Adsorption of ammonia on treated stainless steel and polymer surfaces

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Abstract. Adsorption of dynamically diluted ammonia at part-per-billion to low part-per-million concentrations in dry nitrogen was studied with treated and non-treated stainless steel and polymer test tubes. The treatments included electro-polishing and two types of coatings based on amorphous silicon. Cavity ring-down spectroscopy with an external cavity diode laser operating at the near-infrared wavelength range was used to monitor the adsorption process in real-time in continuous flow conditions to obtain quantitative assessment of the adsorptive properties of the studied surfaces. The investigated polymers were all less adsorptive than any of the treated or non-treated stainless steel surfaces. Some of the commercial coatings reduced the adsorption loss of stainless steel by a factor of ten or more. Polyvinylidene fluoride (PVDF) was found to be superior to the four other studied polymer coatings. The number of adsorbed ammonia molecules per surface area obtained in different ammonia gas phase concentrations was found to follow a Langmuir-Freundlich isotherm for stainless steel and Teflon surfaces. The time behavior of the adsorption-desorption process occurring in the time scale of seconds and minutes was simulated with a kinetic model.

Keywords: adsorption, ammonia, cavity ring-down spectroscopy, fluoropolymers, stainless steel, trace gas measurements

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1. Introduction

Ammonia (NH_3) is an abundant gaseous pollutant in the atmosphere where it contributes to acid deposition, eutrophication and secondary particulate aerosol formation [EEA2011, Korhonen1999]. Its normal atmospheric mixing ratio varies from below one part-per-billion-by-volume (ppbv) to more than ten ppbv [Whitehead2007], but the concentration may rise to part-per-million-by-volume (ppmv) levels in heavily contaminated areas [Shah2006a]. Ammonia is mainly produced by agricultural activities linked to animal manure and fertilizers [vanderHoek1998] but also by traffic and industrial processes [Sutton2000]. NH_3 is also an important indoor air contaminant [Järnström2008] and a potential biomarker in human breath [Schmidt2013].

The National Emission Ceilings (NEC) directive (2001/81/EC) covering four air pollutants including NH_3 has set binding emission ceilings to be achieved by each member state by 2010 and not to be exceeded thereafter [Directive2001]. This necessitates traceable measurement methods to reliably quantify the prevailing NH_3 levels. Gas phase NH_3 concentration can be measured with *e.g.* acid scrubbers, filter packs, denuders and optical methods [Shah2006a]. Metal-oxide, catalytic and conducting polymer NH_3 sensors used in ammonia analysis are reviewed in [Timmer2005] and selected inter-comparison studies are presented in Table 3 of [Shah2006a]. A field inter-comparison of eleven atmospheric ammonia measurement techniques can be found in [vonBobrutzki2010]. Furthermore, real-time gas phase NH_3 measurement methods are compared in [Schwab2007]. The overall correlation between different methods is generally satisfactory but their inter-correlation tends to worsen at low concentrations. Inlet tubing length and filters, for example, greatly affect the accuracy and time-response of the NH_3 measurement. Because the variation in the measured concentrations is large, no single apparatus is suitable for all applications, and not all methods are appropriate for extremely low concentrations. Ammonia is a challenging reactive gaseous compound due to its high water (H_2O) solubility and polarity. The quantification is strongly affected by water condensation and adsorption/desorption effects occurring on the surfaces of the sampling and detection instrumentation. Accurate and reliable measurement data cannot be obtained if such effects are not properly investigated and understood in the concentration levels relevant to atmospheric air quality monitoring.

Some studies on the adsorption of NH_3 on various metal, glass and polymer surfaces have been performed. Photoacoustic spectroscopy (PAS) was used for testing several materials in [Hennigsen1997] and [Melander1999] in which the ammonia concentrations entering and leaving two to three meter long tubes with inner diameters of 4 mm under low-flow (30 standard cubic centimetres per minute, sccm) conditions were compared. Polished and unpolished stainless steel (SS), quartz, pyrex, polytetrafluoroethylene (PTFE) and perfluoroalkoxy (PFA) surfaces were investigated and the studied gas phase NH_3 concentration varied between 0.5 and 50 ppmv. The researchers used two photoacoustic (PA) cells in both ends of the test tubes to measure the gas phase concentration and showed that the adsorption of ammonia leads to a considerable time delay of the signal in the second cell. They found that the surface coverage tends to zero with decreasing concentration for pyrex, quartz and the polymer surfaces whereas for stainless steel a sizeable adsorption persists even at the lowest studied concentrations. The adsorption on electro-polished SS was further observed to be larger than on non-treated SS. Schmol *et al* used PAS to investigate the effects of adsorption processes on the response time and accuracy of NH_3 detection under stopped and continuous flow conditions [Schmol2001]. The adsorption was investigated within PA cells made of brass and polypropylene (PP). Their observations established that stopped flow measurements of NH_3 are never reproducible, and reliable measurements require continuous-flow conditions. Furthermore, the authors provide a short list of recommendations to substantially reduce the adsorption effect in trace NH_3 quantification.

