CHEM 489 Directed research II

Conversion of NO$_x$ gases to nitrate ions by oxidation with persulfate species for air purification

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The absorption and oxidation of NO$_x$ gases by potassium persulfate has been implemented to remove the NO$_x$ gases from the air by forced ventilation through wet silica gel beads soaked with K$_2$S$_2$O$_8$/K$_2$CO$_3$ and (NH$_4$)$_2$S$_2$O$_8$/K$_2$CO$_3$.The influence conditions: air flow, duration, cartridge packing, concentration of solution on the efficiency of NO$_x$ capturing was studied. The ability to absorb NO$_x$ gases and convert into nitrate ions was confirmed, however low efficiency $\cong$0.1% indicates that improvements of the method are required. The increase of duration decreases the efficiency, and increase of the packing increases the efficiency of absorption, however the exact magnitudes appear inconsistent.

Introduction

One of the major contributors to the air pollution are nitric oxide (NO) and nitric dioxide (NO$_2$), usually referred as NO$_x$. Compared to other forms of N$_x$O$_y$ compounds the combination of reactivity and abundancy makes them the source of several hazards to environment and public health and one of the most important factors of air quality assessment.[1] NO$_x$ under UV radiation produce radicals that participate in conversion of ozone (O$_3$) to oxygen (O$_2$) leading to ozone layer depletion, and react with various compounds in the air that results in formation of smog and acid rains. In the scope of this research it is important to indicate the health risks that NO$_x$ posess: depending on the concentration and exposure time, the presence of NO$_x$ is associated with development of asthma and severing the existing asthmatic symptoms, damage to lung tissues and forming other dangerous compounds when mixing with other compounds during inhalation.[1,3,4]

Several methods of reducing the exhausting NO$_x$ are well known and widely implemented: use of catalytic converters and exhaust gas recirculation,[5] development of new energy sources and development of alternatives to combustion engines[6], use of industrial exhaust fumes burners etc. Nevertheless, the high concentration of NO$_x$ in the air of major cities with huge daily traffic remains a serious issue for the health of local population, specifically for drivers and people who tend to work and live in the buildings close to the roads.[7]

There is a certain progress in development of NO$_x$ capturing/removal techniques, relying on different methods and chemical processes: the photocatalytic oxidation (e.g. TiO$_2$ nanopowder),[8]

Selective catalytic reduction[9], oxidation by peroxides/persulfates[10] etc. However the commercial realization of products that would utilize such methods to purify the room air has not been established yet, compared to widespread existing air purifiers that usually target particulate matter (PM), moisturizers and deodorizers.

The purpose of this research is to implement the oxidation of NO_x to nitrate ions by passing the air through a solution of potassium persulfate ($K_2S_2O_8$) and potassium carbonate (K_2CO_3) holded by porous silica gel beads in a cartridge form. Then, substitute potassium persulfate with ammonium persulfate (($NH_4)_2S_2O_8$) to compare with previous potassium persulfate. The investigation of the amount of captured nitrates and the influence of the parameters: duration of the experiment, concentration of the solution and amount of packing are also investigated for determining optimal condition.

Experimental Details

Materials. potassium persulfate ($K_2S_2O_8$, powder, $\geq 99.0\%$), potassium carbonate (K_2CO_3, anhydrous powder, $\geq 99.0\%$) ammonium persulfate (($NH_4)_2S_2O_8$, powder, $\geq 99.0\%$), sodium nitrate ($NaNO_3$, anhydrous powder), ammonium sulfate (($NH_4)_2SO_4$, anhydrous powder, $\geq 99.5\%$), silica gel beads.

Experimental procedure.

Preparation of standards and examination of the interferences. The standards of NO_3^- ions concentration are prepared using the $NaNO_3$ dissolved in DI water to 500 ppm stock solution, diluted to standards of 50, 25, 10, 5, 2, 1, 0.5 ppm concentrations that are used to construct a calibration curve for the ion chromatography measurements (Dionex ICS 6000, C18 column) demonstrated by Figure 1. The samples of 50 ppm $K_2S_2O_8$ /50ppm K_2CO_3 and silica gel wash (20g of silica gel beads in 200 ml DI water, after 12 hours a water sample is filtered and stored) are measured to confirm that no interferences to nitrate ions signal are present demonstrated by figure 2 and 3 respectively. The NO_3 interference from the saliva gel beads is mitigated by multiple washing of the silica gel beds prior the experiment to the point of conductivity of silica gel wash is identical to DI water.

