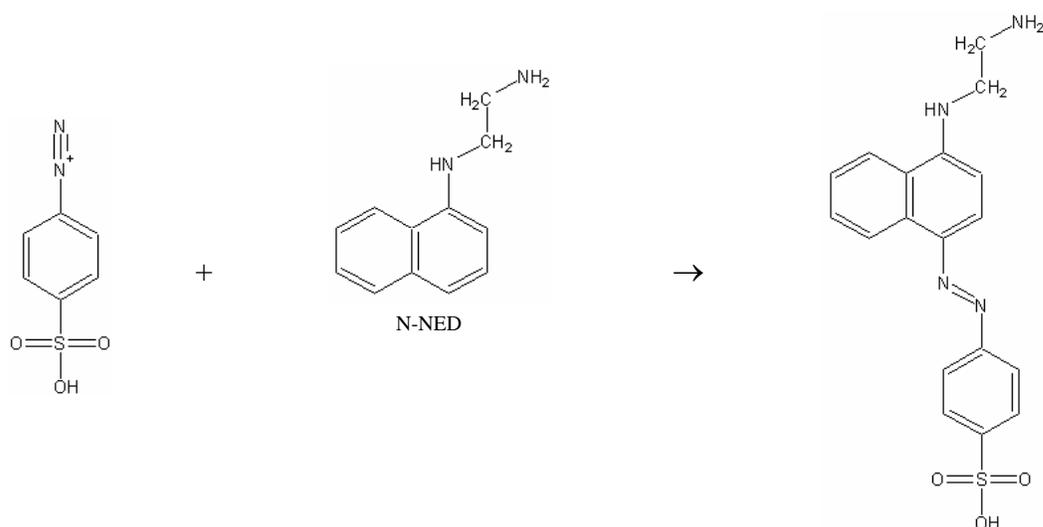
This kind of reaction is known as *diazo coupling* (characterized by the -N=N- group) and always results in a colored compound. The acid-base indicator *methyl orange* is one example of this type of compound and many synthetic dyes have related structures. In this instance the final compound is pink and absorbs at 550 nm.

Mechanically the process for air sampling is the same in the case of both ozone and nitrogen dioxide [the air intake train must be rubber-free for ozone]. Air is pulled through a solution containing a mixture that reacts with the gas of interest. After a sufficiently large air sample has been processed the solution is placed in a spectrophotometer and the absorbance recorded. Standards prepared with known concentrations are used to construct calibration lines that enable the determination of the concentration of the gas in the air sample.

For ozone determination a buffered solution of KI (containing boric acid and a tiny amount of hydrogen peroxide) is exposed to air with an intake rate of 250 mL/min. A 7.5 L sample is generally sufficient to detect typical ozone concentrations. Starch is added to the sample and it is cooled in ice water for 10 minutes to speed up the formation of the blue complex. It is then placed in room temperature water for 10 minutes so that a cold sample in the spectrophotometer will not cause condensation to form inside the instrument. The absorbance is recorded at 574 nm.

The solution used to detect NO_2 contains sulfanilic acid, acetic acid and a trace amount of N-NED. After a sufficient amount of NO_2 has passed through the solution (400 mL/min, 20 L minimum) a pink color develops completely after 15 minutes. The determination of the NO_2 concentration is not that straightforward, however, for a number of reasons. First, the original reaction which produces HNO_2 from the NO_2 in water has alternate pathways, some of which produce N_2O_4 (which is always present in equilibrium with NO_2). So the apparent stoichiometry of the process is misleading. Second, the preparation of standards from a gas is very difficult. It happens that nitrite ion (NO_2^-) will react in the same way as NO_2 in this process but the yield is not the same. However, preparation of nitrite solutions is simple and Saltzman examined the differing results in detail, concluding that **1 mole of NO_2 produces the same color intensity as 0.72 mole of sodium nitrite**. This conversion must be applied to the final determination in order to compare with the standard nitrite solutions.