Ellis *et al* studied the effect of humidity and heat on the adsorption of NH_3 on PFA sampling line using a quantum cascade tunable infrared laser differential absorption spectrometer (QC-TILDAS) at concentrations of 30-1000 ppbv in humid and dry conditions [Ellis2010]. They modelled the decrease of gas phase NH_3 concentration (due to adsorption) by a bi-exponential decay where, according to the authors, the first, fast decay corresponds to gas exchange time of the system and the second, slow decay corresponds to adsorption in the inlet, sampling line and sample cell. On the basis of the model, the authors deduced that the relative contribution of adsorption is higher at lower concentrations, under humid conditions and without heating. A similar bi-exponential decay model was employed in [Whitehead2008] to compare five meter long inlet tubes (inner diameter of 4.32 mm) made of plain SS, Silcosteel (current trade name SilcoNert^{TM} 1000, SilcoTek Corporation) coated SS tubes, PTFE, and polyethylene (PE). The NH_3 concentration in the experiments was 100 ppbv, and the authors utilised the value of the first, short (corresponding to fast processes) time constant to assess the strength of adsorption and desorption. They found that the polymer tubes, which were both quite similar in their adsorptive qualities, outperformed (less adsorption) both Silcosteel coated and plain SS tubes although the coating clearly improved the adsorptive quality of SS.

Shah *et al* [Shah2006b] evaluated five different polymer tubing materials (PTFE, PFA, fluorinated ethylene propylene (FEP), high density polyethylene (HDPE) and polyvinylchloride (PVC); Teflon is often used to refer to the three firstly mentioned fluorinated polymers although it is also used exclusively as a trade name for PTFE; moreover, acronym TFE is also occasionally used to designate PTFE Teflon) for ammonia adsorption at two nominal concentrations (1 ppmv and 10 ppmv) at room temperature (297 K). They used 2.5 m long tubes with an inner diameter of 4.32 mm and a gas scrubber as the detection method. The authors did not find statistically significant differences in NH_3 adsorption between different tubes. They further conclude that even the cheapest PVC tube, which had the lowest adsorption, might be the best option under the conditions of their study. Mukhtar *et al* measured gas phase NH_3 concentration at the inlet and outlet of PFA (referred to as Teflon in the paper) and low density polyethylene (shortened as LDPE or PELD) tubes using a chemiluminescence analyser [Mukhtar2003]. The tubes were 15 or 46 meters long, had an inner diameter of 3.2 mm and the measurements were performed at six nominal concentrations between 2 and 35 ppmv at two different temperatures (298 and 310 K). Ammonia adsorption on LDPE was found to be significantly higher than the adsorption on PFA. Adsorption (the difference between the inlet and outlet mixing ratios) on PFA was independent of the gas phase concentration or temperature. The adsorption on LDPE, on the contrary, increased with the gas phase concentration and temperature.

In the current study, we have systematically assessed the adsorption of gas phase NH_3 on various surface materials. The studied stainless steel based materials were non-treated SS316L, electro-polished SS316L, and three commercial (SilcoTek Corporation) coating materials deposited on SS 316L substrate: SilcoNert^{TM} 1000, SilcoNert^{TM} 2000, and Dursan^{TM}. The investigated polymers were PTFE, PFA, FEP, PELD (low density polyethylene) and PVDF (polyvinylidene fluoride). The work was performed using a laser spectrometer based on cavity ring-down spectroscopy (CRDS) operating at the 1.5 µm spectral region. The time-resolved (< 1 s) adsorption of ammonia was studied in controlled conditions using test tube (TT) samples with the tested surface materials. The effects of gas phase NH_3 concentration, temperature and H_2O content of the experiment were investigated. The observed results were fitted to an adsorption isotherm and attempted to be explained by a simple kinetic model. The gathered information facilitates the choice of materials and procedures to reduce the measurement time and uncertainty owing to adsorption effects in atmospheric trace gas NH_3 measurements.