Capturing and oxidation of NO_x gases. The working solutions of 1% $K_2S_2O_8$ / 1% K_2CO_3 and 2% $K_2S_2O_8$ / 2% K_2CO_3 are prepared using the said reagents and DI water. The solution is added to the dry silica gel beads to completely cover the beads and left for one hour. Wet silica gel beads are transferred into the cylindrical plastic cartridge (R=3 cm, h=20 cm) with double walls, allowing air to be pumped though center to flow though the wet beads and vent outside. The excess solution is used for wetting the bottom sponge (Figure 4). Fans of varying power output (1.36 to 3.6 W) are used to seal the container and force the ventilation of the wet beads when turned on. After the experiments silica gel beads and sponge are washed in 500 ml DI water for two hours, three samples from the solution are filtered and collected for determination of nitrate ions concentration by ion chromatography.

Investigation of influencing parameters. Varying parameters are specified and investigated for the testing, specifically:

- Loading of cartridge (mass of dry beads loaded) for 120g and 225g
- Air flux passing through the beads for 31.8 m^3/h, 45.9 m^3/h and 55.6 m^3/h
- Duration of the experiment for 1 hour and 2 hour
- Concentration of working solution for soaking the silica gel beads for 1% $K_2S_2O_8$ / 1% K_2CO_3 and 2% $K_2S_2O_8$ / 2% K_2CO_3

The obtained staples are used to calculate the mass of NO_x gases captured based on the concentration of the nitrates in the samples, allowing to evaluate the influence and magnitude of changing one of the parameter to the capturing of the NO_x. Then the procedure was repeated with identical parameters with $K_2S_2O_8$ substituted to $(NH_4)_2S_2O_8$
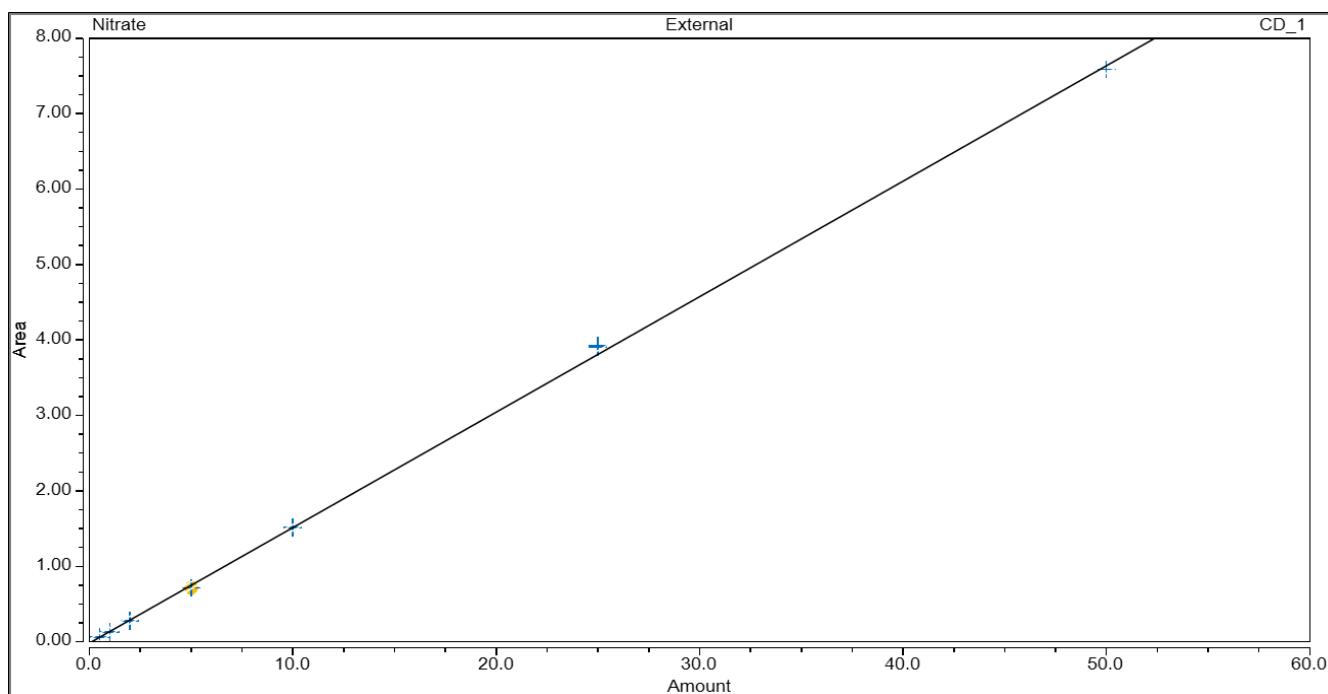

