# **LOPAP - LO**ng **P**ath **A**bsorption **P**hotometer

# Measurements Of HONO

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# Abstract

The LOPAP device is a systematic mechanism which uses an aqueous scrubbing technique to absorb nitrous acid (HONO) from the atmosphere by converting it into a diazonium salt by reacting with sulfanilamide (SA) and then with N-(1-naphthyl)ethylenediamine dihydrochloride (NED), into a highly absorbing azo-dye. this azo-dye can be analyzed once passed through a liquid waveguide capillary cell to increase its absorption for a spectrometer to detect and return numerical values on SpectraSuite, the program used to operate the spectrometer which returns a positive correlation of actual HONO concentration up to parts per trillion by volume.

This is an important technique because other methods of detecting HONO use indirect methods such as the Differential optical absorption spectroscopy (DOAS) which measures HONO's narrow band absorption while the LOPAP measures the physical particulates.

This device was meant to be deployed atop the roof of Petrie Science and Engineering building to detect HONO concentrations during various times throughout the day, month, and year. Measurements during the winter were of particular interest and importance because it was suspected that there may be a change in HONO concentration compared to other times during the year during snow fall. However, due to the malfunction of the liquid waveguides, a key component of the LOPAP, no consistent calibrations were able to be made and therefore no measurements were recorded.

Therefore, the purpose of this assignment was to build and optimize a new LOPAP. New parts and pieces were found from various suppliers with some particular

difficulty because many parts were not specifically designed with the LOPAP in mind and some customization was required such as the stripping coil glassware.

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# Introduction

The long path absorption photometer (LOPAP) is a device designed to detect the concentration of HONO in the troposphere. HONO is an important trace gas found in the lower atmosphere because it can be the main source of hydroxyl radicals during the early morning hours when other sources have yet to accumulate [Kleffman et al., (2008)].

HONO undergoes photolysis during the day time to produce hydroxyl radicals by the following reaction;

$$\mathrm{HONO} + h\nu\ (300\text{-}400\mathrm{nm}) \rightarrow \mathrm{NO} + \mathrm{OH} \qquad ...(R1)$$

The rate of HONO production is constant as long as the proper precursors are present. Therefore, at night large accumulations of HONO exist because at very small amounts are photolyzed when the only source of light is from the reflection of the moon or human intervention. However over the last decade, it has been found that there are other detectable sources of trace amounts of HONO during the day time as well. The concentration of day time HONO in the lower atmosphere is typically several parts per billion in urban areas and ten to one hundred parts per trillion in rural areas. [Wentzel, (2009)]

The dangers of HONO are that it may react with secondary amines to produce nitrosamines, a carcinogenic substance. The use of some amine based home cleaning products may have some potential danger if HONO is present, such as in apartment buildings with open windows (R2).

$$\mathrm{R_2NH} + \mathrm{HONO} \rightarrow \mathrm{R_2NNO} + \mathrm{H_2O} \qquad ...(R2)$$

## Sources & Sinks

HONO may be formed homogeneously by recombination of OH and NO (R3) during times when the concentration of OH is high relative to HONO and there are few other substances to react with.

$$NO + OH \rightarrow HONO \qquad \text{...(R3)}$$

Heterogeneous formation can also occur by $NO_2$ and water vapour, this is the process expected to occur in greater abundance in the presence of snow fall.

$$NO_2 + H_2O \rightarrow HONO + OH \qquad \text{...(R4)}$$

Another method of HONO formation is directly through combustion, such as from burning biomass or automobile engines. Some traffic studies have found that HONO/$NO_X$ ratios to be approximately 0.03%-1.0% in Europe while they were approximately 0.06% in North America [Wentzel, (2009)]. This may be attributable to the fact that many European vehicles have engines that consume diesel which produces a greater variety of gases than alternatives such as ethanol which only produces carbon dioxide and water. Currently, HONO chemistry is still a topic of research and therefore is imperative to take accurate and precise measurements to determine its mechanism of formation.

This research project was originally intended to be collection and analysis of HONO measurements in the troposphere, however due to malfunctions and technical difficulties this was not possible. Therefore, the subject of this research was to build and optimize a new LOPAP. This consisted of finding parts from individual suppliers, and testing the equipment and calibrating to check proper function. However, there was no time for HONO calibrations due to the liquid waveguide capillary cells not functioning properly.

# EXPERIMENTAL

## LOPAP

The LOPAP is an important device used to collect and analysis the concentration of atmospheric HONO. This is an important process because HONO is an important atmospheric source of hydroxyl radicals. These radicals are important for atmospheric reactions such as the oxidation of atmospheric hydrocarbons, and may play a significant role to some unknown positive or negative processes occurring in the atmosphere.

## Solution Making

Stock solutions of sulfanilamide (SA), N-(1-naphthyl)ethylenediamine dihydrochloride (NED), and sodium nitrite ($NaNO_2$) were first made at 0.06M, 0.2 mM, and 0.01M respectively (See Appendix C). MilliQ water was used to solvate the sodium nitrite and NED, but 1 M HCl was used for SA instead of milliQ water because the acid helps to minimize possible interferences such as $SO_{2(g)}$ and $NO_{2(g)}$. Although acidic conditions reduce the solubility of HONO in water, it was the SA which quickly reacts with HONO to form diazonium salts. [Heland et al., (2001)].

Next, to create a calibration curve, the SA was spiked with varying degrees of $NaNO_2$. Concentrations of 50 µm, 100 nM, 50 nM, 10 nM, 8 nM, 6 nM, 4 nM, 2 nM, 0.6 nM and 0.2 nM were made in order to take measurements at varying concentrations (See Appendix D)

As the SA solution passes through the stripping coil from the inflow to the outflow, it dissolves the HONO when the hydroxyl oxygen atom abstracts a proton which creates a very good leaving group, $-OH_2$ , next a lone pair on the oxygen atoms opposite of the water molecule attacks the O-N bond and creates a triple bond. This expels the water molecule from the nitrogen creating the $NO^+$ ion .

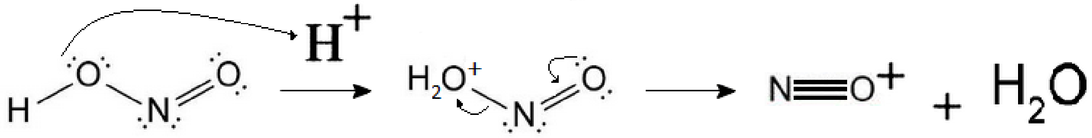

Figure 1. HONO Dissociation

Next, the $NO^+$ ion reacts with SA to form a diazonium ion and liquid water. The lone pair of the amine group bonded to the six carbon aromatic ring undergoes nucleophilic attack on the $NO^+$ ion and a positive charge is obtained on the nitrogen. To relieve this instability, a proton is lost and -NHNO remains on the benzyl portion. After, the lone pair on the internal nitrogen forms a double bond between its adjacent nitrogen atom and forces the remaining proton to migrate onto the terminal oxygen atom, to create a hydroxyl group. The final lone pair on the internal nitrogen atom will bond with its adjacent nitrogen atom again which creates the triple bond, the excess electrons are pushed onto the terminal hydroxyl group which will reclaim the proton which was originally lost in the prior steps and leave as a water molecules, completing the diazonium ion.