2. Experimental setup and measurement protocol

2.1. Cavity ring-down setup

Cavity ring-down spectroscopy is a highly sensitive absorption technique where a laser beam interacts with an optical cavity usually consisting of two highly reflective mirrors [Romanini1997, Berden2009]. We used a home-built continuous-wave CRD spectrometer based on a tunable external cavity diode laser (ECDL). The details of the spectrometer are given in [Schmidt2010] and a simplified schematic diagram of the setup is presented in Figure 1. A ring-down cell (RDC) made of stainless steel and with a length of 50 cm and a volume of 40 cm^3 was used in the measurements. The RDC is coated with SilcoNert^{TM} 2000 coating. At 1000 sccm gas flow rate and 100 mbar pressure, the theoretical gas exchange time of the cavity is about 240 ms. During the measurements, the high reflectivity mirrors had a ring-down (RD) time constant between 140 and 160 µs. The sensitivity (minimum detectable absorption with a single exponential decay) [Lehmann2009] of the spectrometer is $\sim 2 \times 10^{-10}$ cm^{-1}.

To measure the mixing ratio of gas phase NH_3 prior to each adsorption measurement (see Chapter 2.3 for the measurement protocol), the laser wavelength was scanned over the region 6548.45 - 6549.05 cm^{-1}. A typical spectrum for a low (90 ppbv) NH_3 concentration is shown in Figure 2. The spectrum shows three strong lines which all belong to NH_3 [Webber2001]. Fifty RD events were averaged for each spectral point and altogether 200 spectral points were recorded using a pressure of 100 mbar. Three Voigt profiles were fitted to the spectrum using the peak fitting software Fityk [Fityk]. The estimated detection limit (3 times the standard deviation, 3σ) for NH_3 was ≤ 1 ppbv for these measurements.

High time resolution is needed to follow the dynamics of adsorption in real time. For this reason, the laser wavelength was kept fixed (without active stabilization) at the top of the NH_3 absorption line at 6548.79 cm^{-1}. The line strength of this transition is 1.667×10^{-21} cm/molecule at 296 K [Webber2001]. The specified wavenumber was continuously monitored using a wavemeter (EXFO, WA-1500), which has a frequency uncertainty of 40 MHz (0.0013 cm^{-1}). The full-width at half maximum (FWHM) line width of the NH_3 transition is about 0.032 cm^{-1} at the measurement pressure of 100 mbar. Altogether 25 RD events were averaged for each point and the average repetition rate for the RD events was about 50 Hz. Thus, the time resolution of the experiment was about 0.5 s. The detection limit for these measurements was calculated (from > 20 successive measurement points) to be ~ 1.5 ppbv (3σ) for low concentrations ($\leq$ 500 ppbv). In the highest measured concentration (~ 9 ppmv), the noise in the ringdown signal corresponded to ~ 15 ppbv (3σ).

2.2. Gas generation and test tube setup

The required NH_3 gas phase concentration was generated by dynamic dilution of a bottled NH_3 standard in nitrogen (AGA). Calibrated mass flow controllers (MKS Inc.), and (usually) by instrument nitrogen (specified H_2O content of < 3 ppmv and NH_3 content of < 1 ppbv) (AGA). The concentration of the standard was verified to be 8750 ppbv by the CRDS setup and it was within the specifications provided by the manufacturer.

A schematic diagram of the gas generation and TT setup is presented in Figure 3. The gas generating line and its connection to the RDC was made of PTFE tubing, except for the connectors, valves, mass flow controllers and the input appendix (short and narrow tube made of SS) of the RDC. The TT was directly connected to the appendix of the RDC (which was coated with SilcoNert^{TM} 2000) with a short (about 70 cm) PTFE tube.

2.3. Measurement protocol

The measurement protocol consisted of three successive stages (1-3).

1. The test tube was flushed with indoor air for at least an hour. Indoor air (with H_2O content of $\leq$ 1% by volume and NH_3 content of about 5 ppbv) instead of pure nitrogen gas was used because the H_2O molecules in indoor air aid to remove NH_3 from the TT and the rest of measurement setup surfaces. Without the water “treatment”, it is not possible to remove the adsorbed NH_3 in a reasonable time and produce reproducible results on two successive adsorption measurements. Then the TT was flushed with pure nitrogen gas for at least 30 minutes to remove H_2O and the remaining adsorbed NH_3 of the system. The NH_3 concentration was ~ 1 ppbv and the H_2O content 20 - 30 ppmv after the flushing procedure. The H_2O vapour mixing ratio was measured with the current CRDS setup using a line at 6549.763 cm^{-1} with a line strength of 3.313×10^{-24} cm / molecule at 296 K [Macko2004]. Care was taken to ensure that the flushing time for all test tubes with different surface materials was the same and always exceeded the minimum time specified above. Removing the adsorbed NH_3 and H_2O completely *i.e.* achieving the specified NH_3 and H_2O concentrations of the “dry and pure” nitrogen gas would require considerably longer flushing times, up to days. Furthermore, even a minor and undetectable leak somewhere in the vacuum system leads to ppmv level of H_2O contamination from the indoor air. This possibility cannot always be ruled out. The flushing time was therefore a compromise between a reasonable total measurement time (at least one measurement per day) and minimal NH_3 and H_2O contamination of the TT. Heating of the test tubes in an oven was also tested as an alternative to the flushing procedure but because it did not produce superior results and was found to be impractical, this option was abandoned. At the end of the first phase, the nitrogen gas was switched to flow through the by-pass line depicted in Figure 3 using electronic 3-way valves (Bio-Fluidics). Thus, after this stage, a clean TT contained pure nitrogen at a pressure of about 150 mbar (the pressure behind the RDC and further away from the vacuum pump is always higher than the pressure of 100 mbar in the RDC).