The Experiment

There are four parts to this experiment:

- synthesis of NO
  -testing for water solubility
  -testing for oxidizing/reducing strength with $Br_{2(aq)}$ and $I^-_{(aq)}$
- synthesis of NO_2
  -testing for acid behavior with water
  -testing for water solubility
- determination of local atmospheric ozone concentration
- determination of local atmospheric nitrogen dioxide concentration

The following non-locker materials will be provided:

- two 60 mL gas syringes w/sample holder, cap and delivery tube
- 24-well plate
- solid $NaNO_2$
- 1.2 M $FeSO_4$ in 1.8 M H_2SO_4
- 1 M NaOH
- dilute $Br_{2(aq)}$
- 0.3 M KI
- slightly basic water w/universal indicator
- 25 x 200 test tubes w/bubbler assemblies
- eight 18 x 150 test tubes w/stoppers in rack
- Fisher Model 415 Spectrophotometer and cuvettes
- micropipettor w/tips
- approx. 3×10^{-5} M $NaNO_2$ standard [**record exact value**]
- N-NED/sulfanilic acid/acetic acid absorbing solution
- 0.06 M buffered KI absorbing solution
- approx. 7×10^{-5} M I_3^- standard [**record exact value**]
- starch solution

The Chemicals

   Sodium nitrite is a white or slightly yellow crystalline solid, soluble in 1.5 parts cold water, slightly soluble in ethanol. It is decomposed by even weak acids with the evolution of brown fumes. It is used in the manufacture of dyes and in bleaching flax, silk and linen. It also had medical and veterinary applications, mainly as a relaxant for smooth muscle tissue.

   Iron(II) sulfate occurs in several hydrated form, the heptahydrate being common and sometimes referred to as *copperas* or *green vitriol*. The blue-green crystals lose water in dry air. It is soluble in water but solutions are quickly oxidized to iron(III). It is used in iron plating baths, fertilizers, and as a food and feed supplement. It can also be used in weed killers and photoengraving processes.

   Starch (soluble starch, *amylodextrin*) is a white, odorless, tasteless powder which is soluble in water when heated. It is frequently used in the lab as an indicator for iodometric analysis since it forms an intense blue-to-black complex with I_2 but not with I^-.

   Sodium hydroxide is commonly known as lye or caustic soda. It is a very hygroscopic white solid (absorbs water from the air rapidly) and also absorbs CO_2. It is very corrosive to vegetable and animal matter and aluminum metal, especially in the presence of moisture. Dissolving NaOH in water generates considerable heat.

   Besides its use in the laboratory, sodium hydroxide is used in commercial drain cleaner preparations, to treat cellulose in the manufacture of rayon and cellophane and in the manufacture of some soaps. It is corrosive to all tissues and can be detected on skin by the "slimy" feeling associated with bases. It should be rinsed off thoroughly upon contact. It can damage delicate eye tissues and cause blindness.

   Bromine is a dark reddish-brown fuming liquid at room temperature, consisting of diatomic molecules. In dilute water and hexane solutions its color varies from golden to dark orange. In basic solutions at room temperature it slowly reacts to form bromide and hypobromous ions. It is a member of the halogen family and has a chemistry similar to chlorine. It attacks all metals and organic tissues and vaporizes readily at room temperature. Fumes are highly irritating to eyes and lungs.

   Bromine is used for bleaching silk, disinfecting spas, and manufacturing anti-knock compounds. Pure liquid bromine on the skin can cause painful, serious burns which heal only slowly.

   Potassium iodide (the source of I^- in this experiment) is a white solid, slightly deliquescent, and prone to oxidation in air. It is used in the manufacture of photographic emulsions, and in table salt and some drinking water to help prevent iodine deficiency disease.

   Acetic acid (or ethanoic acid) has a pungent odor and in concentrated form (17 M) produces painful burns on the skin. It is soluble in water and is itself an excellent solvent for many organic compounds. While it is a weak acid, concentrated solutions are extremely irritating to tissue, especially mucous membranes. It is used in the manufacture of various acetates including plastics and textiles, in dyeing, preserving foods and in many organic syntheses. Household vinegar is 5% acetic acid. Ingestion of more concentrated solutions may cause severe corrosion of the mouth with vomiting, circulatory collapse and eventual death.

