Investigation of the Efficiency for the Cadmium Reduction Method of Nitrate to Nitrite Conversion for the Application in the LOPAP Instrument

4000 Undergraduate

Research Thesis

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Table of Contents

Abstract

A newly developed, highly sensitive instrument for detecting atmospheric nitrous acid (HONO) has been modified to detect nitric acid (HNO_3). The LOPAP (Long Path Absorption Photometer) has been developed to be cheap, sensitive, compact and continuously running HONO monitor. HNO_3 is sampled in a stripping coil, and is converted to nitrite. Cadmium is used to quantitatively reduce $NO_3^-{}_{(aq)}$ to $NO_2^-{}_{(aq)}$ (Nydahl 1976). The technique is based on aqueous scrubbing of HONO in a neutral buffer and then derivitization of nitrite into a highly light absorbing azo dye with sulphanilamide (SA; ≥99%) and (1-naphthly) –ethylenediamine (NED; 98%). After conversion into a strong light absorbing dye, HNO_3 is detected in a long path absorption in a special Teflon® AF 2400 tubes used as a liquid core waveguide (LCW). Two channels are used in order to correct for interferences. The first channel HNO_3 is quantitatively sampled in a stripping coil after which it is reduced to nitrite and measured. This Channel will measure [HNO_3 + HONO] but HNO_3 is for the most part expected to be much greater than HONO. The second channel without the reduction of HNO_3 HONO, it is used to measure HONO. The difference between the two channels yields the HNO_3 concentration in the atmosphere.

Introduction

Within the atmosphere, nitrous (HONO) and nitric acid (HNO_3) are among the reactive nitrogen species, NOy (=NO + NO_2 + HNO_3 +HONO + PAN and organic nitrate + HO_2NO_2 + NO_3+…) which play an important role in the chemistry in stratosphere and troposphere (Crutzen, 1979; Finlayson-Pitts and Pitts, 1986). It is by and large believed that HONO within the atmosphere is formed mainly through heterogeneous reactions of NOx and water vapor (R1 and R2) in NOx^- rich environments (Calvert 1994; Harris 1982; Reisinger 2000).

$$NO + NO_2 + H_2O + \text{surface} \rightarrow 2HONO \qquad (R1)$$

$$2NO_2 + H_2O + \text{surface} \rightarrow HONO + HNO_3 \qquad (R2)$$

During the night HONO has been observed to accumulate and become a major OH source upon photolysis (R3) in the morning, in particular in urban environments (Andres-Hernandes 1996; Harris 1982; Pitts 1994; Reisinger 2000; Vecera and Dasgupta 1991). Environments where there are low levels of NOx, formation mechanism for HONO, along with its chemistry are still uncertain.

HNO_3 is highly significant as it is a sink for both HOx and NOx families. Nitrogen oxides (NOx = NO + NO_2) control the formation of ozone (O_3) particularly during summer smog durations, and furthermore they have a strong influence on stratospheric O_3 levels (Finlayson-Pitts 2000; Wennberg 2007). Nitric acid is primarily formed by a gas phase three body reaction of NO_2 with OH radicals during the daytime (R3), and by the heterogeneous conversion during the night time of N_2O_5 (R4).

$$NO_2 + OH + M \rightarrow HNO_3 + M \qquad (R3)$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (R4)$$

Once the relatively reactive nitric acid gas is formed, it can be effectively be removed from the troposphere via wet scavenging and dry deposition, leading at least in part to, the formation of acidic rain (Huang 2002; Seinfeld 1998).

Over the years different techniques have been developed for the detection of HNO_3, due to its considerable importance within the atmosphere. Table one lists and briefly describes some of these techniques along with their advantages and disadvantages.

Table 1: HNO_3 Detection Techniques

Detection technique	Description	Advantages/Disadvantages
Filter	First measurement of HNO_3 in the atmosphere, by which HNO_3 is sampled on a Nylon filters after separation from particles by a Teflon filter (Appel 1980). After elution with water, HNO_3 is analyzed ion chromatography.	-poor time resolution -HNO_3 can be lost by adsorption on the first particle filter or on the filter holder (Goldan, 1983) -HNO_3 concentration may be overestimated due to displacement of particle nitrate on the first filter by strong acids (Finlayson-Pitts and Pitts, 2000)
Dry Denuder	HNO_3 measured by dry annular denuders coated with NaCl or sodium carbonate. After elution with water, HNO_3 is analyzed ion chromatography.	-low time resolution -negative artefacts and interferences (Bai, 2003)
Wetted Wall Diffusion Denuders	HNO_3 sampled on wetted wall diffusion denuders, and analyzed by ion chromatography.	-very sensitive -adsorption on inlet, used to create a laminar flow, can lead reduction instrument time response -Denuder inlet not directly in the atmosphere, so adsorption on sampling line can further reduce time response (Vecera, Dasgupta, 1991).
Thermal Dissociation	HNO_3 is measured by thermal dissociation into NO_2 at >500°C,	-fast and sensitive -expensive system components

	and then detected by laser induced fluorescence (Day, 2002), Other nitrogen compounds lead to the formation of NO_2 under these conditions, so HNO_3 is determined by the subtraction of the signal from a second channel, where a lower temperature than the threshold value for HNO_3 dissociation is used.	-HNO_3 is quantified from difference of two signals, so the accuracy can be low under certain conditions, i.e. low HNO_3/NOy ratios -significant interferences from thermal dissociation of particle nitrate (Day, 2002).
Chemiluminescence	Chemiluminescence of nitrogen oxide (NO) after conversion of HNO_3 on heated metal converters (Fahey 1985; Yamamoto 2001). NOy components are converted into NO, and HNO_3 is measured by a two channel system. One channel HNO_3 removed by a nylon filter and the concentration determined by the difference of the two channels.	-high time response -low accuracy may result from the two channel system (Yamamoto, 2001).
Chemical Ionization Mass Spectroscopy (CIMS)	Most promising technique for the detection of HNO_3 in the atmosphere.	-selective, sensitive and fast -expensive system components -positive interferences by particle nitrate (Hanke 2003)

A recently developed instrument for HNO_3 detection technique is the aqueous scrubber/HPLC technique. In this technique the HNO_3 is sampled in a stripping coil after which it is reduced to nitrite, and finally analyzed by HPLC (Huang 2002). This instrument is sensitive to nitrite, so it therefore measures the sum of HONO and $HNO_{3.}$ Due to this, a second channel without the reduction of HNO_3 to HONO is used to strictly measure HONO in the atmosphere (Kleffman 2007). From the difference between the two channels, the HNO_3 concentration within the atmosphere is determined. This technique for measurement has an estimated detection limit in the pptv range for HNO_3.

Even though there is a great variety of different techniques available for the detection of HNO_3 , there is a still a great need for development of a simple reliable HNO_3 instrument. HNO_3 within the atmosphere covers a range from a few pptv up to several ppbv (Finlayson-Pitts and Pitts 2000), so a large dynamic range and a highly sensitive HNO_3 instrument is required (Kleffmann 2007).