2. The ring-down cell and the rest of the vacuum line excluding the TT were exposed to a desired dynamically diluted NH_3 concentration utilizing the by-pass line. Depending on the NH_3 concentration, from one to two hours was usually required for the RD signal to adequately stabilize to the studied concentration (absolute signal stabilization would require considerably longer times, even days and even if these longer stabilization times were used, other long term effects, such as drifting of the mass flow controllers and gas

bottle regulator pressures would step in). This time is necessary for all the surfaces of the vacuum line to be saturated with NH_3. After stabilization, the gas phase concentration of NH_3 in the current measurement was measured by scanning the laser frequency over the spectral region mentioned in Chapter 2.1.

3. After the system had been cleaned and stabilized, and the initial gas phase concentration determined, the actual time-resolved adsorption measurement took place. This stage consisted of three phases (a-c). a) The NH_3 gas flow by-passed the (pure N_2 containing) TT; this phase took about 5 minutes. b) The NH_3 flow was switched to pass through the TT with the help of the 3-way valves; this step was instantaneous and results in a fast decrease of the measured NH_3 concentration in the RDC. The sudden concentration drop is due to the rapid gas exchange in the unexposed TT filled with pure N_2 and fast NH_3 adsorption on the surface of the TT. c) The NH_3 concentration signal was slowly recovering and it finally reached the same level as in phase 1; this phase took up to about 15 minutes depending on the type of the TT and NH_3 concentration.

The measurement protocol was repeated using different surface materials. The same TT was used for three consecutive measurements with a given surface material but tests with tubes belonging to other manufacturing batches were also performed. For comparing the total adsorption of different SS and coated SS surfaces, NH_3 gas phase concentration of about 425 ppbv and a total flow rate of 1000 sccm were employed. Three consecutive measurements with the same experimental conditions were performed without touching the setup except actions required for flushing it. For SS316L surface, the gas phase NH_3 concentration was varied between 100 and 8750 ppbv using flow rates between 200 and 2000 sccm. In another experiment, the SS316L TT temperature was raised stepwise from 295 to 333 K to test the temperature effect on adsorption at a NH_3 gas phase concentration of about 425 ppbv. These measurement were performed only once in the same conditions. The TT length was 30 cm and inner diameter 4 mm in all the above-mentioned measurements. For the comparison of the total adsorption in various polymer surfaces, non-diluted bottled NH_3 standard with a concentration of 8750 ppbv was used. Additionally, the TT length was increased to 200 cm and a flow rate of 200 sccm was used. The increase of NH_3 concentration and TT length were necessary to observe the adsorption phenomenon with an adequate signal-to-noise ratio for all of the studied polymers in similar conditions.

The measurement temperature in the RDC was the room temperature (295 K). This was also the estimated temperature of the NH_3 gas in the experiments when the TT itself was heated. Small changes in the room temperature (± 1 K) occurred during the measurement campaign but this has only a minor (~ 1%) effect on the retrieved concentration, and it has not been taken into account because it is well within the experimental uncertainty.

3. Results

3.1. General remarks

In Figure 4, the time-evolution of the recorded gas phase NH_3 concentration in an experiment where the concentration was changed in a step-wise fashion (step size ~ 90 ppb and 20 min) by diluting a bottled NH_3 standard with indoor air (H_2O content ~ 0.6%). Careful inspection of the data presented in the figure reveals several phenomena, which are ubiquitous in the context of adsorptive molecular species such as NH_3. First, if no adsorption were present, the concentration steps would be square and evenly-spaced and the corresponding observed concentrations should be the same on the both sides of the concentration “ladder”, which is clearly not the case. Second, the shape of the “ladder” form is skewed: the decrease of concentration on the right hand side of the figure is always steeper than the respective increase of concentration. Third, the calculated (on the basis of the dilution ratio) NH_3 concentration value is closer to the right hand side concentration at the end of each 20 minute step. This means that it is easier to remove than to enrich NH_3 molecules on a surface, and the rise time from 0 to 90 percent of actual concentration in an experiment is slower than the corresponding decay time from 100 to 10 percent.