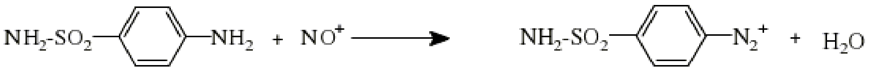

Figure 2. Diazonium ion Formation.

The diazonium ion then reacts with NED to product an azo-dye, the nitrogen atoms of the diazonium ion are strongly ortho-para directing which cause them to undergo nucleophilic attack at the aromatic ring of NED. Since the aromatic ring is very bulky, at the para position due to the long amine and hydrocarbon chain, the diazonium ion must form a bond at the para position. This is the final product of the reaction, the azo-dye has a pale transparent pale pink colouration. The concentration of this compound is directly proportional to the concentration of atmospheric HONO collected. As the azo-dye passes through the waveguide the intensity of refraction is presented on SpectraSuite.

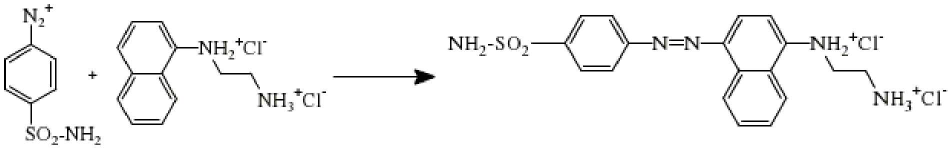

Figure 3. Azo-dye Formation.

Reaction Time

The change in time required for the reaction to complete from the point the SA and NED is drawn to the point where the diazonium salt is analyzed through the liquid waveguide is approximately five minutes. The intensity of pink by the azo-dye can be altered by changing the concentration of sodium nitrite present, a higher concentration increases the intensity and a lower concentration decreases the intensity. The optimal pump speed found to accommodate this reaction time was at 3.8V which translates to 0.4

mL/min. This was found through physical measurements of liquid volume passing through the pump after one minute.

Stripping Coil

This coil is used to collect atmospheric air at one end, where it is introduced to SA solution from the inflow and collected back through the outflow one. Any residual HONO is captured by SA solution from channel two and collected back through outflow two. The other end is attached to a pump which generates a vacuum for the SA solution to be drawn through the SA inflow to SA outflow at a rate of 1 L/min.

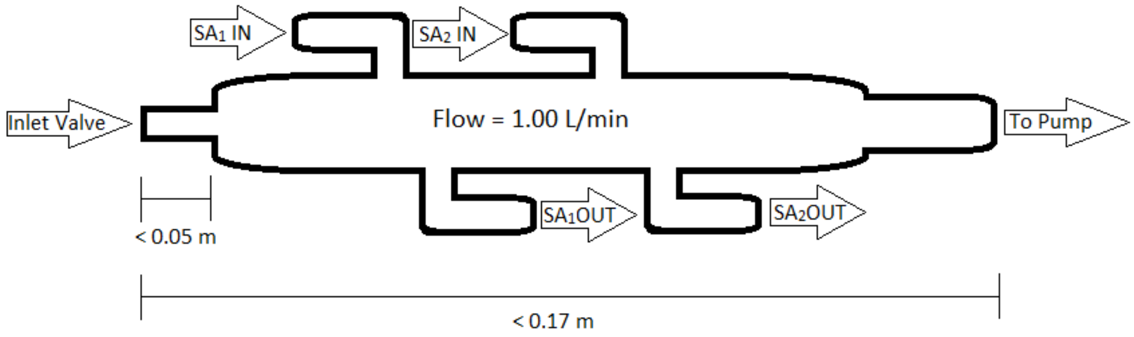

Figure 4. Stripping Coil Schematic.

Generally, the first channel for SA inflow collects approximately 99% of atmospheric HONO and the second channel for SA inflow collects the remaining trace amounts, approximately 1%.

The stripping coil must be less than 17 cm in length, this was the convention by Heland et al, the designers of the LOPAP. In addition, the inlet of the stripping coil must be less than 5 cm in length to reduce the probability of particulates becoming adsorbed on the surface which may cause undesirable reactions and contamination to the whole system [Heland et al, (2001)].

### De-bubblers & Mixing Coils

These are glass tubes in a "Y" shape which help eliminate bubbles created by the pump when drawn from the bottles. Before the SA and NED solution pass through the liquid waveguide they pass through these debubblers at one of the upper points of the "Y" and bubbles are lost through the other upper point of the "Y" and the bubble-free solution is drawn down through the bottom point of the "Y" is drawn through the pump and into the liquid waveguide.

Bubbles make accurate data acquisition impossible because they block or distort the signals created by HONO while passing through the liquid waveguide capillary cells. The waveguides analyze the refractive index of the liquids passing through and air bubbles which have no refractive index disrupt the signal.

Mixing coils are glass coils spun in a loop used to help mix the SA solution after it has passed through the stripping coil with the NED solutions, they are coiled because it increases the volume and surface area to increase the magnitude of mixing while saving space.

### Tubing, Connectors & Fittings

Tubing was an important component for the LOPAP because the inner diameters will affect the flow rate and pump speed, they must also be the correct size for fittings to be attached. Also, outer diameter must also be considered because they must fit tightly with connectors and glassware. All tubing used was tygon tubing, PEEK tubing, PEEK connectors and PEEK fittings, this was in order to reduce the amount of bubbles produced that was associated with being made of teflon, PFA, or silicon.

The tubing used had an inner diameter of 0.76 mm which is consistent with pump speed and liquid flow rate. The only exception was the tubing over the pump which brought the SA solutions into the mixing coils after exposed to atmospheric HONO, this tubing had an inner diameter of 1.02 mm, a larger diameter was required to prevent irregular pressure such a vacuums being created in the opposite direction causing the solutions to propagate in the wrong direction or create an inconsistent liquid flow rate.

## Liquid Waveguide Capillary Cell - LWCC

The liquid waveguide capillary cells are a vital portion of the LOPAP because they physically bring about the refraction of light through the solution which would contain trace amounts of HONO in the form of azo-dye. The waveguides significantly increase the absorbance because it has a greater path length which is directly related to beer's law, which states absorption is the product of concentration, path length and an absorption coefficient.