The most recent and highly sensitive nitric acid detection instrument developed, which is mobile, cheap, compact, a continuously running HONO monitor and a reliable on line instrument, is the LOPAP (*L*ong *P*ath liquid *A*dsorption *P*hotometer). Like the aqueous scrubber/HPLC technique, a known Cadmium reduction technique is used to reduce $NO_3^-{}_{(aq)}$ quantitatively to $NO_2^-{}_{(aq)}$. Once $NO_3^-{}_{(aq)}$ is converted to $NO_2^-{}_{(aq)}$, continuous detection of HONO can be detected by the in situ instrument, LOPAP. The simple HNO_3 instrument for the sensitive detection of HNO_3 in the atmosphere has a detection limit in the pptv range. Sampling artifacts and interferences are also minimized by the use of an external sampling module and by the two channel aqueous scrubber concept of the instrument. However being able to quantify the collection and conversion efficiencies need to be well known to allow for broader field applications of spectroscopic methods of the trace gas, such as HNO_3.

Experimental

Reagents and Materials

The reagents sulphanilamide (SA; ≥99%) and (1-naphthly) –ethylenediamine Dihydrochloride (NED; 98%) were purchased from Sigma Aldrich. The 0.06M SA in 1M HCl and 0.2mM NED were prepared by dissolving 10.332g SA and 0.0518g NED in 1L of Milli-Q water respectively. These stock/working solutions were stable for approximately 3 months when stored in the dark under refrigeration at 4^oC. The high purity NaOH (99.99%) and NH_4Cl (99.998%) and reagent grade chemical's including 37% HCl, $NaNO_2$ (≥99%), $NaNO_3$ (≥99%), EDTA, Imidazole and Cd, 30-80 mesh(99%) granules were from Sigma Aldrich. The Cupric Sulfate (≥98.5%), was purchased form the British Drug House Ltd. Laboratory Chemical Division. The $NO_3^-{}_{(aq)}$ and $NO_2^-{}_{(aq)}$ stock solutions were from the A.C.S. reagent sodium nitrate and sodium nitrite respectively once a month using Milli-Q water and also stored in the dark at 4^oC. Since both sodium nitrate and sodium nitrite are hygroscopic, both of the reagents were placed overnight in an oven at 80^oC before they were used to remove the water. $NO_3^-{}_{(aq)}$ and $NO_2^-{}_{(aq)}$ stock solutions of concentration 1mM, were prepared by dissolving 0.0849g and 0.0689g in 1L Milli-Q water respectively. All chemicals were used without further purification. The water was purified with Millipore Milli-Q water system, with resistivity ≥17MΩ.

Absorption Spectroscopy

Absorption spectroscopy measures the absorption of radiation (net absorption is nearly monochromatic; single frequency) as a function of frequency or wavelength, as a result of the interaction with a sample. The Bohr Frequency condition shows that the net energy ($\Delta E=E_2-E_1$) of a photon absorbed depends on the frequency (v), of the radiation absorbed and Planck's constant:

$$\Delta E=E_2-E_1 = hv \qquad (1)$$

Within this experiment the radiation source was a white light tungsten-filament diode. The tungsten filament used was unlike a tungsten light bulb used within a home, as this radiation source emitted light in the range of $320nm \leq \lambda \leq 2500nm$. The light is collected and detected with a mini-spectrometer (Ocean Optics, SD 2000) using a diode array detector (Kleffmann

2002). Two intensities are recorded. The first absorption, I_{abs}, is recorded at a wavelength where the sample absorbs energy. The second absorption, I_{ref}, is recorded at a wavelength on the spectra where the sample has no absorption (Kleffmann 2002). Since I_{ref} is directly proportional to the background intensity at the absorption maximum, the logarithm of (I_{ref}/I_{abs}) becomes linearly dependent of the concentration, c, of the sample according to Lambert-Beers Law:

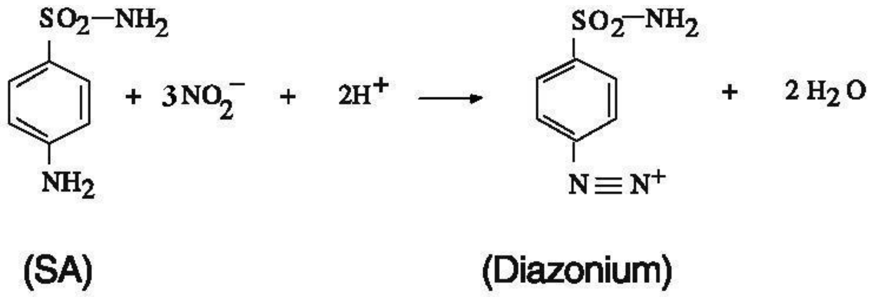
$$ABS = \mathrm{Log}(I_{ref}/I_{abs}) = k_{\lambda} \times l \times c \qquad (2) \quad \text{(Kleffman 2002).}$$

From the equation l is the absorption path length, c is the sample concentration, and finally k_{λ} is the absorption coefficient of the sample.

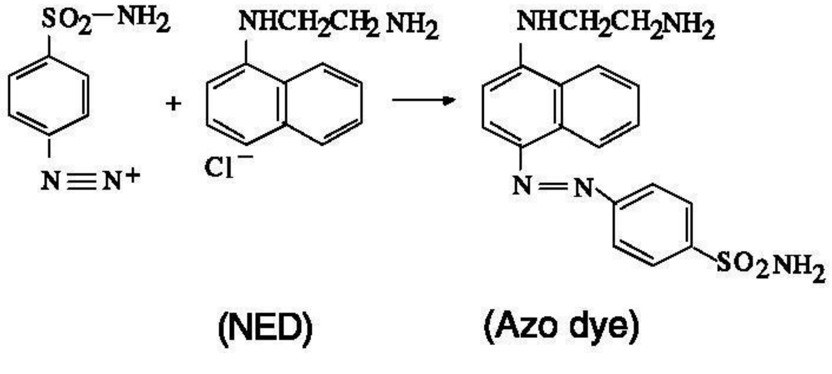
From Beers law stated above, it is evident that the absorption (ABS) is proportional to the path length. Therefore as the path length increases, the sensitivity of the instrument increases as well. In order to do so, a liquid core waveguide (LCW) is used as the absorption cell. The liquid core waveguide has a total path length of 2.5m and is coiled and placed in a 10cm diameter chamber to prevent any introduction of ambient light(Yao 1998).The tubing within the liquid core waveguide is made of low refractive Teflon® AF 2400 (0.6mm ID, 0.8mm OD) (Yao 1998). The light from the tungsten lamp is guided to the Teflon® AF 2400 tubes by a glass fibre (200µm O.D.) and injected into a T-connector (Kleffmann 2007). The visible light is focused into the LCW and since the refractive index of the Teflon is lower than that of the liquid, the light undergoes multiple total internal reflections on the inner walls of the tubing, allowing for adsorption by the liquid. The light from the long path absorption tube is than transferred by a glass fibre to the mini-spectrometer (Ocean Optics, SD 2000). A spectrum is collected and stored using Ocean Optics IBase32 software on a laptop which was connected to the mini-spectrometer. So with the use of the LCW, it allows for an increase in the path length inside the absorption cell for a few meters, resulting in an increase in the sensitivity of the instrument.