3.2. Calculation of total adsorption

Figure 5 shows the time evolution of the adsorption signal during the measurement protocol. There are two processes which contribute to the observed loss of gas phase NH_3 molecules: gas exchange (within the TT) and adsorption (on the surface of the TT). Therefore, in the figure, the fast decrease of the signal can be associated with gas exchange and "fast adsorption component" of NH_3 and the slow re-increase with "slow adsorption component". The number of "lacking" molecules in the TT due to gas exchange, N_g, can be calculated from the ideal gas law. The number of adsorbed molecules N_{ads} is achieved by reducing N_g from the total number of the lost molecules N_{loss} obtained by integration (see Figure 5):

$$N_{ads} = N_{loss} - N_g = \int_{t0}^{\infty} \frac{\partial N(t)}{\partial t} \mathrm{d}t - N_g \, .$$

where t is time, t_0 is the time point when the adsorption process starts and N is the number of NH_3 molecules. The total number of adsorbed molecules per unit surface area, N_s, is then obtained by division of the surface area of the TT.

3.2. Treated and non-treated stainless steel surfaces

Table 1 presents the results obtained for the SS and treated SS surfaces. The NH_3 concentration of the measurements was about 425 ppbv and the gas flow rate was 1000 sccm. The TT pressure was 176 mbar and temperature 296 K. The variation in three consecutive measurements performed with an identical setup and in the same experimental conditions using the same TT was always within 20%. In Figure 6, a typical example of the reproducibility of two consecutive measurements is presented. The calculated standard deviation is in the case of the lowest adsorbing coating, SilcoNert™ 2000, considerably smaller than the stated 20%. However, the actual error in the adsorption value is estimated to be about 3×10^{12} molecules cm^{-2}, which is about 50% of the observed total adsorption. This stems mainly from the uncertainty in the process of integration in such a case of modestly adsorbing coating and low gas phase concentration. This induces a possibility for a systematic error bigger than 20%.

Table 1. Adsorption of ammonia N_s (10^{12}molecules/cm^2) on SS surfaces.

SS / coating	N_s	σ^a
SilcoNert 2000	5.7	0.6
SilcoNert 1000	14.6	0.9
EP SS316L[b]	72	11
Dursan	101	5
SS316L	138	21

[a] σ is the standard deviation of the number of adsorbed molecules N_s.
[b] EP = electropolished

Conspicuous adsorptivity inconsistencies of about a factor of two were occasionally observed also for exactly the same individual SS316L tube with a reassembled (but schematically identical) setup in measurements performed a few months apart, despite the fact that no obvious problems in the setup or in the measurement protocol (*e.g.* obvious leakages or sudden pressure changes due to irregular closure or opening of the 3-way valves) was observed. A definite explanation for such a behavior is currently not known. Possible explanations include a leakage of indoor air (leading to H_2O contamination) to the TT during the saturating phase of the protocol or, more likely, variable H_2O content of the trace gas used in the measurements. Water plays an important role through competitive adsorption with ammonia, and the adsorption of NH_3 is observed to be strongly dependent on the H_2O concentration of the measurement (Figure 7). Because it was not possible to monitor the H_2O concentration in real-time with the current measurement set-up, the actual H_2O mixing ratio at the time of adsorption event of individual measurements is not exactly known. According to the data in figure 6, a change by a factor of two in H_2O concentration, which is conceivable, even though the same protocol was always employed, might lead up to a factor of two change in the recorded NH_3 adsorption. In order to obtain identical conditions, the whole measurement setup was leak-tested before a series of the three consecutive measurements. However, because our simple leak-testing procedure is not impeccable and it is not possible to monitor the pressure changes in the TT during the saturation phase, minor and variable leaks may have existed during the protocol. For these reasons, care should be taken in interpreting the results presented in Table 1 and in estimating their uncertainty. The adsorption values should rather be considered as minimum values at a H_2O concentration of about 20 ppmv which was the smallest concentration achieved.

Despite these insufficiencies, our results compare well with the literature values obtained for similar coatings [Hennigsen1997, Melander1999] considering the measurement conditions (higher gas phase concentration was used in the these studies) and match qualitatively with the data provided by the manufacturer of the silicon-based coatings [SilcoTek, Barone2012]. In [Hennigsen1997, Melander1999], the H_2O concentration of the trace gas was not quantified and phrasing "dry" was used for apparently water-free conditions. However, the authors in [Melander1999] have observed that ammonia can almost completely be degassed at room temperature by using H_2O containing gas flow. This notion corroborates our observations and the data presented in Figure 7. The fact is also the foundation of our TT cleaning procedure.