Both pairs of waveguides have an internal volume of 500 µL, but an important difference between the old waveguides and new waveguides are the path lengths. The older waveguides have a path length of 200 cm while the new ones have 250 cm. This allows a greater absorbance of HONO because according to Beer's law, absorbance is the product of the concentration of the species, its absorption coefficient, and path length. This provides the potential for more accurate readings because there is a greater amount of transit time for light to path through before reaching the spectrometer

The critical angle for the liquid waveguide is 14.1 degrees, this is due to the internal glassware being coated in teflon AF 2400 having a refractive index of 1.29 which is required because the water in the aqueous core of waveguides has a refractive index of 1.33 and the teflon must have a lower refractive index in order to create the proper refraction. This causes the critical angle to be 14.1 degrees because the total internal reflection is less than 14.1 degrees.

Another difference between the two waveguides are that the old waveguides were close to being a decade old and was not as sturdy as the newer models, hence leaks were common. One method of cleaning the waveguides is to use a syringe and inject milliQ water through the inflow and then through the outflow as many times as desired to remove debris and air bubbles. The older waveguides could not withstand this pressure and some internal components may have come loose when water was injected which caused leaks through the sides.

## Fiber Optic Cables

The newer fiber optic cables used have 600 μm pinhole compared to 300 μm pinhole of the older fiber optic cables. This allows the new fiber optic cables to let twice the magnitude of light to enter the waveguide than the old ones.

In addition, the newer fiber optic cables are longer, more durable and flexible than the older ones which allow greater flexibility in keeping the work bench clean and organized. The older fiber optic cables must be kept straight at all times because they could easily have their internal glassware shatter if they were bent.

## Spectrometer

The spectrometer is an important component of the LOPAP because it detects the light being transmitted from the waveguides which detected the absorbance of atmospheric HONO and relayed this message through the fiber optic cables to return a numerical value for the intensity of HONO collected from the stripping coil.

Dark and reference spectrums must be taken for baseline values to be used to calculate the actual percent transmission of HONO concentrations. To collect these values, the stock solutions of SA and NED, 0.06 M and 0.2 mM respectively, were connected to the pump and flushed through the LOPAP. The reference spectrum represents the intensities found when there is pure SA and NED passed through the system without any sodium nitrite, this provides a baseline value to find the difference of any non-HONO related noise that may be also taken through the solution. The dark spectrum is taken after blocking out the light source completely, the intensity recorded should be approaching zero, however there would still be a small amount of "noise" intensity that is not negligible which may be due to imperfect manufacture or leaks of light.

The actual percent transmission of HONO can also be determined by SpectraSuite by using  a formula which also uses its baseline dark and reference spectrums to directly determine the percent transmission;

$(S_\lambda - D_\lambda)/(R_\lambda - D_\lambda)$

where;

$S_\lambda$ = Sample intensity at $\lambda$

$R_\lambda$ = Reference intensity at $\lambda$

$D_\lambda$ = Dark intensity at $\lambda$

Channel one should always be the more saturated channel with channel two significantly lower because 99% of the HONO was already collected from channel one and only ~1% residual levels of HONO remain in channel two.

## Light Source

The light source used was a tungsten halogen lamp which generates light within the range of the visible spectrum to near infrared spectrum. There is no ultraviolet radiation emitted. It was discovered that this was not a reliable light source for operating with the LOPAP because of its tendency to become unstable and increase the chance of recording false data due to an effect called *drifting*.

Drifting is the effect where initial wavelengths of light detected will consistently change once the light source is turned on until a certain amount of time has passed for the light source to warm up and stabilize. Any data found before this time are incorrect. Therefore, the amount of time must be found for the light source to have stabile wavelengths must be found.

Initially, twenty minutes were thought to be enough time for the light source to stabilize, however once the wavelengths were measured, another fourty minutes were found to be required. This means one hour is required for the light source to be ready for use, which is a significant delay before any calibrations or real measurements may even begin to be recorded. After the first hour, another thirty minutes were timed at a different initial intensity to determine if there was any deviation once the intensity was changed, there was not. However, for the initial hour, there was an astonishing 25% drop in intensity, this is a significant amount of change and would certainly affect the results if it had not been discovered, therefore the old light source was calibrated as well.

## Mass Flow Controller #2 Calibration

The newly purchased mass flow controller from Aalborg has a range of 0-2 L/min was found to have an error of ±1.5% the maximum flow rate, which translated to ±0.03L/min. This meant that the first mass flow controller, which had a range of 0-15 L/min has an error of ±0.225L/min, and for the purpose of the LOPAP which only operates at 1L/min would carry a ±22.5% error, which is significant.

The mass flow controller was calibrated using a Gilibrator. This device is a small cylindrical tool used to generate bubbles which travel through the tubing at a rate directly proportional to the actual flow rate. There are two holes at the centre of the bubble generator, the top one connects to the mass flow controller and the bottom is used to pour a soapy solution into the lower cylinder where a circular pad is pressed down by a pump to generate bubbles.

Figure 5. Gilibrator

It is imperative to have only one bubble produced at a time or else the measurement is inaccurate. It was found that a reading of 1.04 L/min on the mass flow controller actually has a flow of 1L/min. [See Figure 11. Mass Flow Controller Calibration]

During calibrations there is also a mass flow controller attached to the compressed air cylinder to ensure a constant rate of release at 1.02 L/min. The mass flow controller two is attached to a stainless steel "T" where 1.00 L/min is diverted into the stripping coil inlet. The remaining excess air is diverted from the third end of the "T" through a tube into a glass beaker full of water at 0.01-0.02 L/min. The excess air is diverted because it serves as an indicator to ensure air is indeed released from the compressed gas cylinder, in addition it serves as a fail safe mechanism if there may be a momentary lapse in the flow rate. This is important because there must be more air supplied from the compressed air cylinder than pulled from the pump otherwise a vacuum forms and the flow rate is in the wrong direction.