Derivatization within the LOPAP Instrument

The LOPAP instrument allows for the concentration of $NO_2^{-}{}_{(aq)}$ to be measured through the use of simple chemistry. After conversion of nitrate into nitrite, behind the Cd reduction columns, a mixture of sulphanilamide (10.332g/L) in 1M HCl and (1-naphthly) – ethylenediamine (0.0518g/L) is added. After a reaction time of ≥1min a strong absorbing azo dye is quantitatively formed (Grasshoff, 1983). All reactions are in a one to one ratio, therefore the concentration of the azo dye detected by the spectrometer is the same concentration as the $NO_2^{-}{}_{(aq)}$. So once a consist and quantitative reduction technique is developed, the concentration of $NO_3^{-}{}_{(aq)}$ can be determined due to the 1:1 ratio of the reactions. First $NO_2^{-}{}_{(aq)}$ reacts with SA in the presence of an acid to form a diazonium cation (R5). The diazonium cation then reacts with NED to form the azo dye (all reactions 1:1 ratio) (R6).



(R5)



(R6)

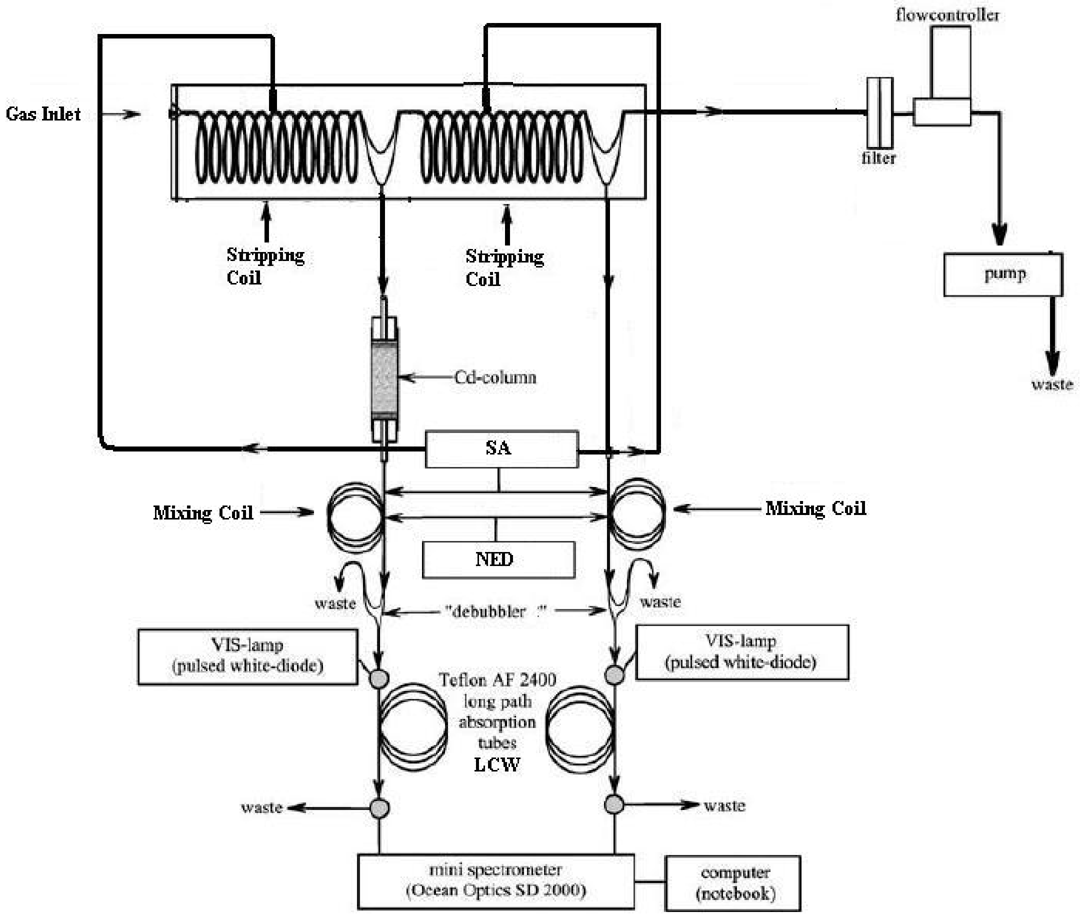
Like most azo dyes, the azo dye produced in R6 is a strong absorber of light. The diode array detector measures a range between 350-1000nm and the azo dye produced, absorbs energy at a wavelength of 544nm, and the intensity observed refers to I_{abs} from equation (2) stated above. I_{ref} from the same equation is taken at 700nm, a point on the spectrum where no absorption by the azo dye occurs (Grasshoff, 1983).

Instrumental Setup for the LOPAP

The instrument is setup up with two channels which are connected in a series to correct for interferences, which are a known common problem for wet chemical instruments, which measure all species that form nitrate in the liquid phase (Kleffmann, 2007). Figure 1 shows the LOPAP experimental setup used for atmospheric HNO_3 sampling. In the sampling unit, there are two stripping coils (Channel 1 and Channel 2) setup up in a series, and air is sampled from the atmosphere (gas phase) by a membrane pump at a flow rate of 1.0L/min through the stripping coils. During external sampling of nitric acid (HNO_3), inlet of the stripping coil is optimized for minimal absorption, as the stripping reagent, SA (0.06M), is injected only approximately a few cm's behind the inlet of the coil as shown in figure 1. The first channel HNO_3 is quantitatively sampled in a stripping coil after which it is reduced to nitrite and measured. This Channel will measure [HNO_3 + HONO] but HNO_3 is for the most part expected to be much greater than HONO. The second channel without the reduction of HNO_3 HONO, it is used to measure HONO. The difference between the two channels yields the HNO_3 concentration in the atmosphere. Next, the contents within channel one and channel two which are mixed with SA are then pumped using a peristaltic pump (flow rate 0.3ml/min) through the Cd reduction column (1-2g cupperized Cd, Aldrich 30-80mesh,99% in a glass tube 2mmID, inlet and outlet protected with glass wool. The nitrate to nitrite reduction technique is explained later within the paper.

After the Cd column nitrate is reduced into nitrite and under goes R6 forming diazonium ion. The diazonium cation solution is then pumped into a mixing coil (2mmID and 4mmOD) where it is mixed with 0.02mM NED solution to form an azo dye. The azo is sent through a debubbler, to separate all the gas bubbles, and it is then sent through the liquid core waveguide and a spectrum of data is then collected from the mini-spectrometer. The LOPAP technique for $NO_{2}\text{-}_{(aq)}$ detection is very sensitive with detection limits of $NO_{2}\text{-}_{(aq)}$ in the nM range resulting in pptv detection limits for HONO (Kleffmann 2002). Therefore the sensitivity of the LOPAP can be used to measure any species that can be quantitatively converted into $NO_{2}\text{-}_{(aq)}$.