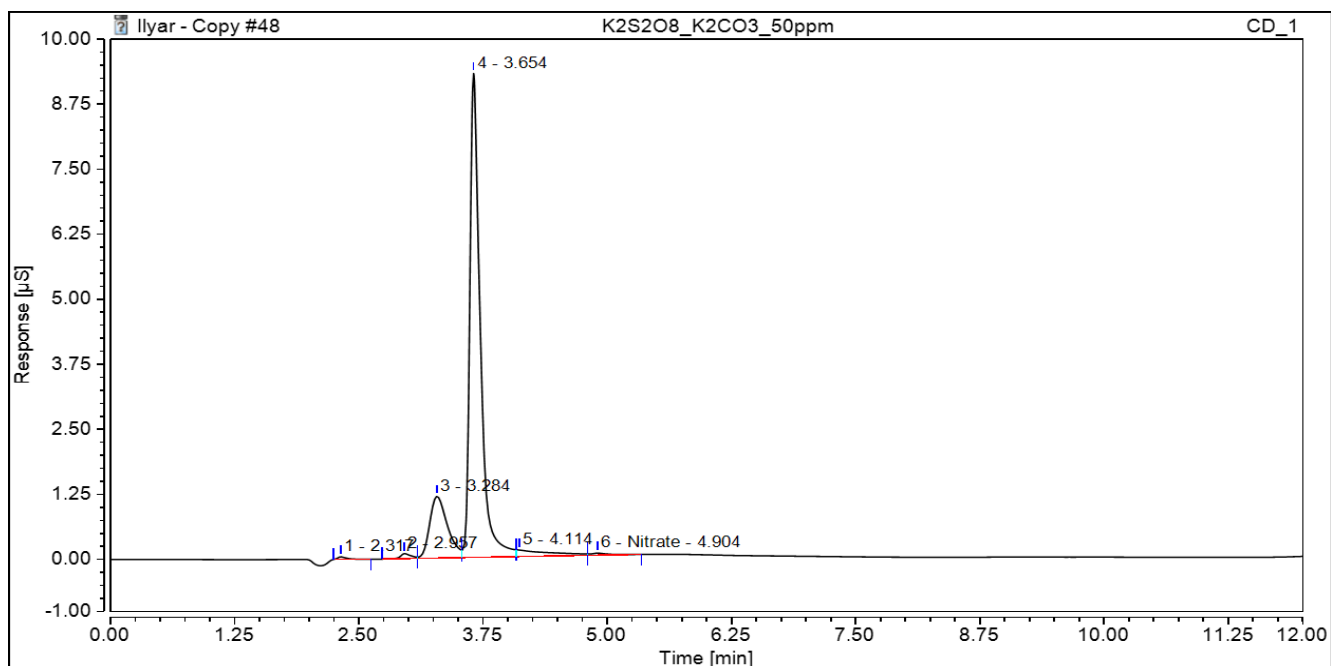Figure 1. Calibration curve based on IC peak area vs concentration of the standards.

Figure 2. Ion chromatogram of background ions solution. Concentration of nitrate is 0.151 ppm
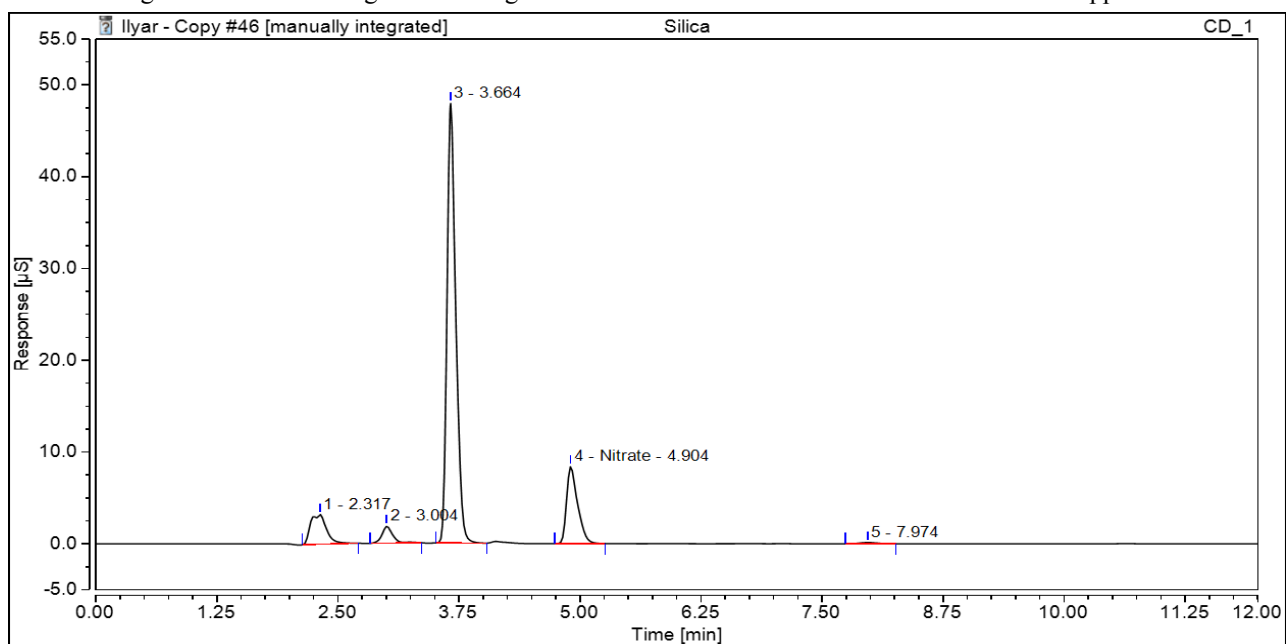