In [Melander1999], at a concentration of one ppmv, total adsorption of 2×10^{14} molecules/cm^2 for SS316 was observed. This matches well with our result of 1.4×10^{14} molecules/cm^2 for SS316L taking into account the fact that in their measurement the mass concentration was four times higher due to increased NH_3 concentration and pressure. Electropolishing does not seem to improve much, if at all, steel's adsorptive properties. Electrolysis used in the electropolishing process simply removes atoms from the SS surface but does not change the surface qualitatively. Melander *et al* observed, analogously to our results, more adsorption on electro-polished SS316 than on non-polished SS304. They, however, compared two different SS types which likely has an effect on adsorptivity (there is 2 % of molybdenum on SS316 which improves its corrosion resistivity; otherwise these two SS types are similar). On the other hand, in the current study, direct comparison is also compromised because the non-polished and polished SS test tubes were from different batches (and therefore have possibly somewhat different composition) and due to possible reproducibility problems addressed earlier.

SilcoNert^{TM} 2000 coated surface was the least adsorptive of the studied metal-based materials with an improvement by a factor of 25 over non-treated SS316L. SilcoNert^{TM} 2000 has two layers: a hydrogenated amorphous silicon (a-Si) layer on plain SS substrate and an extra alkyl layer on top of the a-Si layer for capping the remaining active adsorption sites [U.S. Patent]. This additional layer may also explain the three-fold superiority of SilcoNert^{TM} 2000 over SilcoNert^{TM} 1000 which has only a single a-Si layer. For quartz surface, Melander et al measured total adsorption of about 1×10^{13} molecules/cm^2 using a corresponding NH_3 concentration. This is approximately the same value as we have observed for our "quartz" surfaces, SilcoNert^{TM} 1000 and SilcoNert^{TM} 2000 (both of these coating are often referred as quartz). There is not enough information available from the manufacturer of the possible reasons for the third coating produced by SilcoTek Corporation, Dursan^{TM}, being clearly more adsorptive than the other studied SilcoTek coatings. In any case, this observation has also been confirmed by real-time proton-transfer-reaction mass spectrometry (PTR-MS) studies performed elsewhere [Barone].

When the SS316L TT temperature was increased stepwise from 295 to 333 K, there was a decreasing trend in adsorption, as expected. However, the overall change in the total adsorption was surprisingly small and almost within the experimental uncertainty of 20 %. This is an interesting result in the sense that the adsorption effects of NH_3 are often claimed to be considerably alleviated even by a relatively small increase of temperature, especially in humid samples. This superficially contradictory (with respect to our study) observation can be explained by the role of H_2O (which is almost always present at percent level in *e.g.* atmospheric trace gas analysis if no action is taken to remove it): even minimal H_2O condensation results in NH_3 dissolving from the gas phase and reducing its apparent concentration. This happens every time the relative humidity reaches 100 % anywhere in the sampling and recording apparatus.

In addition to the surface materials listed in Table 1, adsorption on plain copper surface was measured to be about double ($\sim 2.5\times10^{14}$ molecules/cm^2) to that of SS under similar conditions. For comparison, Schmol et al observed higher but comparable adsorption of $\geq 4.4\times10^{14}$ molecules/cm^2 for a brass surface in a *desorption* study employing a considerably higher NH_3 concentration (61 ppmv) than in our experiment [Schmol2002].

3.3. Polymer surfaces

Polymer surface adsorption results are displayed in Table 2. The NH_3 concentration of the measurements was about 8750 ppbv and the gas flow rate was 200 sccm. The TT pressure was 119 mbar and temperature 296 K. The standard deviation of three consecutive runs was within 25 % in these measurements. However, in the case of the least adsorbing polymer, PVDF, the actual maximum error in the total number of adsorbed NH_3 molecules is estimated to be as much as 50% corresponding to 5×10^{11} molecules/cm^2. This is due to the low adsorptivity of this material in relation to the sensitivity of the measurement, which causes uncertainty in the integration of N_{loss}. Furthermore, as with the SS coatings, the absolute H_2O concentration is not exactly known, and therefore the uncertainty in the measurements could be larger than the given standard deviation. Similar large variations in adsorption as in the case of SS surfaces were on the other hand never observed which gives more confidence on the equality of the H_2O concentration in the studies and the correctness of the results. In any case, the N_s values should, again, rather be taken as minimum values than absolute quantities. In the case of polymer surfaces, where adsorption is, in general, less significant than in the case of SS surfaces, the effect of gas exchange is considerable. For example, for PVDF, the gas exchange constitutes ~ 70% of N_{loss}. Once again, despite these effects, our results for PTFE and PFA match those of [Melander1999] taking into account measurement conditions. They, however, did not observe any difference between those two very similar fluoropolymers.

Table 2. Adsorption of ammonia N_s (10^{12}molecules/cm^2) on polymer surfaces.