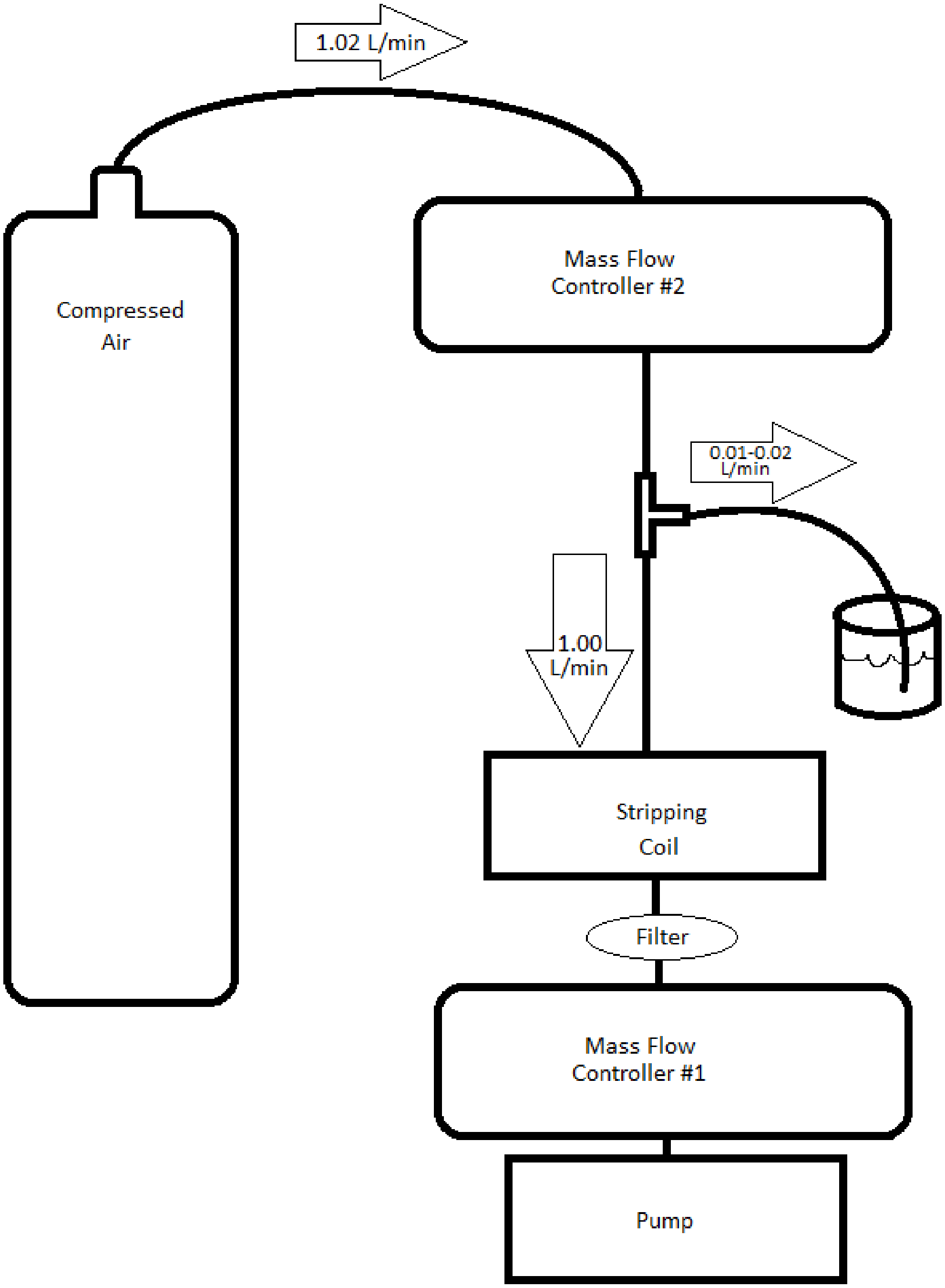

Figure 6. Mass Flow Controller #2 Schematic

The reason there is a diversion for excess air to leave through the mass flow controller two because the pressure from the mass flow controller must be greater than the flow rate of air from the mass flow controller one to ensure the proper direction of flow. If the flow rate of mass flow controller one is greater than mass flow controller two, a vacuum forms and the flow rate of air is turned to the opposite direction which causes the liquid flow of SA through the stripping coil to also turn to the opposite direction which causes it to not pass into the $SA_{OUT}$ valve which contaminates the tubing with SA where only air is supposed to pass through.

## Mass Flow Controller #1 Calibration

The mass flow controller is the device used to monitor the flow rate of the pump to help draw the SA solution through the stripping coil from the inflow to the outflow at a constant rate of 1L/min. On one end, it is connected to a filter to prevent debris from entering the mass flow controller which is connected to the end of the stripping coil opposite the inlet. On the other end of the mass flow controller it is connected to a dial used to increase or decrease the flow rate of the pump which is connected to the other side of the dial.

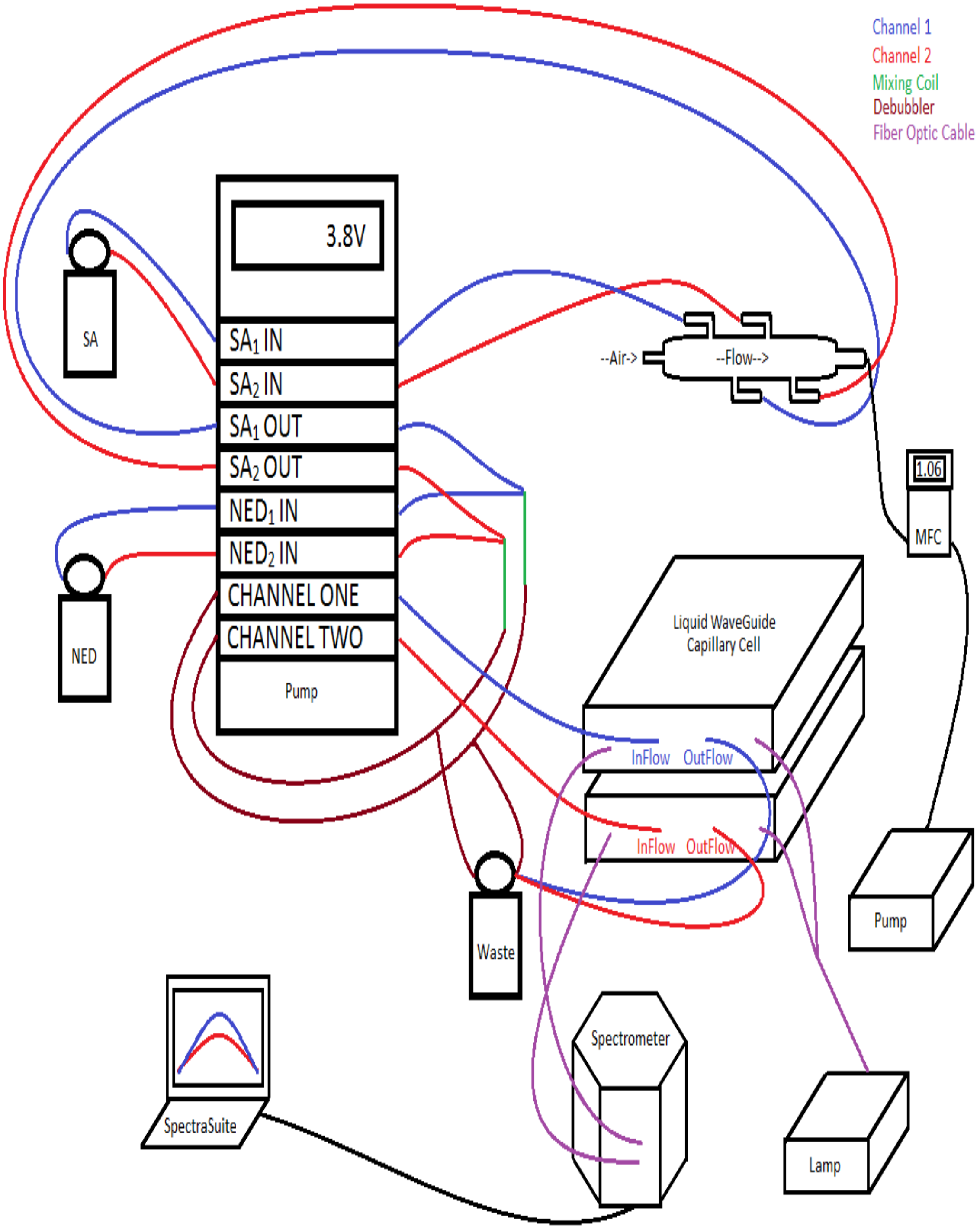

Figure 7. LOPAP Schematic.