Figure 3. Ion chromatogram of silica gel beads wash. Concentration of the nitrate ions is 7.85 ppm.
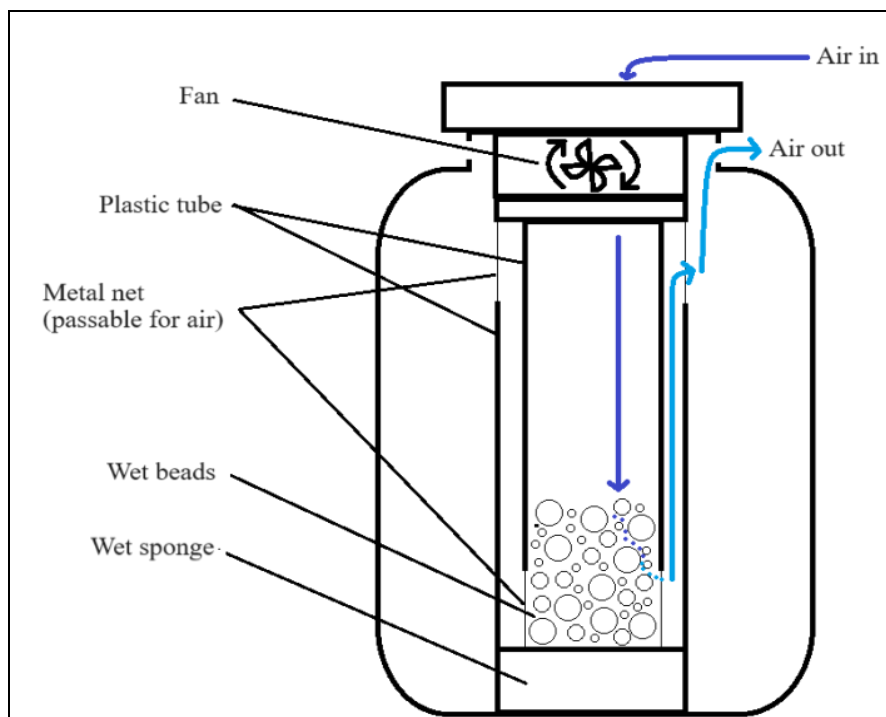
Figure 4. The scheme of an operating device.