Figure1: Experimental setup of the LOPAP with external atmospheric sampling unit



Reduction Conversion of NO_3-$_{(aq)}$ to NO_2-$_{(aq)}$

A known reduction technique was used to reduce NO_3-$_{(aq)}$ almost 100% quantitatively to NO_2-$_{(aq)}$. The standard reduction potential for the Cd/Cd^{2+} couple (R7) is -0.403V. If cadmium contains metals of lower reduction potential, its reduction power will be increased. This effect, of Cd containing metals of lower reduction potential is brought about by the treatment of the Cd granules with copper sulphate ($CuSO_4$) prior to being packed into the glass columns. The Cd granules are initially washed with acetone to remove any organic contaminates on the surface. The granules are then washed with 6M HCl twice, immediately followed by water each time. Next the Cd is washed with a. Upon contact with the copper solution, the surface of the Cd granules was coated with copper and the silvery granules turned grey (Zhang, 1999). It necessary to swirl the granules in the copper sulphate solution, to insure there is a uniform coating. While swirling, brown flakes of colloidal copper appeared, and the blue copper sulphate solution faded (Zhang, 1999). The copper from the copper sulphate solution precipitates out and partly adheres to the cadmium as a porous layer (Nydahl, 1976). A galvanic cell is produced with the copper as the cathode. As the standard reduction potential of the Cu/Cu^{2+} couple is +0.337V, the emf of the cell under standard conditions will be 0.740V, and the "cupperized Cd" has a reducing power which is much higher than that of Cd alone (Nydahl, 1976).

From the following three step reactions (R7) (R8) (R9)

NO_3-$_{(aq)}$ $+ 2H^+ + 2e^- = NO_2$-$_{(aq)}$ $+ H_2O$ V=+0.01 (R7)

$HNO_2 + 5H^+ + 4e^- = NH_3OH^+ H_2O$ V=1.356 (R8)

$HNO_2 + 7H^+ + 6e^- = NH_4^+ 2H_2O$ V=1.3598 (R9)

It is apparent that the hydrogen-ion concentration has a strong influence on the reduction process (Nydahl, 1986). It is important to maintain a certain hydrogen-ion concentration, for quantitative reduction of nitrate to nitrite. Nitrite from (R7) is able to react with H^+ to form NH_3OH^+ H_2O in (R8) and NH_4^+ $2H_2O$ in (R9) which would cause further reduction of nitrite. Therefore it is important that the pH of the solution should be adjusted (pH 5-10) (Nydahl, 1976) to minimize further nitrite reduction. Initially a buffer of EDTA-NH_4Cl was used. The buffer was prepared by dissolving 13g of NH_4Cl and 1.7g of EDTA in 1L Milli-Q H_2O. The pH was adjusted to 8.4 with NH_4OH and allowed for the reduction of hydrogen-ion in the solution, getting rid of the chance of further nitrite reduction. Later, an Imidazole buffer was used. This buffer was prepared by dissolving 6.9g of Imidazole in 1L of Milli-Q H_2O. The pH was ~9.0 so adjustment of the pH was not required.

The reduction process of $NO_3^-{}_{(aq)}$ to$NO_2^-{}_{(aq)}$ can also lose efficiency due to the precipitation of cadmium hydroxide on the surface of the cadmium particles within a packed column (Nydahl, 1976). Cadmium ions in the reductor can form from the following reaction

$$2Cd + O_2 + 4H^+ = 2Cd^{2+} + 2H_2O \qquad \text{(R10)}$$

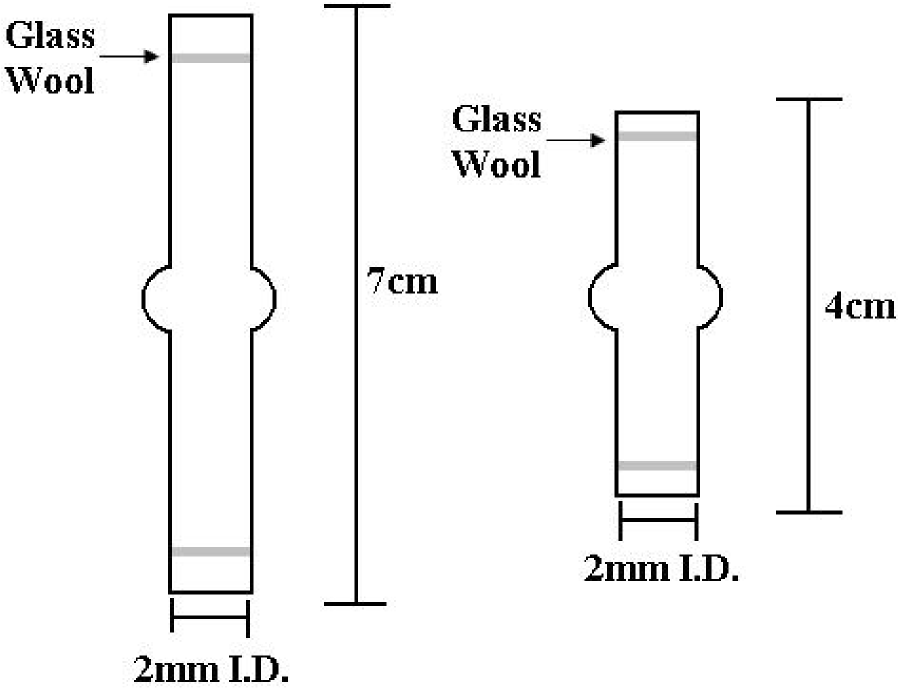
And eventually interact and react with water to form cadmium hydroxide. To avoid this buildup, it is essential the packed column is washed with dilute sulphuric acid.

Packing and Cleaning Cadmium Columns

The cupperized Cd granules are then packed into a glass tube with an inner diameter of 2mm, and held in place with glass wool at the inlet and the outlet. It is essential to use Cd, which is 30-80 mesh, (purchased from Aldrich, 99%) as 100 mesh was proven to be too compact. Cd 30-80 mesh increases the surface area of cupperized Cd which allows for better reduction of nitrate to nitrite, and also allows for higher flow rates through the column without an increase in the pressure within the LOPAP instrument. Once the column is tightly packed with the cupperized Cd, the column is washed with 5-10ml of buffer solution at a flow rate of 0.3-0.7ml/min.. Initially EDTA-NH_4Cl buffer with a pH of 8.5 was used, but Imidazole with a pH of 9.0 had proven to be more efficient for the reduction, so was eventually used to wash the packed column. Washing of the column with the buffer ensures that the pH of the column is adjusted before any other solution is passed. Once each column was packed and whenever the column was not in use, a rubber tube was connected to one end of the column, and with a disposable pipette, the tube long with the column was completely filled with the buffer solution and then the tube was connected to both ends of the column forming a closed loop.

Several columns were made in the glass shop, each being 4cm or 7cm in length. The glass tube was not just a straight glass tube, but it was made with a bulb in the middle of the tube (see Figure 2). The bulb was inserted due to the fact that it was previously known, that a pressure issue was a common problem. With straight glass column tubes, the pressure would be too high within the column as the solution was being pumped out of the column into the tubes. The tube connected at the outlet of the column would constantly pop off, thus disrupting the instrumental measurement. With the use of the bulb in the column, the pressure issue was resolved and the outlet tube remained connected to the column at all time.

