Passive Nitrogen Dioxide Sampler: Preparation and Analysis

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This page provides instructions for preparing and analyzing passive samplers for measuring gaseous nitrogen dioxide. This method was originally described by *Palmes, et al.* (1976). It is highly recommended you read through all of the instructions once before beginning, as there are many side notes.

**Washing Components**

It is essential that all of the parts of the diffusion tube are clean before construction. The stainless screens are best cleaned by soaking in phosphoric acid and distilled water, then rinsed at least three times. Caps and tubes ideally are washed in a sonic bath with distilled water and a detergent such as automatic dishwashing soap or Sparkleen. I have also had luck with generic dishwashing soap, but these have a tendency to leave behind residue and odors. If using a sonic bath, the parts should be left for at least one hour; otherwise, soaking in detergent for several hours will work. After either the bath or soaking, RINSE, RINSE, RINSE with distilled water. All components may be laid out on paper towels to air dry, and should be thoroughly dry before construction.

**Constructing tubes**

Components necessary for tube construction. See Shopping List at end of document for relevant catalog numbers and pricing.

Two (orange) polyethylene caps, 0.5" ID  
Two Stainless steel mesh screens, 0.5" diameter  
One acrylic tube: 0.5" OD; 3/8" ID  
Triethanolamine (TEA)  
Brij-35 (Wetting agent)  
Distilled water  
Scale  
Cleaning detergent (see below)  
Phosphoric acid  
Clean glassware: 100ml graduated cylinder, 25ml and 200ml beakers  
100-1000uL micro-pipettor  
20-50uL micro-pipettor (optional)  
clean paper towels

There are two methods for preparing the tubes which achieve satisfactory results, although one is preferred over the other. If you have access to micro-pipettors capable of 25-50uL, use the preferred method. Both are illustrated below. Before putting the tubes together, however, the TEA solution must be...
Prepared.
--Weigh out 1 gram of Brij-35 on a scale. Place in a small beaker and add 9mL distilled water. Heat briefly on a hot-plate to dissolve the solution; the boiling point of Brij-35 is near 110 degrees F.
--In another beaker, combine distilled water and TEA in a 80:20 solution. That is, for 80ml of distilled water, add 20ml of TEA.
--To the 100ml total water/TEA solution, add 167uL (that's micro-liters) of Brij-35. Stir to mix thoroughly.
NOTE: it does not take much to prepare even a large number (e.g. 200) of tubes. If you want, you may cut down the total amount of solution by scaling appropriately. The limiting factor in the solution preparation will be how little Brij-35 solution you are accurately able to measure.

Preferred method

For one cap in each pair of caps you have, arrange open side up. Into each cap, place two stainless steel mesh screens, pushing them all the way to the bottom so they lay flat, one on top of the other. Into each cap that now has a pair of screens, use a micropipettor to put 25-50uL (again, micro-liters) onto the surface of the screens. NOTE: the reason a range is given is that not all micro-pipettors have the same volume increments. I always put in 50uL, but any more than that can cause excess to run down the sides of the tube. Choose a volume in the range that will allow you to only have to put solution in each tube once.

Figure 1. Caps arranged, screens pushed to the bottom, and ready for TEA.

Alternative method

If you do not have a micro-pipettor that will measure down to 50uL, use this method. Take a pair of stainless steel screens and sandwich them together. Using a pair of tweezers or needle-nose pliers, grip the screens together and dip into the TEA solution. Lightly dab off the screens on a clean cloth or paper towel and put into the bottom of a cap. Repeat for one cap in each pair of caps.

At this point, there are two options. One is to shove an acrylic tube into each cap that now has a screen, making sure the tube makes contact with the screens, and cap the open end of the tube. It is crucial here not to shove the closing cap on too hard or too far, as it can force excess TEA up into the crack between the outside of the acrylic tube and the inside of the cap with the screens. Placing the closing cap on about half way is good enough. Once all tubes are capped, put them in a sealable bag, label the outside with the date and method of preparation, and put them in cold storage (a normal refrigerator is fine) until ready to use.