Polymer	N_s	σ^a
PVDF	1.0	0.1
PELD	4.4	0.6
PTFE	7.5	1.9
FEP	8.6	0.3
PFA	13.9	1.0

$^a\sigma$ is the standard deviation of the number of adsorbed molecules N_s.

The least adsorbing polymer is, according to our studies, PVDF. We have two potential explanations for this observation. First, PVDF has both hydrogen (H) and fluorine (F) atoms attached to its carbon chain, and there is a possibility of hydrogen bonds between H and F atoms belonging to different polymer branches. This possibly makes the polymer more inert against adsorption due to decreased surface energy. The second explanation stems from the fact that PVDF is able to uptake (absorb) more water than the other fluoropolymers listed in Table 2 [Hansen2001]. This explanation is counterintuitive in the sense that while recording the ammonia concentration in a trace gas containing several percent of water vapor, we have consistently in appropriate circumstances, *i.e.* at dew point, observed *absorption* (dissolution) of NH_3 to the condensed H_2O droplets on the surfaces of the sampling equipment. Consequently an apparent large decrease in the recorded NH_3 concentration is observed. However, it has also been confirmed in this study that *adsorption* of H_2O on any surface effectively suppresses NH_3 adsorption. Therefore, it is not unconceivable that H_2O absorption into the polymer without the condensation effect (which is not possible in the temperature, pressure and H_2O concentration of the adsorption experiment) is associated with a high concentration of H_2O also on the surface (adsorption). This inhibits the adsorption of NH_3 molecules. Intriguingly, Shah *et al* discovered that another polymer, PVC, which has a similar, relatively high water absorption propensity as PVDF, had lower adsorptivity than the other studied polymers [Shah2006b]. It should be noted, however, that the possible adsorptive edge of PVDF over the other studied polymers in dry conditions might be lost when the H_2O concentration of the measured trace gas becomes high, as happens in the case of actual atmospheric conditions.

We observed similar adsorptivities for all Teflon polymers (PTFE, PFA, FEP) although PFA reproducibly produces almost a factor of two higher values than PTFE or FEP. This matches the studies of Shah *et al* who found no statistically significant difference between PTFE, PFA, FEP and HEPD/PEHD (high density polyethylene). In contrast to our results, Mukhtar *et al* [Mukhtar2003] observed that PELD is more adsorptive than PFA. The authors also claimed that adsorption on PFA does not depend at all on NH_3 gas phase concentration. On the light of the adsorption isotherm presented later in this paper, the latter claim seems untenable.

4. Model / adsorption isotherm

Adsorption isotherms are used to model the adsorption as a function gas phase concentration. The two traditional and the most widely used isotherms were proposed by Langmuir [Langmuir1918] and Freundlich [Freundlich1909]. The Freundlich isotherm is purely an empirical formula describing the adsorption phenomenon especially at small concentrations (pressures) with no theoretical justification. The Langmuir isotherm is, on the contrary, derived theoretically based on two simple main assumptions: 1. all adsorption sites are equivalent and can accommodate at most one molecule (therefore only a monolayer of adsorbate is possible) and 2. there is no interaction between the adsorbed molecules on adjacent sites. Although being theoretically elegant, the Langmuir isotherm often fails in higher concentrations where the theory predicts saturated adsorption independent of temperature.

The so-called Langmuir-Freundlich isotherm [Sips1948] combines Langmuir and Freundlich isotherms and has been employed successfully in current adsorption studies [Jeppu2012]…more text about adsorption isotherms and real-time modeling by Markus

5. Discussion and conclusions

Our results agree to a large extent with previous published investigations. The adsorption of NH_3 on plain and coated SS surfaces falls in the same rank order as the data presented in the literature or provided by the coating manufacturer. This happens despite the fact that the measurement methods (*e.g.* PAS, CRDS, chemiluminescence and PTR-MS) and protocols used to estimate the adsorptivity differ drastically. The common observation that polymers generally adsorp less NH_3 than stainless steel or even the best coated metal surfaces was also reinstated in this study. Due to the low adsorptivity of polymers in general, a comparison of our results to the literature is more ambiguous.

On the basis of their model, Whitehead *et al* ranked their studied polymer and stainless steel surfaces in the order of increasing adsorption: PTFE = PE < SilcoNert^{TM} 1000 < non-treated SS [Whitehead2008]. This is exactly the rank order of our study with a trivial side note that we found a small difference (same order of magnitude as the maximum measurement error) between polyethylene (PELD in our case) and PTFE. The order is also in accordance with other studies where both treated and non-treated stainless steel and polymer surfaces have been investigated [Melander1999, Barone]

The relative contribution of adsorption to the measurement uncertainty of gas phase NH_3 concentration is higher at lower concentrations as corroborated by the observations in [Ellis2010]. However, on the contrary to their further claim that added humidity would increase the surface interactions (more NH_3 adsorption), we have established that NH_3 adsorption is decreased as H_2O content is increased. This effect is demonstrated in Figure 7. The apparent disagreement between the studies can simply be explained by H_2O condensation on the measurement system of [Ellis2010]. Indeed, the authors of the study observed a significant decrease of "adsorption" when heating the tested PFA line to 313 K and they further hypothesize that the temperature change might reduce the H_2O condensation within the sampling line. In our separate non-published studies we have also observed that increasing the temperature of a polymer might actually increase its adsorption as in [Mukhtar2003].