Figure 2: Dimensions of the Reduction Columns Used



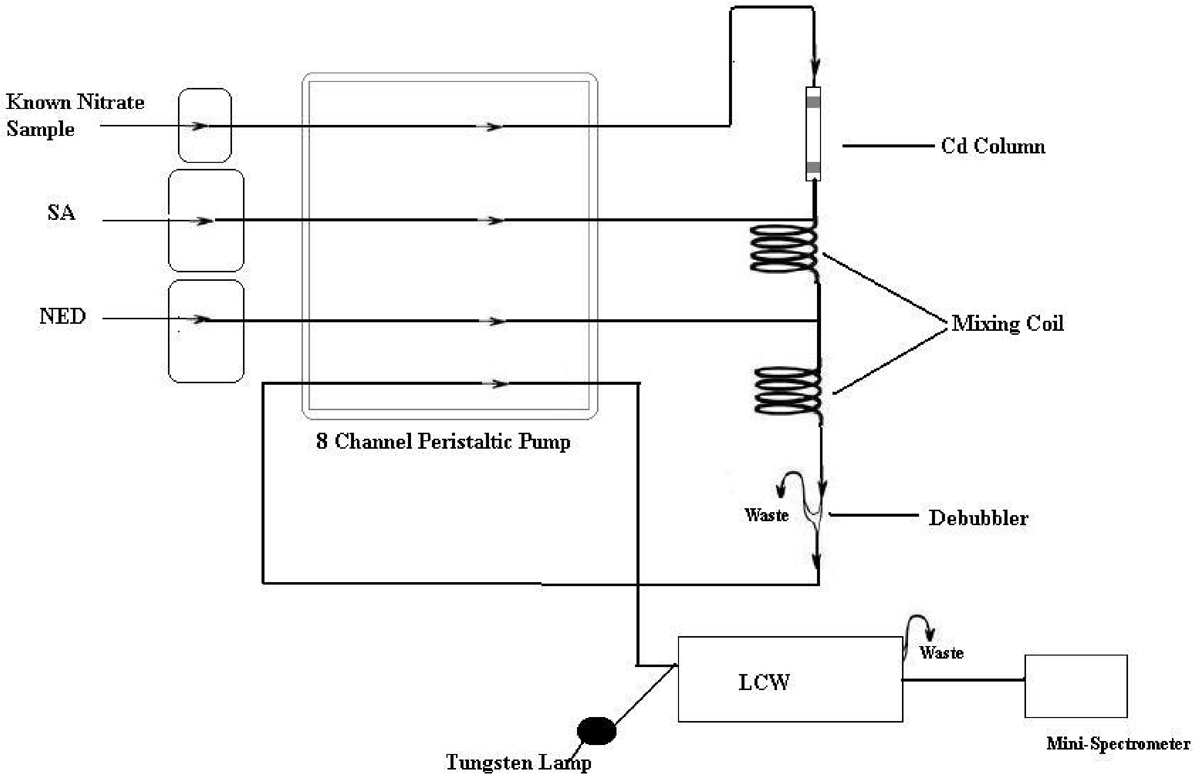
Activation of the Packed Cadmium Columns

All columns prior to being used from reduction of $NO_3^-{}_{(aq)}$ need to be activated with a buffer solution. 5-10ml of the buffer should be passed through the reduction column at a flow rate between 0.3-0.7ml/min..Washing the column with the buffer conditions it before the sample is passed through. The efficiency of the reduction of the column is not known exactly for how long it stays efficient, but for safe measure it is best to reactive each column every two weeks if under constant reduction. The efficiency begins to decrease as the partly adhered copper begins to precipitate off the Cd granules, so the columns need to be reactivated with $CuSO_4$ once again and than washed with a buffer solution as previously stated.

Detection of reduced $NO_2^-{}_{(aq)}$ in the LOPAP

In order to quantify the reduction efficiencies of the cadmium columns a few changes were made to the LOPAP system (see figure 3). There was no need for the external sampling unit, as a known concentration of $NO_3^-{}_{(aq)}$ was passed through the column. Also there was no need for a second channel, since the experiment was of known concentration of aqueous solution. Therefore subtracting out a background reading of possible interfering substances was not required. The known samples of $NO_3^-{}_{(aq)}$ were made in the concentration range of 10nm-400nm from the stock solution of 1mM $NO_3^-{}_{(aq)}$. All samples were of various concentrations of $NO_3^-{}_{(aq)}$ were made to concentration with Milli-Q water. The samples of $NO_3^-{}_{(aq)}$ were sampled into the LOPAP by a 8 channel peristaltic pump (0.3ml/min) and pushed though an activated cadmium column. After reduction with the column, $NO_2^-{}_{(aq)}$ is pushed into a mixing coil (2mmID and 4mmOD), where it mixes with SA, to form diazonium cation. The diazonium cation solution is then pushed into another mixing coil where it mixes with NED and forms an azo dye. The azo dye formed in the in the mixing coil, is then pushed into a debubbler to allow for all gas bubbles to be separated from the liquid solution. The gas free solution of azo dye is then pumped into the liquid core waveguide (LCW) where light is reflected through the Teflon tubing containing the light absorbing dye. The light is then sent by a glass fibre to a mini-spectrometer from which a spectrum is obtained.

Figure 3: Experimental setup of the LOPAP during measurement of reduction efficiencies of the Cadmium Columns



Gas Phase $HNO_{3(g)}$ Source

Prior to gas phase calibration and collection efficiency tests, a gas phase permeation source for nitric acid was built. A Teflon tube was filled with concentrated HNO_3 (~1-2mls). The sealed Teflon tube was placed into a glass sleeve through which N_2 gas was flowed through, at a rate of 20ml/min. The tube was inserted into a copper jacket, which was temperature controlled to 0.1 °C with the use of a heating pad and a thermocouple. To ensure temperature stability, the whole system was insulated.

LOPAP Maintenance

The LOPAP instrument is very sensitive, and due to its high sensitivity it is very essential that periodic maintenance on the instrument is maintained. The light intensity from the long path absorption tubes are able to decrease significantly, so it is important that the whole LOPAP instrument is washed out with a dilute base (0.5N NaOH) followed by Milli-Q water and then by a dilute acid (0.5M HCl) and followed by Milli-Q water once again. Each solution should run through the system for an hour minimum. Fine particulates over time bind to the Teflon tubing's or the stripping coils and mixing coils, and may clog the system decreasing the flow rate and affecting the signal. This cleaning procedure should be carried out every month. It is always beneficial to run Milli-Q water through the system kept over night, a few times a month.

To ensure high conversion efficiency, the Cd columns should be reactivated every two weeks with 2% by volume $CuSO_4$ and washed with buffer solution. If the column is used constantly it is important to wash the column with dilute sulphuric acid (25mL 0.05M at max flow rate) to get rid of the CdOH build up, and then washed with buffer. This should be done each day before the first series of reductions, however if the column is not used everyday, once a week is fine.

Blanks and Calibration

A reagent blank was obtained by directly pumping SA/NED into the working system of the LOPAP. The SA and the NED are made up with Milli-Q water, and they both show absorption at 544nm (azo dye wavelength; $_{\text{Iabs}}$) and the reference wavelength, 700nm. So a blank calibration is obtained every time a new solution of SA or NED is made. The solutions are run through the system and an average absorption is obtained from Log($_{\text{Iref}}$/$_{\text{Iabs}}$) (equation (2)), by

Ocean Optics IBase32 software. The blank is subtracted from any nitrite or nitrate sample which is being analyzed in the system. For example when a known concentration of nitrate is being passed through the Cd column an average nitrite signal is obtained; the blank is subtracted away from the average nitrite signal, so the adjusted signal is strictly from the reduced nitrite. A calibration of known $NO_2^-{}_{(aq)}$ concentration is also run through the working system of the LOPAP. By detecting the absorption for a range of specific $NO_2^-{}_{(aq)}$ concentrations, a graph is obtained. When $NO_3^-{}_{(aq)}$ is run through the LOPAP working system and through the Cd column and converted to $NO_2^-{}_{(aq)}$, the absorption is compared to the graph and a reduction percentage, can be determined. It is important to obtain a quantified conversion of $NO_3^-{}_{(aq)}$ to $NO_2^-{}_{(aq)}$.