Discussion

The optimal time for the extraction was determined from a series of samples taken at different time after the start of beads washing. It was concluded that the optimal time for the extraction is two hours (Figure 5). The concentration of the nitrate ions in the obtained samples are demonstrated in Table 1. The specific conditions of each sample are represented further in Table 2.
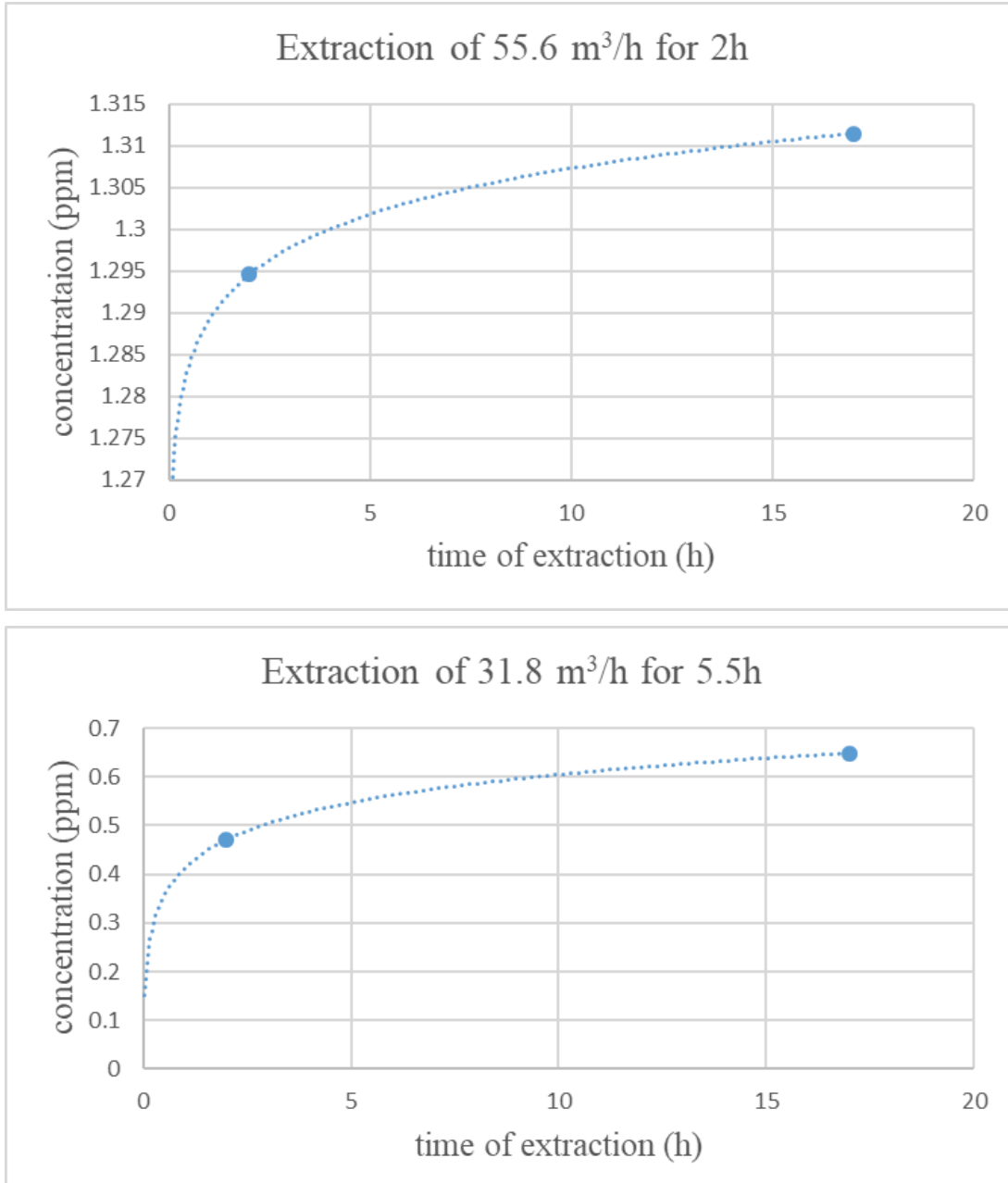
Extraction of 55.6 m³/h for 2h

Extraction of 31.8 m³/h for 5.5h

Figure 5. Concentration of NO_3^- ions vs extraction time for 55.6 m³/h for 2h and 31.8 m³/h for 5.5h sample

Table 2 represents the results of the absorbing of nitrate ions depending on the varying conditions. The obtained concentration of NO_3^- is used to approximate the mass of captured NO_2

$$m(NO_2) \ in \ mg = \frac{[NO_3^-](ppm)*m(DI \ H_2O)(mg)}{10^6} \times \frac{M(NO_2)}{M(NO_3^-)}$$

Where m(DI H₂O) is the mass of the water used for extracting nitrate ions, that was set to 500 g
The obtained mass is used for calculating the decrease of NO_2 gas concentration in the total volume of air passed through the device.
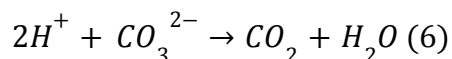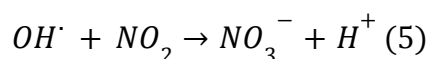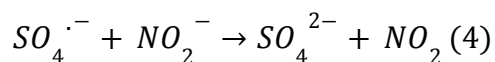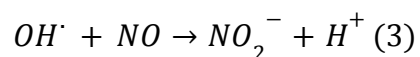
Sample	[NO$_3^-$] (ppm)	Average and 95% CI (ppm)	Sample	[NO$_3^-$] (ppm)	Average and CI 95% (ppm)	Sample	[NO$_3^-$] (ppm)	Average and 95% CI (ppm)
A1	0.85	0.83±0.039	D1	0.32	0.35±0.034	G1	0.38	0.40 ±0.030
A2	0.82		D2	0.36		G2	0.39	
A3	0.88		D3	0.38		G3	0.43	
B1	0.58	0.61 ±0.034	E1	0.25	0.28 ±0.040	H1	0.33	0.39 ±0.108
B2	0.64		E2	0.28		H2	n.a.	
B3	0.62		E3	0.32		H3	0.44	
C1	0.50	0.50 ±0.028	F1	0.32	0.36±0.043	I1	0.36	0.37 ±0.020
C2	0.48		F2	0.38		I2	0.38	
C3	0.53		F3	0.39		I3	n.a.	

Table 1. The concentration of NO$_3^-$ ions in the samples.