Sulfanilic acid (4-aminobenzenesulfonic acid) is a white solid which is slowly soluble in water and common organic solvents but reasonably soluble in acetic acid. It is used in the manufacture of various dyes and other organic chemicals.

N-(1-naphthyl)ethylenediamine (N-NED) is a yellow, viscous liquid with low water solubility. The pale green dihydrochloride salt (used in this experiment) is readily soluble in alcohol, dilute acid and hot water. It is used in the determination of sulfanilamide in body fluids; also for determining potassium, nitrites, and sulfates.

Technique Discussion

For the sake of efficiency there is a logical order to the work that is involved in this experiment. The atmospheric sampling operations for both NO_2 and O_3 take about one hour. The instructor will monitor the collection of a few samples of each which will be mixed to average out sampling errors. Once the sampling has begun there is time to prepare standards for the calibration graphs. After that has been done, the short study of NO and NO_2 can be done while waiting for the atmospheric sampling to finish.

To pump air through a number of sample tubes at a constant rate is not a simple matter-- especially if the tubes are all attached to the same pump. To get around problems of pressure drops and inconsistent bubblers the following procedure is used. First, all of the sample tubes (one for each student) are connected to a large vacuum hose through 22-gauge hypodermic needles. The hose is attached to a vacuum pump. The physics of this situation need not concern us here, but when air is drawn through very small orifices it is possible to have a uniform draw through all of the openings at the same time.

The needles lead back to the head space in the sampling test tubes. As air is drawn out of the tubes by the vacuum pump it must be replaced. This is accomplished by air flowing in from the atmosphere through the bubblers which are immersed in the absorbing solution. The entire assembly is placed on a cart outside the lab. The air flow can be adjusted by a bleeder valve on the vacuum pump line. *This adjustment will be made before class*. Once the 10 mL samples have been attached to the vacuum line and sampling has begun they do not require further attention.

Subsequent calculation of the volume of NO_2 or O_3 present in the air sample will require room pressure and temperature values.

During the sampling period data should be gathered to allow the construction of a calibration graph for the absorbing solution.

The fundamental law governing the absorption of *all* types of electromagnetic radiation is known as **Beer's Law**. It is generally expressed as

$$\log P_o/P = \epsilon bc = A$$

where **P** is the *power* of the incident and transmitted light, **A** is the logarithmic term known as *absorbance,* and the constant ϵ is called the *molar absorptivity* when the concentration **c** is expressed in terms of moles of absorber per Litre, and the path length **b** is given in centimetres.
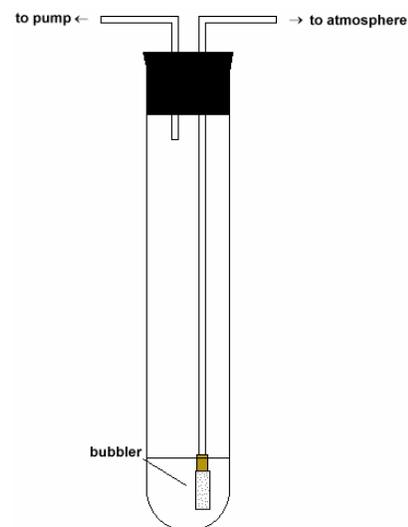
When other units are given for concentration or path length, ϵ is simply called the *absorptivity* and is given the symbol **a**. Beer's Law also applies to solutions in which there is more than one kind of absorbing substance, the total absorbance being the sums of the individual absorbances (assuming no interactions among species).

Another quantity frequently encountered in colorimetric analysis is *transmittance*, T:

$$-\log T = A$$

[on many instruments a dual scale is provided, one for Absorbance--which is logarithmic and therefore difficult to read at the condensed part of the scale--and one for *percent* Transmittance which is linear; in the formula above, **T** stands for the <u>decimal</u> value of the transmittance, *not* the percent; our instrument is digital and so it is more convenient to simply read absorbance]

The linear relationship between absorbance and concentration at a fixed path length of absorbing substances is a generalization which is true for many solutions as long as they are not "too dark" or "too light". However it is unwise to rely on Beer's Law and take only a single reading, assuming that a line can be drawn (or a proportionality set) from that point to 0,0. Random experimental error is enough to make the measurement of small concentrations unreliable without additional data. For that reason it is usual to prepare a number of standard samples on the high and low end of any anticipated unknown concentration and use their absorbances to establish a "best-fit" calibration graph. The table below gives a range of samples utilizing the supplied standards $NaNO_2$, and I_3^-.