Results and Discussion

Calibration of the Gas Phase HNO_3 Source

The gas phase $HNO_{3(g)}$ perm source was supposed to initially be calibrated using ion chromatography, however due to instrumental malfunction, the concentration of $HNO_{3(g)}$ from the perm source was determined based on acid-base titration. The perm source had previously been calibrated several years ago and was setup with the same apparatus explained previously. An averaged concentration of the perm source from the past was used as an estimate for the concentration of the $HNO_{3(g)}$. Using this concentration as a starting point, the concentration of the base was determined for the titration procedure. The average $HNO_{3(g)}$ concentration from the perm source which was bubbled in 10mL of Milli-Q water for 10minutes was 8.405µM. Therefore a weak acid and weak base titration with dilute NaOH was used. A 2.101µM solution of NaOH was prepared, and titrated into a 20mL solution, which was made by bubbling the gas from the perm source into 20mL of Milli-Q water for 40 minutes. A neutralization point is required to be determined where the amount of acid in the solution is in equilibrium with the amount of base as shown in (R11).

$$HNO_3 + NaOH \leftrightarrow NaNO_3 + H_2O \qquad (R11)$$

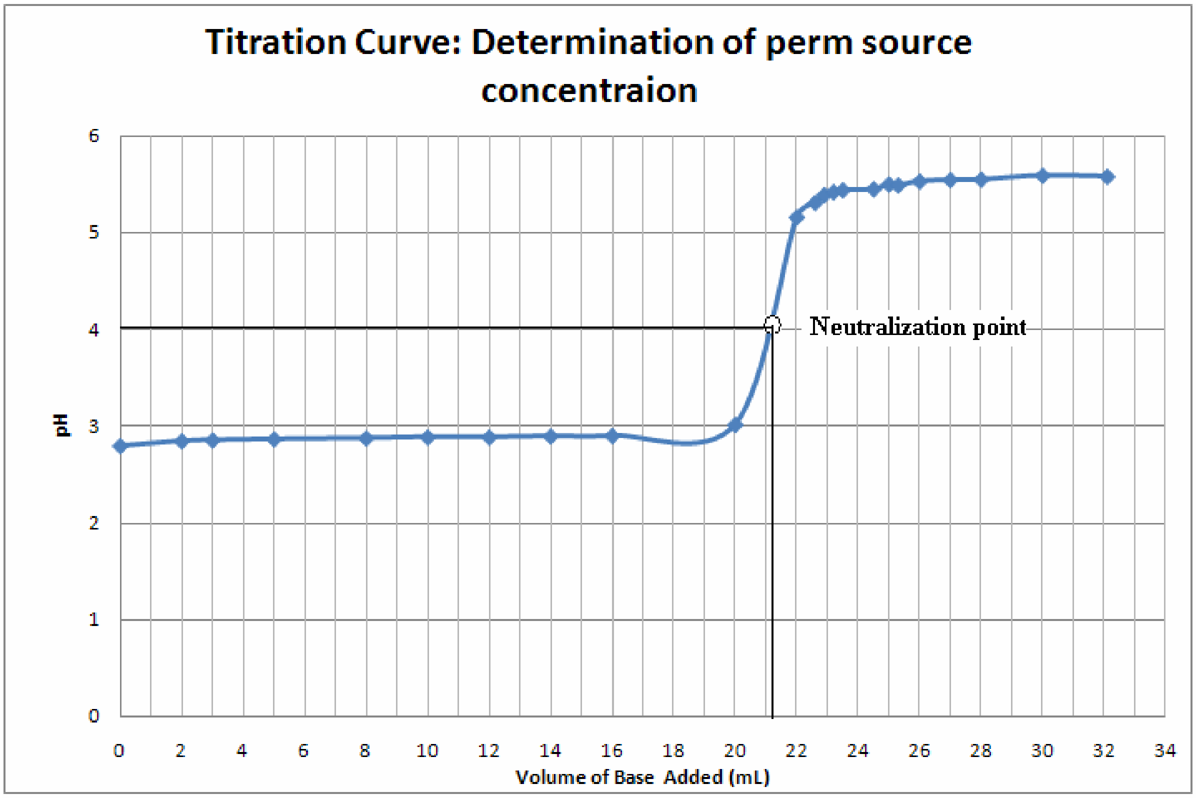
Once the neutralization point is known, the amount of base added to reach it, is determined from a titration curve (see figure 4), thus the unknown concentration of the $HNO_{3(g)}$ from the perm source is determined. The following equation is used to determine the unknown concentration of the HNO_3;

$$C_aV_a = C_bV_b \qquad (3)$$

As V_a (volume of acid; 20mL) is known, C_b (concentration of base; 2.101µM) is known and V_b (volume of base added to reach neutralization point; 21.2mL) is known (see figure 3), therefore using equation three, C_a, the concentration from the gas phase $HNO_{3(g)}$ perm source is 2.227 µM.

During the preparation of the dilute NaOH base, nitrogen gas (N_2) was bubbled into the solution during mix up. Also when the base was being titrated from the burette into the 20mL solution of HNO_3, nitrogen gas was also bubbled into the 20mL solution of HNO_3. It is important to bubble nitrogen gas into the base and the solution of HNO_3 to avoid neutralization with carbon dioxide (CO_2).

Figure 3: Titration Curve: Weak NaOH Base Titrated into Weak Acid HNO_3 from Perm Source



We are also interested in the perm rate of our gas phase $HNO_{3(g)}$ perm source. This is commonly represented as mass/time, and in our case ng/min. The concentration of the perm source determined from the titration (see Table 2), is converted to moles and then multiplied by the molar mass of HNO_3 (84.99g/moles) to find the mass and then divided by the time the sample was collected.

$[HNO_3]$ x V x molar mass of HNO_3 = $(2.227\text{x}10^{-6}\text{M})(0.020\text{L})(84.99\text{g/moles})$ = 3785.454ng

Dividing this mass by the time the perm source was sampled into 20ml of Milli-Q water (V), yields a perm rate of 94.636ng/min

Table 2: Solutions and Volumes used for the Calibration of the Perm Source

Solution	**Concentration (μM)**	**Volume (mL)**	**Perm Rate (ng/min)**
NaOH	2.101	21.2 (Neutralization point)	
HNO_3	2.227 (Perm Source)	20	94.636

$NO_2^-{}_{(aq)}$ Calibration Curve on the LOPAP

A calibration curve $NO_2^-{}_{(aq)}$ was obtained using the LOPAP instrument. Five sample concentrations of $NO_2^-{}_{(aq)}$, ranging from 10nM-400nM was prepared from the 1µM $NO_2^-{}_{(aq)}$ stock solution previously prepared, and diluted with Milli-Q water. A blank for the calibration curve was performed by running water and SA and NED through the working LOPAP system. I_{ref} and I_{abs} were recorded by Ocean Optics IBase32 software ever 100msec and 800 of there averages were displayed by the software. It is important that the averaging is greater then 45seconds due to the residual time in the liquid core waveguide (LCW).The known concentration samples of $NO_2^-{}_{(aq)}$ were run for 20mins each and the average $\log(I_{ref}/I_{abs})$ was obtained and plotted against concentrations. Note, subtracting out the SA/NED blank was done first. There are two channels within the LOPAP instrument, however only one calibration curve was obtained. This is due to the fact that only one channel was needed for quantifying reduction efficiencies (see figure 3). Therefore a calibration curve only for channel 1 was only obtained. Figure 4 shows the calibration curve, along with the equation for the graph. The equation for channel 1 calibration graph along with the correlation coefficient is shown as follows:

$$y = 0.002x + 0.028 \qquad R^2 = 0.998 \qquad (4)$$

The calibration curve, has a very high correlation coefficient (close to 1) which means that the data between the absorption and the concentration is linear related, as expected.