# Results

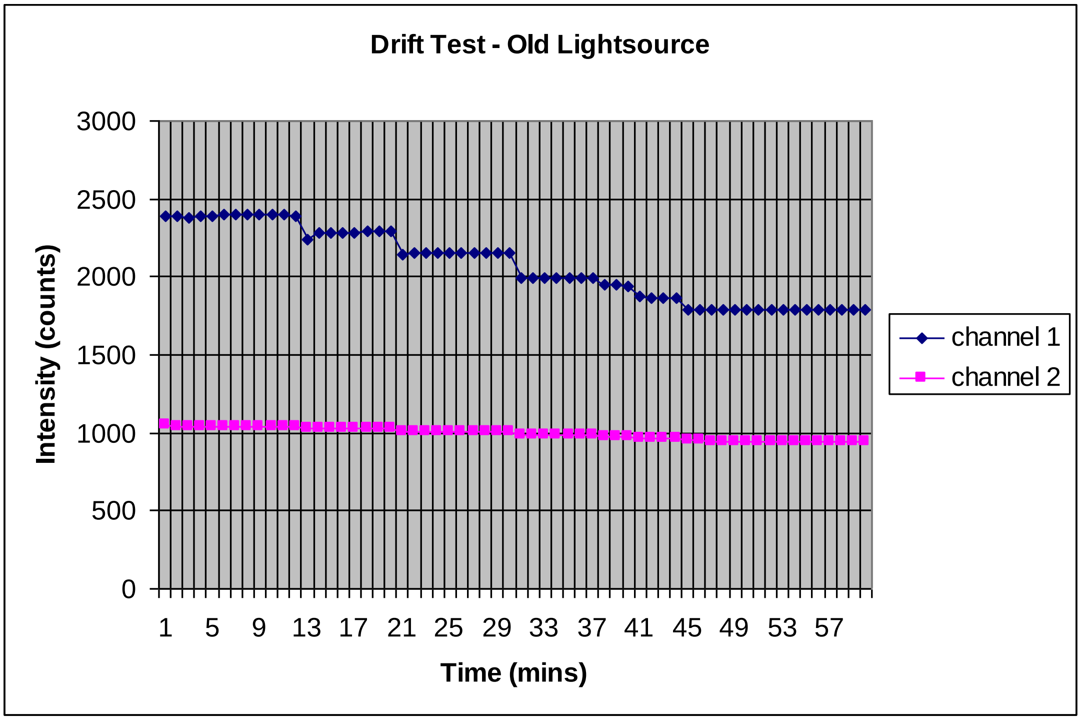

Figure 8. Drift Test - Old Lightsource

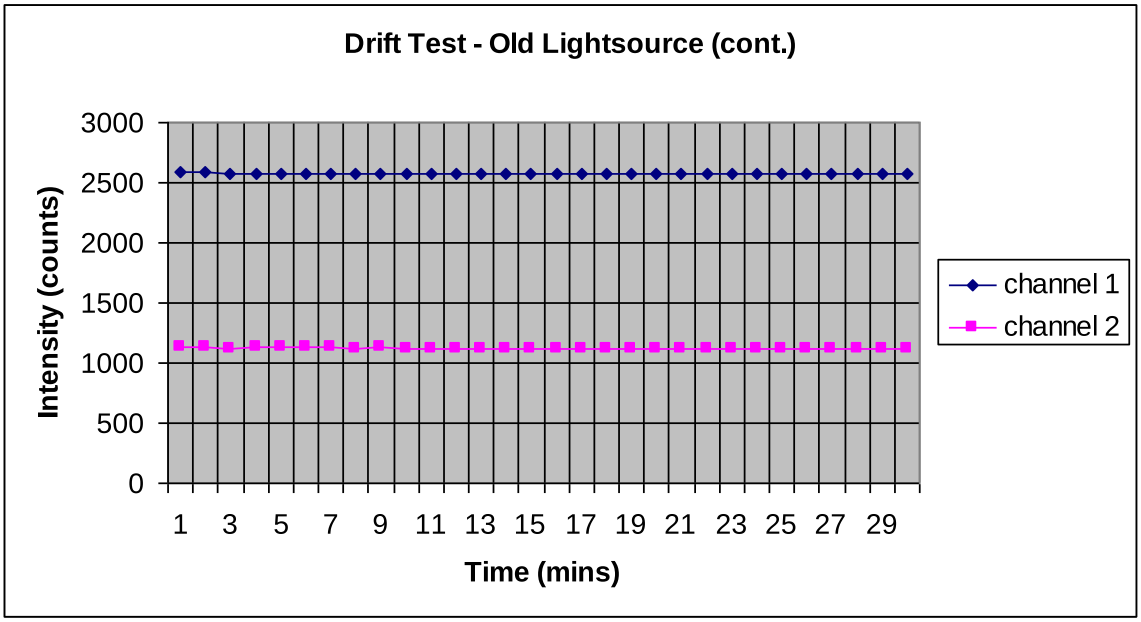

Figure 9. Drift Test - Old Lightsource (cont.)