Sample code	Pumping volume (m^3/h)	Duration of the experiment (h)	Absorbed working solution[a](g)	Working solution (% K$_2$S$_2$O$_8$ /K$_2$CO$_3$)	Captured mass of NO$_2$ (mg)[b]	decrease of NO$_2$ concentration in air volume (ppb)[c]
A	0	1.0	85.0	1/1	0.315	-
B	31.8	1.0	85.0	1/1	0.226	5.90
C	45.9	1.0	85.0	1/1	0.185	3.35
D	31.8	2.0	85.0	1/1	0.130	1.70
E	45.9	2.0	85.0	1/1	0.104	0.94
F	31.8	2.0	122.0	1/1	0.134	1.75
G	45.9	2.0	122.0	1/1	0.148	1.34
H	31.8	2.0	122.0	2/2	0.141	1.84
I	45.9	2.0	122.0	2/2	0.137	1.24

Table 2. The Captured NO$_x$ depending on conditions ([a] the mass of absorbed solution is approximation, determined using the mass of decanted solution left after loading the cartridge. [b] for approximation all NO$_x$ is considered NO$_2$. [c] it is assumed that cleaned air does not recirculate back and density of air at 293 K=1.204 kg/m^3)

The captured amount of NO$_x$ appears to be extremely low. It is considered that the following reactions (1-6) occur in the process[10]. It is calculated that a theoretical load that absorbs 85.0 g of 1%K$_2$S$_2$O$_8$ can oxidize 94 mg of NO or 289 mg of NO$_2$ and 122 g can oxidize 135 mg or 414 mg of NO or NO$_2$ respectively. There are several reasons that could explain such a decrease in the performance. First is an inefficient radical formation in Reaction (1) for example due to low temperature, and inability to reach activation energy. Second is the persulfate reagent being degraded to sulfate form and losing the oxidation ability. Third is inefficient capturing of the cartridge, that may not allow the air flow to pass through or allows it to pass only through surface beads, restricting the air contact in the deeper and core region, resulting in incomplete capturing of NO$_x$. Forth, the air flow causes too rapid evaporation of the moisture in the silica gel bead, that is not countered by moisture supply from the soaked sponge, therefore restricting the reactions.

$$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot -} \ (1)$$
$$SO_4^{\cdot -} + H_2O \rightarrow HSO_4^{-} + OH^{\cdot} \ (2)$$
$$OH^{\cdot} + NO \rightarrow NO_2^{-} + H^{+} \ (3)$$
$$SO_4^{\cdot -} + NO_2^{-} \rightarrow SO_4^{2-} + NO_2 \ (4)$$
$$OH^{\cdot} + NO_2 \rightarrow NO_3^{-} + H^{+} \ (5)$$
$$2H^{+} + CO_3^{2-} \rightarrow CO_2 + H_2O \ (6)$$
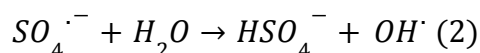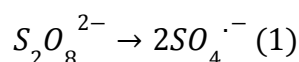
The difference between alternating conditions is present but appears inconsistent, perhaps to the same reasons mentioned above, that reduce the efficiency of the oxidation, so the resulting values are prone to errors.

Figures 6 demonstrate that the increase in air flow decreases the amount of captured nitrates (accordingly, the highest amount of captured nitrates (0.315 g) appeared when the fan was not turned on) for the cases when 125 g of beads were loaded (85 g of working solution). However when the load was doubled (122 g of working solution, increased 1.4 times) the increase of air flow also increased the absorbed NO$_x$ (except in the case of 2% K$_2$S$_2$O$_8$ / 2% K$_2$CO$_3$ solution, which may suggest that the more silica gel is loaded, the less it is prone to increased evaporation caused by increased air flow. Regardless, the relative difference between two parameters is inconsistent among the cases, therefore it is concluded that air flow does not affect the capturing of NO$_x$.

Figure 6a suggests that an increase of the duration from 1 hour to 2 hours of the experiment actually decreases the captured amount by factor 1.74 (31.8 m^3/h) and 1.78 (45.9 m^3/h). The possible reason for such irregular observation may be connected to the increased drying of the beads for more prolonged air flow.

Figure 6b demonstrates the increase of absorbed nitrates with the increase of loading of the cartridge, however the increase varies in the magnitude (by 3% for 31.8 m³/h and 37 % for 45.9 m³/h). The said increase is expected, due to the increase of contact surface area, the limit of absorbing capacity, and slower evaporation of the moisture.