Figure 4: Calibration curve for $NO_2^-{}_{(aq)}$ on Channel 1 using the LOPAP

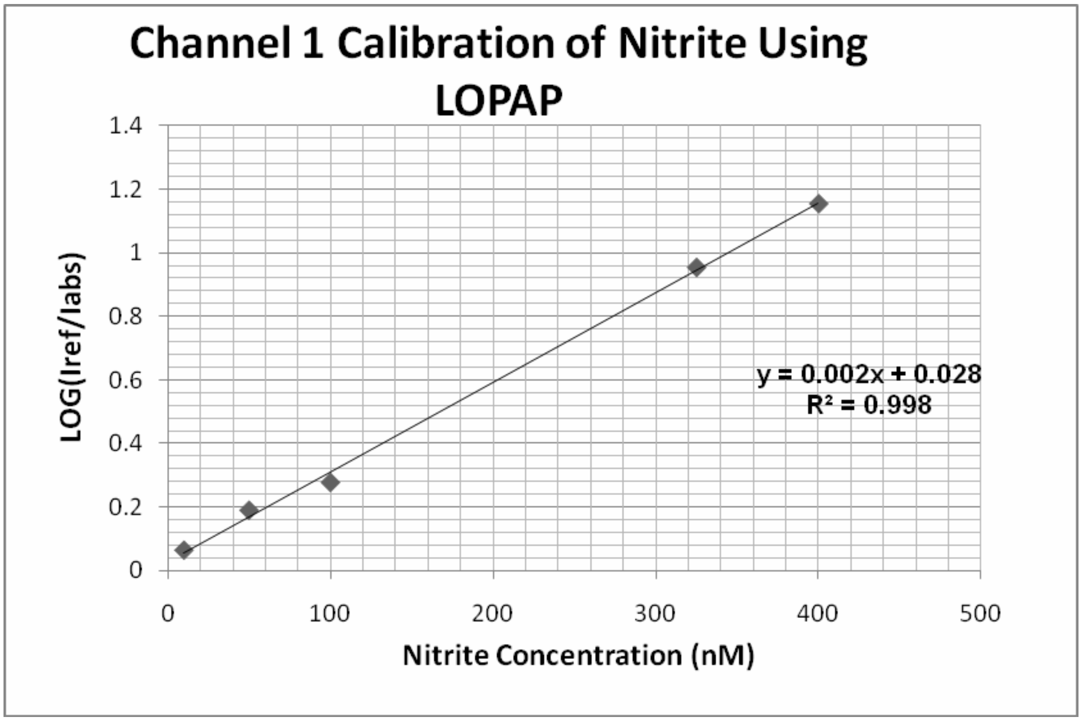


Table three shows channel ones calibration concentration and corresponding absorbance:

	Concentration (nM)	**Absorbance (W/ Blank Subtracted out)**	**SA/NED Blank**
Channel 1	10	0.0632	-0.2890
	50	0.1891	
	100	0.2767	
	325	0.9547	
	400	1.1556	

Table 3: Master and Slave $NO_2^-{}_{(aq)}$ Calibration Curve Parameters

Cadmium Column Parameters for Reduction

Two different length cadmium columns were made and prepared as described above. The lengths of the column were 4cm and 7cm's. Each column was made with a bubble in the center length of the tube as seen in figure 2. The bubble was inserted into the tube to increase the surface area of the cadmium granules within the column, and most importantly to reduce the pressure as the liquid $NO_3^-{}_{(aq)}$ and SA are being pumped through the column during reduction. The flow rate at which the solutions are being pumped through the column is important factor to consider. It is essential that the solution being pumped through the column is at a rate between 0.3-0.7ml/min (Zhang, 1999). The peristaltic pump was set so the solution was being pumped out of the column at 0.3ml/min. This allows for optimal time of contact of the nitrate solution with the Cd granules. The flow rate set on the peristaltic pump was also optimally set allowing a good reaction time to allow the converted nitrite to react with SA and NED to form the azo dye (R5 and R6).

Reduction Experiment with the 4cm Column

Throughout the reduction experiments the LOPAP system was setup as seen in figure three. Prior to each activation EDTA buffer was washed through the column as stated above. The known concentration of $NO_3^-{}_{(aq)}$ samples which was used, was 325nM. The experiment using the 4cm column was carried out five times. I_{ref} and I_{abs} was recorded using Ocean Optics IBase32 software. Points were averaged over no less then 45 seconds due to resonance time within the LCW. $Log(I_{ref}/I_{abs})$ of the sample runs was determined and the blank was subtracted out (table 3). These numbers where averaged and fit into the calibration curve (figure 4). During all of the reduction experiments only the master channel was used in the LOPAP system (channel 1).

Table 4 shows the percent reduction for the $NO_3^-{}_{(aq)}$ conversion to $NO_2^-{}_{(aq)}$. Run one and run two show zero conversion. This was a system error due to the fact the LOPAP system was not cleaned out recently prior to that. The LOPAP system was washed out with weak NaOH and weak HCl, along with Milli-Q water. Once this was done run 3 was performed. There was a reduction conversion of 166%, and this high percentage conversion was thought to be due to not washing out the system with Milli-Q water for long enough, after the cleaning process. Due to this, particulates may have been in the LOPAP instrument, as they were not entirely washed out, giving an inaccurate instrument reading. Also, due to improper washing of the instrument, the system may have had a high acidity from the HCl solution which was used to clean the LOPAP system after being washed out with dilute NaOH and some water (refer to LOPAP maintenance), leading to the inaccurate reading. The system was washed out overnight with water, and run 4 and 5 were performed next. A conversion was obtained of 47% and 31% for run 4 and 5 respectively. The column was never washed with 0.05M sulphuric acid to remove any cadmium hydroxide which may have possibly formed and accounted for the low percent reduction.