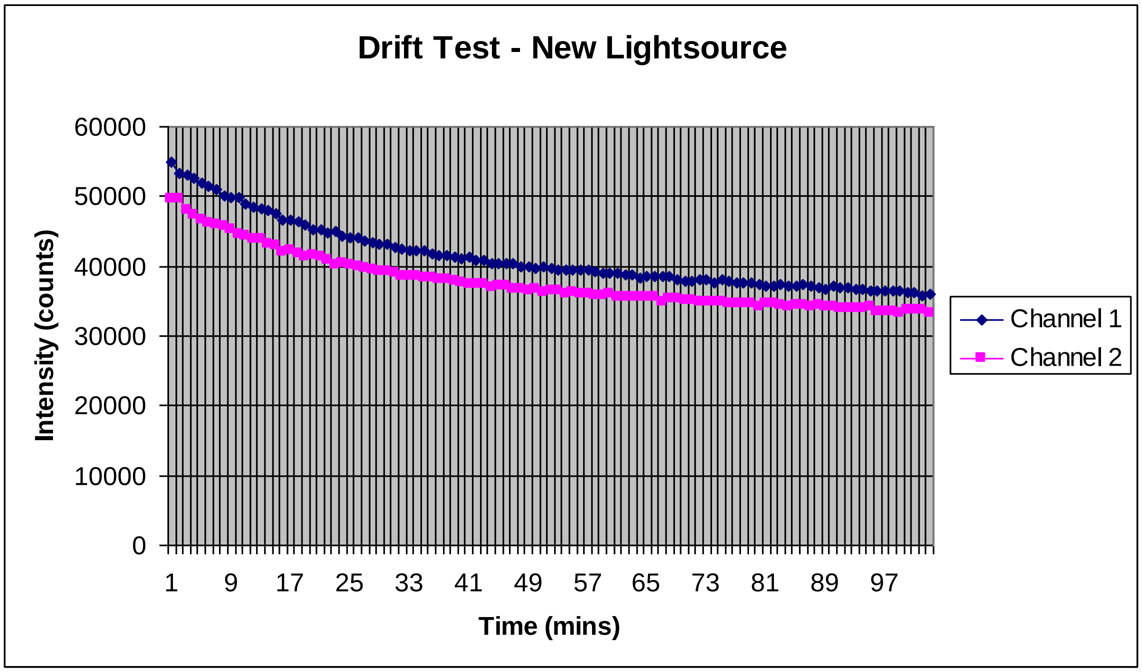

Figure 10. Drift Test - New Light source

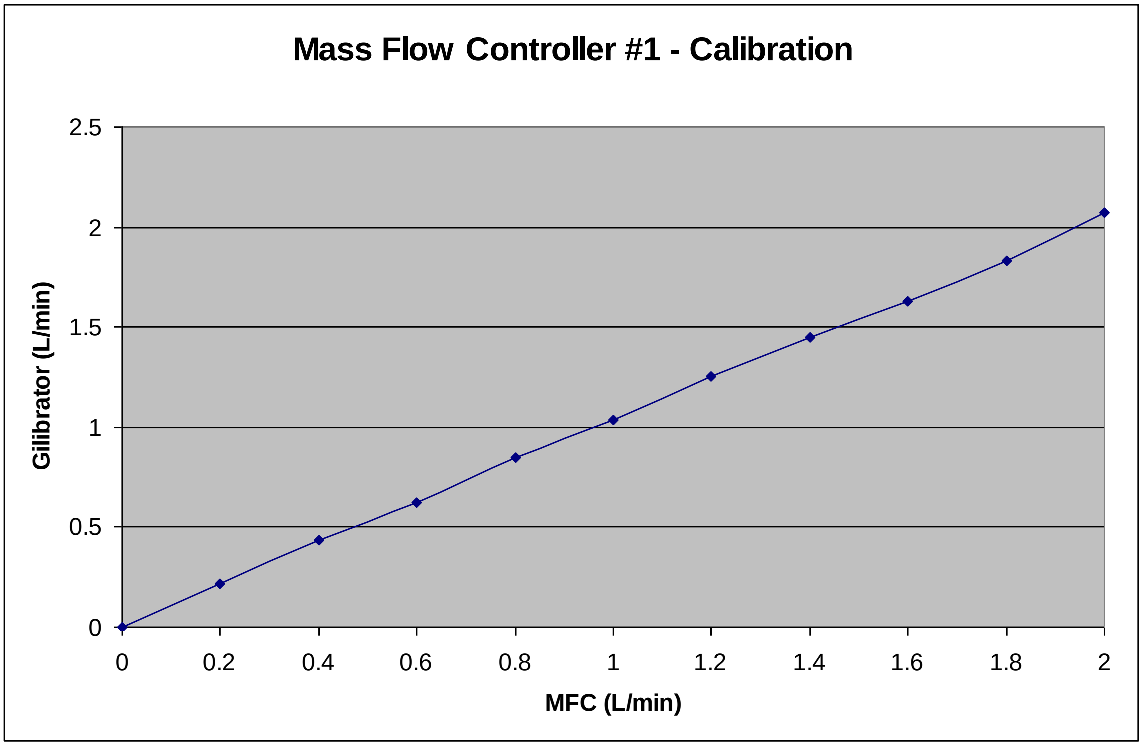

Figure 11. Mass Flow Controller #1 Calibration

## Discussion

### Weather Conditions

No measurements were taken on days with overcast, rain, or fog because HONO is taken up by the moisture.

Snow is associated with higher concentrations of $NO_2$ which are precursors for HONO synthesis in the atmosphere. Therefore, it was particularly important component in the original research project for collecting ambient HONO during the winter when snow fell. However, due to the LOPAP be unable to function properly, the project was converted to building and optimizing a new LOPAP.

### Light Source

An alternative light source suggested by the Kleffman group at the University of Wuppertal in Germany was to use an LED light source because LED light sources are capable of a consistent generation of light at a specific wavelength. In addition, LED lights do not overheat and risk the possibility of burns or fire that the halogen lamp possesses.

### Optimal Wavelengths

The wavelengths of interest that were analyzed on the spectrometer were 544 nm, 590 nm, and 700-710 nm. These wavelengths are important because 544 nm is the maximum absorption wavelength for ambient HONO, 590 nm is the alternate wavelength used to analyze ambient HONO, however it is generally not required because the spectrometer is calibrated for optimal function at 544 nm. Also, the 700-710 nm wavelength is important for analyzing the concentration of HONO in the atmosphere because it is the baseline reference spectrum and should not have any absorption.

The new liquid waveguides are still malfunctioning, they are fully saturated intensities when milliQ water is passed through and when there is only air inside there are also high intensities detected by SpectraSuite. This should be impossible because air has such a low refractive index (1.000293) and should not create such high absorption. This problem may be due to a translucent particle being trapped inside of the waveguide which is causing a large refractive index but not blocking the light or else there would be no signal. However, injecting water from the inflow and outflow outlets did not solve the problem.

Old liquid waveguides are still malfunctioning as well, there are very low detectable signals when milliQ water is passed through using the pump, but when milliQ is injected directly through either the inflow or outflow, the proper intensity curves are presented. Therefore the pump and tubing were expected to be the problem, however after cleaning the system multiple times the same problem persisted.

## Conclusion

The LOPAP was successfully assembled with all the correct parts, but one particular portion did not function as expected and many problems have arisen due to the malfunction of the liquid waveguide capillary cells. Many different forms of cleaning have been performed on it such as a custom cleaning kit designed for waveguides specifically. This kit contained a special soapy solution, dilute HCl, and dilute methanol, which are used in this respective order to remove any particulates or contaminations that may be present, however it did not fix the problem. Nor did injecting milliQ water with a syringe, which gave a short term fix but quickly disappeared once the pressure subsided, running milliQ water through the pump did not yield the same result as using the syringe which is peculiar. More tests must be conducted to fix this problem quickly and efficiently.