Figure 6c suggests that increase of the concentration of $K_2S_2O_8$ / K_2CO_3 in the solution does not produce a significant and consistent effect- the amount of NO_x absorbed has increased by 5.2% for 31.8 m³/h but decreased by 7.5% for 45.9 m³/h. It is concluded that the concentration of $K_2S_2O_8$ / K_2CO_3 is not affecting the absorption due to the said concentrations being higher than a maximum concentration that can be absorbed by the beads, therefore saturating the silica gel beads equally.

Considering the slow efficiency of absorbing of the NO_x and inconsistent response to the change of the experimental conditions, it is evident that the experiment requires certain improvements in the materials and methods. The following improvements may be suggested: the increase of temperature or use of catalysts to improve the reactivity of oxidation agent, introducing more efficient way of resupplying the moisture to beads (for example, spraying the beads with the solution at the drying regions), increasing the contact area of the silica gel beads by using smaller and/or more porous variants and analogues, decreasing the air flow for more steady influx of NO_x gases and slower evaporation of the working solution.
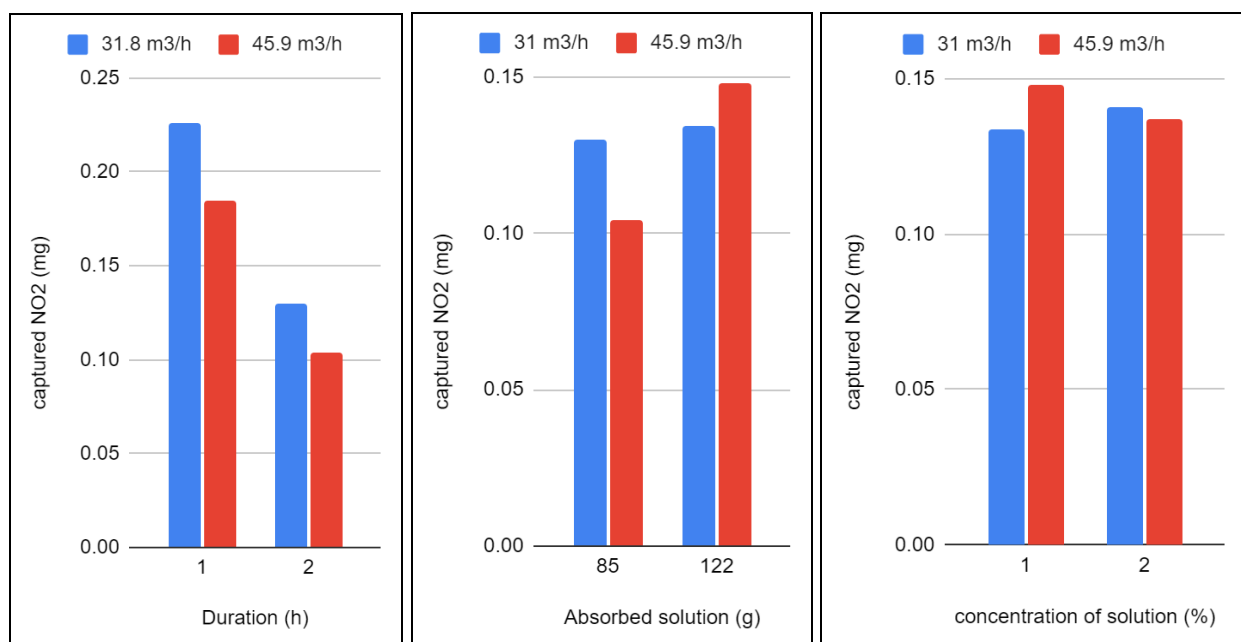

Figure 6. a) The absorption of NO_2 vs the duration of experiment, b) The absorption of NO_2 vs the amount of solution in the cartridge, c) The absorption of NO_2 vs the concentration of the working solution.

Substitution of reagent

When the $K_2S_2O_8$ was substituted to $(NH_4)_2S_2O_8$ there overall efficiency of NO_x capturing was improved and the effect of changing the parameters is more consistent (Table 3)

Sample code	Pumping volume (m^3/h)	Duration of the experiment (h)	Absorbed working solution[a](g)	Working solution (% $(NH_4)_2S_2O_8$ /K_2CO_3)	Captured mass of NO_2 (mg)[b]	decrease of NO_2 concentration in air volume (ppb)[c]
J	31.8	2.0	85.0	1/1	0.475	6.20
K	45.9	2.0	85.0	1/1	0.465	4.21
L	31.8	4.0	85.0	1/1	0.793	5.18
M	45.9	4.0	85.0	1/1	0.954	4.31
N	31.8	2.0	122.0	2/2	1.121	14.64
O	45.9	2.0	122.0	2/2	1.163	10.52

Table 3. The Captured NO_x depending on conditions ([a] the mass of absorbed solution is approximation, determined using the mass of decanted solution left after loading the cartridge. [b] for approximation all NO_x is considered NO_2. [c] it is assumed that cleaned air does not recirculate back and density of air at 293 K=1.204 kg/m^3)