Test Tube	1	2	3	4
mL $NaNO_2$ or I_3^-	0	0.200	0.400	0.600
additional absorbing solution	0	0.800	0.600	0.400

Three sample test tubes are each filled with 9 mL of the absorbing solution (dispensed from a buret). These are samples 2-4. Additional material is then added to each according to the table. Test tube #1 is for a sample of absorbing solution alone which will be used to calibrate the spectrophotometer (i.e., as a "blank") since the solution itself has a small absorbance. 10 mL of solution should be placed in this tube.

The fractional mL volumes are added with an adjustable micropipet, the object being to have a total volume of 10 mL for each sample. The adjustment and use of the micropipet will be discussed in class. <u>It is important that the pipet be held vertically when measuring</u>. You **<u>SHOULD NOT</u>** fill the pipet with liquid and then set it down on the bench on its side. A clean tip should be used for different solutions. Once the samples have been made they should be thoroughly mixed. Saltzman determined that the maximum color intensity of the dye for NO_2 detection was achieved after standing at least 15 minutes. In the case of the I_3^- standards, 1.000 mL of starch should be added to each tube (including the blank) and after thorough mixing the test tubes should be placed in ice water for 10 minutes and then in room temperature water for 10 minutes.

The Fisher Model 415 spectrophotometer is a relatively simple instrument, similar to many other spectrophotometers currently available. It consists of 5 basic parts: a light source, a monochromator to select a certain wavelength of light (in this case, a grating and a set of filters), a compartment to hold the sample and exclude stray light, a detector to receive the light transmitted through the sample, and a display which indicates either absorbance or % transmittance.

In most spectrophotometers, a special glass test tube (called a cuvette) with marks inscribed on it to ensure that the tube is inserted the same way each time is generally used. Variations in the transmittance of the glass make this important for accurate work. Cuvettes are often supplied in matched sets so that a series of solutions can be analyzed but these are expensive so more often a single cuvette is used, rinsed and refilled.

The instrument should be allowed to warm up for about ½ hour for maximum stability. The desired wavelength is selected with the Wavelength Selector knob (5).

A diagram of the Model 415 is shown at the right.

1. Select Absorbance or Transmittance
2. Zero Absorbance/100% Transmittance
3. Function Selector
4. Readout
5. Wavelength Selector
6. Wavelength indicator
7. Sample Compartment

Model 415
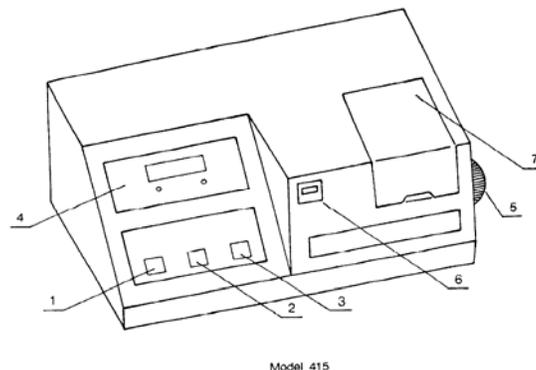
Once the standard samples have been prepared and "aged" the instrument is zeroed (2) with the "blank". A small amount of solution is poured into the cuvette, rinsed along the sides and then discarded. Then the cuvette is filled. Normally this is done to the bottom of the *fiducial mark*, a vertical line segment on the cuvette. Our instrument only requires about half as much liquid, however. The fiducial mark *should* be used to align the cuvette consistently in the light path. There is an arrow inside the sample compartment which is used as a reference point. Once the instrument is zeroed (press 2 and wait for the 0.000 readout), the blank is returned to its sample tube and a small amount of the lightest solution is used to rinse the cuvette, then discarded. The cuvette is then filled and a reading taken as before (although this time there is no need to press any buttons). The process is repeated until all of the samples have been read. By beginning with the lightest sample the effect of sample contamination due to poor rinsing is limited. Use a different cuvettes for the two different chemical systems.