Table 4: Percent Efficiency of Reduction of $NO_3^-{}_{(aq)}$ into $NO_2^-{}_{(aq)}$ using a 4cm Cd Column

Column Length	Run	$[NO_3^-{}_{(aq)}]$	Average Absorbance ± Std.Dev.	$[NO_2^-{}_{(aq)}]$ calculated from calibration curve	% reduction of $NO_3^-{}_{(aq)}$
4cm	1	325nM	-0.3552 ± 0.0217	-191.6nM	0
	2		-0.2526 ± 0.1149	-140.3nM	0
	3		1.1092 ±0.00669	540.6nM	166%
	4		0.3348 ± 0.167	153.4nM	47%

	5		0.2291 ± 0.114	100.6nM	31%

The next four reduction experiments with the same column, was carried out in the same manner except the fact that the column was washed with 0.05M sulphuric acid. Every other run the column was washed with 25mL 0.05M sulphuric acid, at a flow rate of 2ml/min. Table 5 shows the results. The first run (run 6), the column was washed with 25mL 0.05M sulphuric acid then a buffer solution as stated above, and a nitrate conversion of 48% was obtained. This indicated that the column had a CdOH build up, due to the fact that once the column was washed with 0.05M sulphuric acid the reduction increased from run 5 from 31% to 48%. The next run, run 7, a very good reduction of 91% was obtained. The next run, run 8, the reduction decreased to 77%, and run 9, there was a reduction of 135%. The gradual decrease in reduction along with the 135% reduction, made me believe that the column had to be reactivated with $CuSO_4$, to allow cadmium to contain copper, which has a lower reduction potential than cadmium, allowing for te reduction power to increase for the cadmium column.

Table 5: Percent Efficiency of Reduction of $NO_3^-{}_{(aq)}$ into $NO_2^-{}_{(aq)}$ using a 4cm Cd Column Washed with 0.05M sulphuric acid

Column Length	**Run**	**$[NO_3^-{}_{(aq)}]$**	**Average Absorbance ± Std.Dev.**	**$[NO_2^-{}_{(aq)}]$ calculated from calibration curve**	**% reduction of $NO_3^-{}_{(aq)}$**
4cm	6	325nM	0.3416 ± 0.0837	156.8nM	48%
	7		0.6184 ± 0.0228	295.2nM	91%
	8		0.5303 ± 0.0332	251.2nM	77%

	9		0.9079 ± 0.0758	439.9nM	135%

Reduction Experiment with the 7cm Column

The next set of reduction was carried out with an activated column (as stated above), 7cm in length. As before, prior to each run, the column was washed out with the EDTA buffer, and the column was washed with 0.05M sulphuric acid on a weekly basis. It is important that after each wash with sulphuric acid, the column is washed with a Milli-Q water for 15-20min's to neutralize the column. Stabilization and conditioning was also a concern of interest for the next reduction experiments. To achieve 100% recovery from sample nitrate it is important to obtain both 100% efficiency of reduction of nitrate to nitrite and no further reduction (0%) of nitrite to lower nitrogen compounds (Zhang, 1999). After the column is washed with the buffer, the sample nitrate is pushed through the column using the peristaltic pump, and it is important to pass the solution through for 15-20 minutes, to ensure a constant output signal. It is not quite clear what the detailed mechanism of this conditioning process is, but it probably involves re-arranging the reactive surface site to create a uniform reactive surface with selective reduction of nitrate to nitrite (Zhang, 1999).

Table 6 shows the results obtained for the 7cm column. Run one, an over reduction was obtained. The column was thought to have a build up of CdOH, which may have developed during preparation and packing of the column. The column was washed with 0.05M sulphuric acid. Run 2, the reduction of nitrate to nitrite was 99%. This therefore indicates that the column had a CdOH build up. Run 3 through 5 the reduction percentage began to decrease after each run, 87%, 77%, and 52% respectively. This decrease in reduction indicated that the column needed to be reactivated with 2% by volume solution of $CuSO_4$. The column was washed with 10ml of this solution through the column at a flow rate of 0.3ml/min. The column was then washed with Milli-Q water for 15 minutes, and then washed with the new Imidazole buffer which was to be used replacing the EDTA buffer. The column was washed for 20-25mins at a flow rate of 0.3ml/min with pH 9.0 Imidazole. Table 7 shows the reduction percentage results for the reactivated Cd column, washed with the Imidazole buffer.

Table 6: Percent Efficiency of Reduction of $NO_3^-{}_{(aq)}$ into $NO_2^-{}_{(aq)}$ using a 7cm Cd Column

Column Length	Run	[$NO_3^-{}_{(aq)}$]	Average Absorbance ± Std.Dev.	[$NO_2^-{}_{(aq)}$] calculated from calibration curve	% reduction of $NO_3^-{}_{(aq)}$
7cm	1	325nM	0.8332 ± 0.0594	402.nM	123%
	2		0.6693 ± 0.168	320.6nM	99%
	3		0.5915 ± 0.0339	281.7nM	87%
	4		0.5302± 0.0349	251.1nM	77%
	5		0.3684 ± 0.0298	170.2nM	52%

Table 7: Percent Efficiency of Reduction of $NO_3^-{}_{(aq)}$ into $NO_2^-{}_{(aq)}$ using a reactivated 7cm Cd Column washed with Imidazole Buffer

Column Length	Run	[$NO_3^-{}_{(aq)}$]	Average Absorbance ± Std.Dev.	[$NO_2^-{}_{(aq)}$] calculated from calibration curve	% reduction of $NO_3^-{}_{(aq)}$

7cm	1	325nM	0.6511 ± 0.024	311.6nM	96%
			0.6745 ± 0.0048	323.3nM	99%

Once the column was reactivated and washed with the Imidazole buffer, the reduction percentage increased from 52% (run 5 in table 6) to 96%. This shows that the column needs to be to be reactivated with $CuSO_4$. The increase in reduction, is also due to the fact the new Imidazole buffer was used. The next run (run 2 in table 7) the reduction increased to 99%. The use of the new buffer has showed to be more efficient for the reduction of nitrate to nitrite.

Conclusion

Summary

Attempts were made to modify a proven method of detecting HONO for application in HNO_3 detection. The LOPAP instrument is a cheap, sensitive and continuously working instrument, making the instrument an ideal choice to attempt to modify for this purpose (Kleffman, 2007). A known cadmium reduction technique was used to reduce $NO_3^-{}_{(aq)}$ into $NO_2^-{}_{(aq)}$ (Nydahl, 1976). Using the LOPAP instrument, the best reduction efficiencies were obtained when using a 7cm column with a bulb at center length. Washing the column prior to each run with a pH 9.0 Imidazole buffer for 5-10 minutes at a flow rate of 0.3-0.7ml/min yielded the best reduction. Once a week the column should be washed with 0.05M sulphuric acid, to remove and CdOH build up. Once the reduction efficiency begins to decrease below 80% reduction the column should be reactivated with 10ml of 2% by volume solution of $CuSO_4$. Stabilization and conditioning is important to obtain 100% reduction, so it is significantly important to pass the nitrate solution though the column for 15-20minutes to receive an optimal and constant output signals.

Future Work

Future work includes: (i) Perm source titration for HNO_3 concentration (ii) gas phase sampling of nitric acid

(i) Since only one perm source titration for the HNO_3 concentration was complete, it is essential that further titrations are performed in order to get an average along with a standard deviation of the perm source concentration. It is very important to determined with high accuracy what the perm concentration is for gas phase sampling.

(ii) Sampling of gas phase source and calibration of the LOPAP system within this phase is the next step to get working. It is important to see if the reduction efficiency is different between gas phase sampling and purely aqueous sampling. Eventually field study measurements of $HNO_{3(g)}$ in the atmosphere will be able to take place.

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