First, the overall absorption ability is significantly improved, as the captured mass of nitrate ions as well as the NO_x depression in the air increase in range of 2 to 9 times, the most probable explanation is that ammonium persulfate reagent was less stale than potassium persulfate.
The effect of increase of air flow is still not pronounced- for J/K pair the 31.8 m^3/h mode is 1.02 times higher, for L/M pair the 45.9 m^3/h mode is 1.20 times higher and for N/O pair the 31.8 m^3/h mode is 1.08 times higher. However, when divided by the volume of the air passed through, the slower air flow is always preferred for stronger depression of air flow.
Contrary to the results of potassium persulfate the increase of duration of the experiment and concentration of working solution both improve the absorption of the NO_x (figure 7) which coincides with the expected results. Prolonged experiment duration allows capturing more ions, without affecting the efficiency (approximately same level of NO_x concentration depression in the air (table 3). Higher concentration increases the capacity of absorbing and the equilibrium of the reaction, allowing stronger formation of nitrate ions.
These observations suggest that absorbing efficiency may be improved and regulated by working parameters, which will allow further optimization for developing the practical applications of this method of capturing NO_x gases. Still, overall low efficiency compared to theoretical capacity suggests that the same previously suggested improvements are needed: increasing reactivity of the components by introducing catalytic mechanisms and introducing moisture resupplying to the beads.
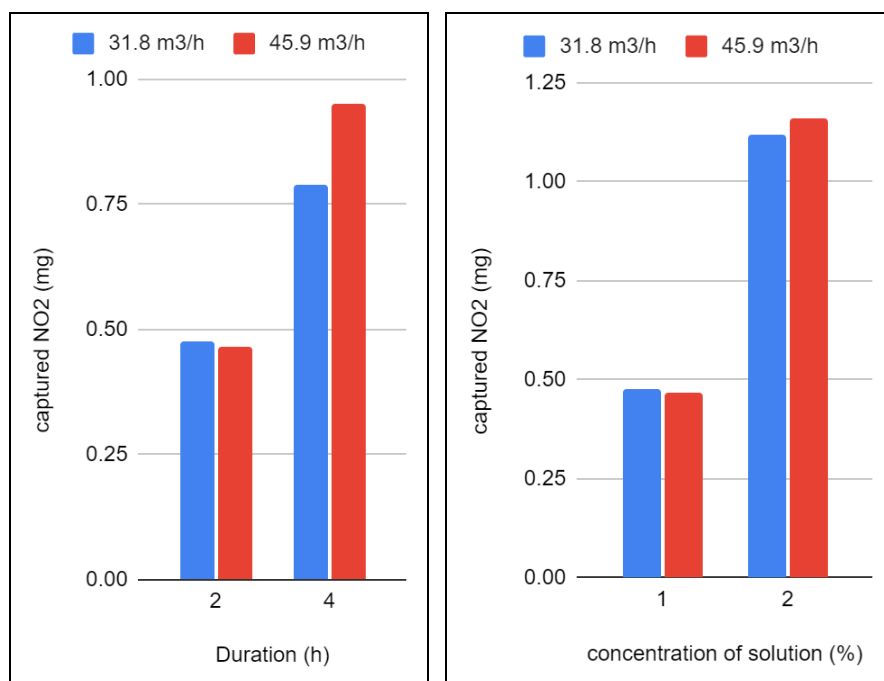
Figure 7. a) The absorption of NO_2 vs the duration of experiment, cb) The absorption of NO_2 vs the concentration of the working solution.

Conclusion

The experiments demonstrated that it is possible to capture NO_x gases from the atmosphere and convert them to nitrate ions, as well as implemented the method in a compact device that can be developed as or integrated into small household appliances. However the effect of the varying parameters (power and duration of air flow, amount of wet beads on the cartridge, the concentration of the reagents in the working solution) were not established to state a certain relationship with the absorbing capability, the general outline is that increase of the duration of the experiment decreases the efficiency (due to enhancing the evaporation), and increase of the packing improves the efficiency due to increase of the contact area and resistance towards evaporation. The effect of increased concentration of the solution or air flow appear inconsistent and possibly having no overall effect on the efficiency of NO_x absorption. Finally the extremely small efficiency for all samples, regardless the conditions (generally $\cong 0.1$ % of theoretical NO_x conversion capacity) requires the attention and development of certain improvement to the concept in order to be practically applicable, the most important direction would be increase of oxidation activity (by modulating suitable conditions and introducing new reagents and catalysts) and decrease of the rate of evaporation (by limiting the air flow rate, increase the ability of silica gel beads to absorb more solution and introducing an efficient method for moisture resupply).

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