When the air samples are ready to measure be sure to use the same spectrophotometer as before and rezero with the same cuvette and some blank.

While the air samples are being processed and after the standard readings have been recorded, the synthesis and testing of the nitrogen oxides should be done. In order to collect nitrogen monoxide, air must be excluded. The gas can be generated in a syringe and dispensed for the various tests from the same.

No more than 0.25 g of solid $NaNO_2$ should be measured into the sample holder. The syringe is then filled with water and the sample holder floated on the column of water which is then allowed to escape, bringing the sample down into the syringe. The plunger is then inserted, pinning the sample holder down. Between 3 and 5 mL of the acidic iron(II) sulfate solution is drawn up in the syringe and the syringe cap is placed securely over the end. Vigorous shaking will mix the contents of the sample holder and the solution, allowing the reaction to proceed. NO should gradually push out the plunger.

sample holder
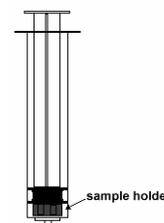
If it appears that too much gas will be generated, take the syringe to the fume hood, turn it so the cap is pointing up and give the cap a quick twist and release the pressure. Replace the cap promptly.

After the reaction is finished, discharge the remaining liquid into a beaker of water. Draw 5 mL of distilled water into the syringe, recap, and shake to wash the gas and the syringe [is the gas soluble?]. Discharge the wash. Repeat if needed.

To check the oxidizing/reducing strength of the NO, slowly bubble some of the gas (via a delivery tube) into half-filled wells of either $KI_{(aq)}$ or $Br_{2(aq)}$. The tube must be kept under the surface of the solution and the gas should be added slowly. Rinse the tube between solutions since bromine will displace iodine from KI.

To make some NO_2 it is only necessary to mix some oxygen (from the air) with the remaining NO in the syringe. Discharge 30 mL of the remaining NO into a DRY, empty syringe via the delivery tube [you can dispose of any remaining NO by bubbling it through 1 M NaOH]. Draw an equal volume of air into the dry syringe containing the NO. NO_2 should form immediately.

To judge the acidic properties of the NO_2, discharge some of the gas slowly *over* (about 1 cm) some of the prepared slightly basic water containing the universal indicator. Retain about half the gas sample.

The water solubility of NO_2 can be checked by drawing 5 mL of water into the syringe. Keep the syringe tip under the surface of the water and shake the syringe a little. Dispose of any remaining material by discharging into 1 M NaOH.

The Report

Your initial calculations should include:

1. The moles of NO_2^-/I_3^- in each of the standard solutions

2. The effective moles of NO_2 in each of the standard solutions
   [remember, 0.72 mol NO_2^- = 1 mol NO_2 in this experiment]

3. A calibration graph for NO_2 at 550 nm (Absorbance vs. mol NO_2) including the best-fit line

4. A calibration graph for I_3^- at 574 nm (Absorbance vs. mol I_3^-) including the best-fit line

5. The volume of NO_2 in the 20 L air sample (determined from calibration graph, P and T)

6. The volume of O_3 in the 7.5 L air sample (determined from calibration graph, P and T)

7. The concentrations of NO_2 and O_3 in air expressed in ppmv

Your conclusion to this experiment should include a comparison of your results for both the tropospheric ozone and nitrogen dioxide with the SCAQMD *forecast* values for the day of the experiment (http://www.aqmd.gov/) [forecasts are available the prior day only].

Summarize briefly the test results on the nitrogen oxides. Compare water solubility. How does NO compare to I^- and Br_2 as a redox agent? Can this be explained using basic principles? Explain the behavior of the water sample when NO_2 was discharged above it. How is this connected to acid rain phenomena?