Alternatively, if one has access to a clean-air source (i.e. air that is scrubbed clean of ozone, NOx, VOCs and other hydrocarbons, and water), an enclosed chamber can be rigged up to dry out the solution in
the open caps before the tubes and closing caps are put on. This will ensure that no excess TEA will run down the inside or outside of the tubes, potentially skewing the analysis. After drying (about 24 hours is sufficient), finish construction as described in the previous paragraph.

![Finished, capped tube. Note number written on cap containing screens.](image)

**Figure 2.** Finished, capped tube. Note number written on cap containing screens.

**Tube Deployment**

The following are some general guidelines to consider when deploying tubes in the field.

The cap without the screen should be removed upon deployment. Tubes should be placed at least 10cm (4 inches) away from any surfaces—a good way to achieve this is with wire. Placing tubes out in pairs or triplets may help increase the accuracy of your data and reduce anomalous results. ALWAYS put out a few capped tubes with your measurement set as blanks as a check against contamination. They are also used in the calculation of NO₂.

Be creative: wire, duct tape, zip ties, and fishing line are your friends. Be sure to place the tubes out of reach and line of sight, 2.5 – 3 meters (8 – 10 feet) off the ground.

![Example of tube placement on a light pole. Tubes are placed in a pair and are set away from the pole by wire.](image)

**Figure 3.** Example of tube placement on a light pole. Tubes are placed in a pair and are set away from the pole by wire.

**Analysis**

Components necessary for analysis
- Exposed passive samplers
- Sulfanilimide
- Naphthylethylenediamine Dihydrochloride (NEDA)
Phosphoric acid
Sodium Nitrite (solid)
Distilled water
Scale
Spectronic-20
Cuvette that fits into Spectronic-20
Five test tubes
Nine 250ml Volumetric flasks; 500ml Erlenmeyer flask; 25ml graduated cylinder
20ml, 10ml, 5ml, 1ml glass pipettors
100-1000uL micro-pipettor
clean paper towels

***Turn on the Spectronic-20 and set the wavelength to 540nm. The instrument needs to warm up for one hour before use.***

Preparation of Reagent Solution

Using the scale, weigh out 0.35 grams of NEDA; put into a 250ml volumetric flask and fill with distilled water to the line. Weigh 5.0 grams of sulfanilamide; put into a 250ml volumetric flask. Add to the sulfanilamide 15ml phosphoric acid; fill the flask to the line with distilled water. Note: combining water and phosphoric acid triggers an exothermic chemical reaction; do not be alarmed if the flask becomes warm. When filling each flask with distilled water, add about half the necessary amount and agitate the solution to encourage mixing. Do not fill to the line until the mixture has completely dissolved.

Once both mixtures are completely dissolved, pour the entire contents of the volumetric flask containing the sulfanilamide solution into the 500ml Erlenmeyer flask. Next, add 35.7ml of the NEDA solution to the 500mL flask. Mix well, and cover with a rubber stopper until ready to use.

Making a Calibration Curve

The method of analysis to determine the amount of NO₂ captured by the tubes involves measuring the absorbance of NEDA that has reacted with NO₂. To determine the mass of NO₂ relative to absorbance, a calibration curve must be done using known amounts of NO₂ in solution.

Weigh out 0.70g (0.01mol) of sodium nitrite and add to a 250mL volumetric flask. Fill with distilled water to the line, making sure the solution completely dissolves. Take 1ml of solution and add it to a second volumetric flask and fill with distilled water to the line. This second solution is the stock solution. From the stock solution add the following amounts into each of 5 volumetric flasks:

<table>
<thead>
<tr>
<th>Solution #</th>
<th>ml of Stock</th>
<th>[NO₂] mol/L</th>
<th>[NO₂] diluted</th>
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<tr>
<td>1</td>
<td>20</td>
<td>1.28x10⁻⁵</td>
<td>5.97x10⁻⁶</td>
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<td>2</td>
<td>15</td>
<td>9.60x10⁻⁶</td>
<td>4.48x10⁻⁶</td>
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<td>3</td>
<td>8</td>
<td>5.12x10⁻⁶</td>
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<tr>
<td>4</td>
<td>3</td>
<td>1.92x10⁻⁶</td>
<td>8.96x10⁻⁷</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>6.40x10⁻⁷</td>
<td>2.99x10⁻⁷</td>
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After making your standard solutions, add 1.4 ml from each into its own test tube, and add 1.6 ml of
sulfanilamide-NEDA solution to each test tube. Let sit 15 minutes. To find the absorbance for each standard solution, follow the steps outlined in the section, "Spectroscopic Analysis of Analyte". Plot your obtained absorbance values versus [NO\textsubscript{2}] and apply a simple linear regression. A valid curve will have $r^2 \geq 0.999$ and an intercept near zero. You now have a way to convert absorbance to mass of NO\textsubscript{2}. See "Calculation of [NO\textsubscript{2}] in Parts Per Billion" for more details.