Every other aspect of the LOPAP had been tested and are working to their expected specifications.

Although no measurements were recorded, there was still a vast breadth of knowledge obtained with the construction and understanding of the LOPAP which provided both academic and applied skills that may be applied to a field in chemistry or related.

## References

Kleffmann, J, Wiesen, P. "Technical Note: Quantification of interferences of wet chemical HONO LOPAP measurements under simulated polar conditions." Physikalische Chemie. 7 October 2008.

Heland, J., Kleffmann J., Kurtenbach, R., Wiesen, P. "A new instrument to measure gaseous nitrous acid (HONO) in the atmosphere." 2001.

Wentzel, Jeremy. "Measurements of HONO in Southern Ontario using Long Path Absorption Photometry. November 2009.

# Appendices

## Appendix A. Drift Test - New Lightsource

| Time (mins) | Channel 1 | Channel 2 |
|---|---|---|
| 1 | 54822.71 | 49529.88 |
| 2 | 53285.43 | 49575.49 |
| 3 | 53113.57 | 47973.45 |
| 4 | 52600.74 | 47301.95 |
| 5 | 51921.98 | 46638.75 |
| 6 | 51466.18 | 46175.99 |
| 7 | 51030.6 | 45968.56 |
| 8 | 50189.44 | 45721.08 |
| 9 | 49799.68 | 45123.46 |
| 10 | 49758.69 | 44508.91 |
| 11 | 49033.23 | 44200.23 |
| 12 | 48541.83 | 43872.22 |
| 13 | 48329.43 | 43767.36 |
| 14 | 47906.92 | 43196.03 |
| 15 | 47566.06 | 42817.18 |
| 16 | 46697.09 | 42112.08 |
| 17 | 46664.24 | 42258.18 |
| 18 | 46447.99 | 41742.61 |
| 19 | 45872.41 | 41402.17 |
| 20 | 45262.55 | 41573.26 |
| 21 | 45204.87 | 41250.5 |
| 22 | 44847.08 | 40765.59 |
| 23 | 44931.14 | 40267.47 |
| 24 | 44405.35 | 40382.59 |
| 25 | 44047.34 | 40167.74 |
| 26 | 44054.6 | 39887.64 |
| 27 | 43594.62 | 39672.57 |
| 28 | 43332.33 | 39461.43 |
| 29 | 43104.21 | 39263.28 |
| 30 | 43116.84 | 39166.27 |
| 31 | 42609.51 | 38921.96 |
| 32 | 42470.61 | 38630.19 |
| 33 | 42311.61 | 38502.3 |
| 34 | 42264.91 | 38648.85 |
| 35 | 42130.63 | 38291.93 |
| 36 | 41656.37 | 38328.15 |
| 37 | 41595.72 | 38054.38 |
| 38 | 41443.42 | 38099.67 |
| 39 | 41261.23 | 37801.67 |
| 40 | 41179.8 | 37694.08 |
| 41 | 41215.52 | 37371.43 |
| 42 | 40834.77 | 37315.56 |

| | | |
|---|---|---|
| 43 | 40754.88 | 37310.43 |
| 44 | 40359.52 | 36870.48 |
| 45 | 40354.57 | 37100.06 |
| 46 | 40487.64 | 37088.71 |
| 47 | 40378.97 | 36662.28 |
| 48 | 39902.84 | 36740.52 |
| 49 | 40014.04 | 36445.69 |
| 50 | 39717.9 | 36667.74 |
| 51 | 39821.41 | 36263.25 |
| 52 | 39598.79 | 36411.86 |
| 53 | 39514.73 | 36350.97 |
| 54 | 39536.37 | 36098.81 |
| 55 | 39352.1 | 36211.74 |
| 56 | 39389.9 | 35944.08 |
| 57 | 39352.98 | 36043.6 |
| 58 | 39226.72 | 35724.65 |
| 59 | 38944.65 | 35833.98 |
| 60 | 39037.5 | 35925.97 |
| 61 | 39042.11 | 35605.6 |
| 62 | 38874.54 | 35596.11 |
| 63 | 38730.04 | 35461.24 |
| 64 | 38372.37 | 35508.27 |
| 65 | 38442.91 | 35578.98 |
| 66 | 38455.55 | 35460.81 |
| 67 | 38581.15 | 34943.49 |
| 68 | 38470.28 | 35195.44 |
| 69 | 38067.77 | 35285.13 |
| 70 | 37846.02 | 34965.53 |
| 71 | 37801.3 | 35003.5 |
| 72 | 37981.18 | 34762.25 |
| 73 | 37985.03 | 34865.14 |
| 74 | 37611.75 | 34773.6 |
| 75 | 38158.75 | 34861 |
| 76 | 37834.59 | 34708.89 |
| 77 | 37608.12 | 34673.1 |
| 78 | 37572.3 | 34556.56 |
| 79 | 37567.14 | 34576.2 |
| 80 | 37426.81 | 34268.83 |
| 81 | 37204.19 | 34577.62 |
| 82 | 37179.14 | 34535.72 |
| 83 | 37455.38 | 34366.81 |
| 84 | 37217.7 | 34202.26 |
| 85 | 37129.58 | 34472.44 |
| 86 | 37309.35 | 34343.35 |
| 87 | 37053.54 | 34184.92 |
| 88 | 36980.68 | 34278.43 |
| 89 | 36628.94 | 34073.18 |
| 90 | 37155.4 | 34094.02 |
| 91 | 37007.06 | 33911.47 |
| 92 | 36971.23 | 33838.8 |

| | | |
|---|---|---|
| 93 | 36754.54 | 33863.9 |
| 94 | 36749.93 | 33822.65 |
| 95 | 36549.94 | 34057.47 |
| 96 | 36480.38 | 33562.19 |
| 97 | 36420.27 | 33546.37 |
| 98 | 36398.63 | 33448.06 |
| 99 | 36349.07 | 33317.44 |
| 100 | 36222.37 | 33630.61 |
| 101 | 36152.71 | 33715.61 |
| 102 | 35831.73 | 33606.16 |
| 103 | 36036.23 | 33231.46 |

## Appendix B. Drift Test - Old Lightsource

| time | channel 1 | channel 2 |
|---|---|---|
| 1 | 2388 | 1049 |
| 2 | 2390 | 1041 |
| 3 | 2380 | 1041 |
| 4 | 2385 | 1042 |
| 5 | 2390 | 1043 |
| 6 | 2395 | 1043 |
| 7 | 2396 | 1044 |
| 8 | 2397 | 1043 |
| 9 | 2396 | 1043 |
| 10 | 2399 | 1044 |
| 11 | 2395 | 1042 |
| 12 | 2387 | 1037 |
| 13 | 2237 | 1026 |
| 14 | 2282 | 1026 |
| 15 | 2284 | 1027 |
| 16 | 2287 | 1025 |
| 17 | 2287 | 1026 |
| 18 | 2290 | 1026 |
| 19 | 2289 | 1026 |
| 20 | 2292 | 1026 |
| 21 | 2148 | 1006 |
| 22 | 2150 | 1006 |
| 23 | 2152 | 1007 |
| 24 | 2155 | 1007 |
| 25 | 2154 | 1007 |
| 26 | 2157 | 1007 |
| 27 | 2149 | 1006 |
| 28 | 2154 | 1007 |
| 29 | 2155 | 1008 |
| 30 | 2150 | 1006 |
| 31 | 1990 | 982 |
| 32 | 1994 | 982 |

|  |  |  |
|---|---|---|
| 33 | 1993 | 982 |
| 34 | 1993 | 982 |
| 35 | 1990 | 981 |
| 36 | 1991 | 981 |
| 37 | 1992 | 982 |
| 38 | 1947 | 974 |
| 39 | 1946 | 974 |
| 40 | 1943 | 974 |
| 41 | 1873 | 961 |
| 42 | 1866 | 960 |
| 43 | 1868 | 961 |
| 44 | 1867 | 962 |
| 45 | 1791 | 949 |
| 46 | 1794 | 949 |
| 47 | 1793 | 948 |
| 48 | 1794 | 948 |
| 49 | 1794 | 948 |
| 50 | 1793 | 948 |
| 51 | 1793 | 948 |
| 52 | 1786 | 947 |
| 53 | 1787 | 948 |
| 54 | 1788 | 947 |
| 55 | 1788 | 947 |
| 56 | 1788 | 948 |
| 57 | 1785 | 948 |
| 58 | 1785 | 947 |
| 59 | 1786 | 948 |
| 60 | 1786 | 947 |

| time | channel 1 | channel 2 |
|---|---|---|
| 1 | 2584 | 1126 |
| 2 | 2583 | 1126 |
| 3 | 2580 | 1125 |
| 4 | 2579 | 1126 |
| 5 | 2580 | 1126 |
| 6 | 2579 | 1126 |
| 7 | 2579 | 1126 |
| 8 | 2579 | 1125 |
| 9 | 2579 | 1126 |
| 10 | 2577 | 1125 |
| 11 | 2575 | 1124 |
| 12 | 2576 | 1125 |
| 13 | 2577 | 1125 |
| 14 | 2576 | 1125 |
| 15 | 2574 | 1123 |
| 16 | 2574 | 1123 |
| 17 | 2576 | 1124 |
| 18 | 2574 | 1124 |

| | | |
|---|---|---|
| 19 | 2576 | 1125 |
| 20 | 2575 | 1125 |
| 21 | 2575 | 1124 |
| 22 | 2575 | 1123 |
| 23 | 2576 | 1125 |
| 24 | 2578 | 1124 |
| 25 | 2575 | 1123 |
| 26 | 2574 | 1125 |
| 27 | 2574 | 1125 |
| 28 | 2573 | 1125 |
| 29 | 2573 | 1124 |
| 30 | 2574 | 1123 |

## Appendix C. Gilibrator Data

| Flow (L/min) | MFC (L/min) | Flow (L/min) | MFC (L/min) |
|---|---|---|---|
| 0.2 | 0.2135 | 1.2 | 1.25 |
| 0.2 | 0.2139 | 1.2 | 1.25 |
| 0.2 | 0.215 | 1.2 | 1.25 |
| 0.2 | 0.2135 | 1.2 | 1.25 |
| 0.2 | 0.2146 | 1.2 | 1.263 |
| 0.4 | 0.4301 | 1.4 | 1.445 |
| 0.4 | 0.4332 | 1.4 | 1.445 |
| 0.4 | 0.4332 | 1.4 | 1.428 |
| 0.4 | 0.4316 | 1.4 | 1.481 |
| 0.4 | 0.4316 | 1.4 | 1.463 |
| 0.6 | 0.6217 | 1.6 | 1.643 |
| 0.6 | 0.6185 | 1.6 | 1.621 |
| 0.6 | 0.625 | 1.6 | 1.661 |
| 0.6 | 0.625 | 1.6 | 1.643 |
| 0.6 | 0.625 | 1.6 | 1.621 |
| 0.8 | 0.851 | 1.8 | 1.818 |
| 0.8 | 0.851 | 1.8 | 1.818 |
| 0.8 | 0.845 | 1.8 | 1.846 |
| 0.8 | 0.851 | 1.8 | 1.846 |
| 0.8 | 0.851 | 1.8 | 1.846 |
| 1 | 1.043 | 2 | 2.105 |
| 1 | 1.043 | 2 | 2.033 |
| 1 | 1.034 | 2 | 2.068 |
| 1 | 1.034 | 2 | 2.033 |
| 1 | 1.034 | 2 | 2.105 |

## Appendix D. Stock Solution Creation

For SA;

MM = 172.21 g/mol

m = 10.3326 g

[ SA ] = ( 10.3326 g/L )( 1.00 mol/172.21 g ) = 0.06 M

Acidify SA Solution; Required: 1M HCl

$V_1C_1 = V_2C_2$

$V_{HCl}$ = ( 1.00L )( 1.00 M) /( 12 M ) = 8.3 mL

For NED;

MM = 259.18 g/mol

m = 0.0518 g

[ NED ] = ( 0.0518 g/L )( 1.00 mol/259.18 g) = 0.2 mM

For Sodium Nitrite;

m = 0.6900 g

MM = 69.00 g/mol

[ $NaNO_2$ ] = ( 0.690 g/L )( 1 mol/ 69g ) = 0.01 M

## Appendix E. Sodium Nitrite Solutions Spiked

$V_1$ = ( 50.0 x $10^{-6}$ M )( 0.1 L )/ ($10^{-2}$ M ) = 0.5 mL

$V_2$ = ( 1.00 x $10^{-6}$ M )( 0.1 L )/ ($50^{-6}$ M ) = 2.0 mL

$V_3$ = ( 250. x $10^{-9}$ M )( 0.1 L )/ ($10^{-2}$ M ) = 0.5 mL

$V_4$ = ( 50.0 x $10^{-9}$ M )( 0.1 L )/ ($10^{-2}$ M ) = 5.0 mL

$V_5$ = ( 1.25 x $10^{-9}$ M )( 0.1 L )/ ($10^{-2}$ M ) = 0.5 mL

$V_6$ = ( 0.20 x $10^{-9}$ M )( 0.1 L )/ ($10^{-2}$ M ) = 0.4 mL