See an example calibration absorbance curve here.

**Preparation of Tubes for Analysis**

Uncap the non-screen end of your exposed tubes and arrange open end up. Using your 100-100uL micro-pipettor (having more than one is helpful here), measure out 1.6ml of the combined sulfanilamide-NEDA solution into each tube AND into the cuvette. Next add 1.4ml distilled water to each tube for a total of 3ml of liquid in each tube AND into the cuvette. The solution will become pink. This coloring is the result of NEDA dye reacting with NO\textsubscript{2} captured by the tubes during exposure. The solution in the cuvette, however, is the blank and should be clear; if it is pink, your sample is contaminated. Let stand for 15 minutes.

![Figure 4. NO\textsubscript{2} in solution reacted with NEDA dye.](image)

**Spectroscopic Analysis of Analyte**

You will now measure the absorbance of each tube. First, the Spectronic-20 needs to be calibrated so we are only measuring the absorbance of the reacted NEDA. This is accomplished by placing the cuvette into the Spectronic-20 with the blank solution and turning the offset dial until the needle reads zero ON THE ABSORBANCE SCALE, NOT THE TRANSMITTANCE SCALE. If the cuvette has a label or marking near the top, always orient the cuvette the same way relative to the marking as the glass will have slight variations in absorbance depending on its orientation. If there is no marking, make one. Remove the cuvette, then empty, rinse, and dry the cuvette.

Now, pour the contents from a tube into the cuvette and measure the absorbance using the Spectronic-20, remembering to orient it the same way for each reading (and the same as the blank reading at the beginning). Record both the absorbance and the tube number. Empty, rinse, and dry the cuvette after each absorbance reading.

Blank tubes should be analyzed in the same manner. The results of all blank absorbance readings may be combined into an average blank absorbance, $b$, to be used the calculation of NO\textsubscript{2}. 

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Figure 5. Spectronic-20 with analyte in cuvette.

Calculation of [NO₂] in Parts Per Billion

Equation 1 below is derived from Fick’s law of diffusion. Several assumptions are made in the calculation of the diffusion rate:
- Constant with temperature
- Not affected by wind or other turbulent flow
- Density of air does not include water vapor, and is for an average temperature of 17°C.

For further discussion of the effects of environmental parameters on diffusion tubes, see Heal, et al. (2000) and Kirby, et al. (2001).

See an example of tube response with increasing NO₂ concentration using this method in a controlled environment here.

Definition of relevant variables:
- \( A_b \) = Absorbance
- \( b \) = Average blank absorbance
- \( l \) = Length of tube [cm]
- \( d \) = Volume of solution [3 mL]
- \( M_w \) = Molecular weight of NO₂ [47 g mol⁻¹]
- \( s \) = Slope of calibration curve [A L mol⁻¹]
- \( r \) = Inner radius of tube [cm]
- \( D_L \) = Diffusion coefficient, 0.154 cm² s⁻¹
- \( t \) = Time of exposure [sec]
- \( r_a \) = Density of dry air (@ 290 K) [1.21 kg m⁻³]

\[
[\text{NO}_2] \text{ (ppb)} = \left[ (A_b - b) \cdot l \cdot d \cdot M_w (10^9) \right] / \left[ s \cdot \pi \cdot r^2 \cdot D_L \cdot t \cdot r_a \right] \quad (1)
\]

Sources


**Shopping List**

Prices and catalogue numbers last checked on 21 November 2005.

**Sigma-Aldrich**

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**Fisher Scientific**

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<td>100-1000uL Pipettor</td>
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<td>21-278-52</td>
<td>101-1000uL pipettor tips (1000)</td>
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