Although the measurement was performed in real-time, the adsorption was not recorded exactly at the point of adsorption (*i.e.* inside the TT). This induces not only a certain time lag in the observed gas phase NH_3 concentration but creates also a potential problem in the quantification of the adsorptivity. During the adsorption measurement, and especially at and immediately after the time point when the three-way valves are switched from the by-pass to the test tube position, there is a dynamic interaction between the TT and the rest of the vacuum system including the RDC. Immediately after ammonia begins to flow through the TT, there will be less NH_3 molecules reaching the RDC due to the gas exchange and adsorption. This means that the adsorbed NH_3 molecules in the saturated surface of the RDC (and elsewhere in the system) will begin to desorp (this is the net effect – both adsorption and desorption processes are evidently always present) to the gas stream. When a new equilibrium (within the whole vacuum system now including also the TT) is again reached within tens of seconds at a lower NH_3 gas phase concentration, the molecules begin to re-adsorb to all surfaces. As a consequence, a rounding effect in the "adsorption valley" (see Figure 4) is observed. Exactly the same concentration as in the beginning is eventually restored after about ten minutes, although somewhat later in time as compared to a hypothetical situation where this interaction between the TT and the rest of the system would not be in force. Fortunately, this interaction does not affect the total measured number of adsorbed molecules because exactly the same number of molecules is re-adsorbed that has initially been desorbed. The interaction within the vacuum system effects only on the time behavior of the observed NH_3 concentration and consequently its real-time modeling. To damp these effects, and to observe the actual real-time profile of the adsorption process in the TT, we tested an extra by-passing PTFE tube to create a faster total flow rate in the RDC than in the TT (see Figure 3). Measurements with this setup confirmed that the within vacuum system interaction effect to the total adsorption is negligible as expected and its contribution on real-time measurements is clearly observable but induces no practical limitation in the real-time modeling; the challenges in the latter are of different origin as will be discussed later.

On few occasions, an identical and apparently fault-free setup and an unchanged measurement protocol produced inconsistent results exceeding the experimental uncertainty. Explanations include variation in the H_2O content of the N_2 gas used for dilution and potential contamination of the test tubes by a minor leakage during the saturation phase of the experiment. Fully reproducible (10 - 20 % standard deviation) adsorption measurements would require real-time monitoring and tight control of these constraints, which is not possible with the current measurement setup and protocol. For example, considerably longer flushing times (days), robust and frequent leak-testing and real-time vacuum control would be required. In fact, it is not feasible to monitor the phenomena occurring in the test tube without compromising the adsorption measurement itself. One solution to this problem could be to measure both the NH_3 and H_2O concentrations simultaneously in real time.

Speculation about modeling here

The results of the current study are qualitatively equivalent to the ones obtained in other meticulously performed literature investigations. In many of them, considerably less complicated measurement setups, straightforward protocols and short waiting times were used as compared to our study. In the light of this, it is, in most cases, sufficient to render to such simple procedures. For example, in choosing the right sampling tube material for NH_3 or other adsorptive trace gas analysis, it is often enough to connect a selection of potential long (several to tens of meters) sampling tubes to the analyzer, allow the analyzed trace gas to flow via the tested tubing, simply follow the time evolution of the recorded signal and rank the tubes on the basis of this basic information. Rather than accentuating the finesse of the adsorption measurement setup and protocol itself, it is more important to ensure that the tests are performed in the same conditions (especially with the same water content) as what will be encountered in the actual trace gas studies such as atmospheric pollution measurement field campaigns.

However, despite the agreement between this study and most of the referenced literature, up to a factor of ten differences in the values of adsorptivity have been presented [Shah2006b, Mukhtar2003]. The competitive adsorption between ammonia and water might explain many of these inconsistencies. Usually no information beyond a statement "dry" or "zero gas" has been given about the H_2O concentration in the adsorption studies even though the actual H_2O mixing ratio has been in all likelihood in the ppmv range. In our opinion, it is meaningless to compare the results of different studies (or results even *within* a study) without at least a rough estimate of the H_2O concentration of the NH_3 trace gas used in the adsorption measurement. The interaction between ammonia and water molecules calls for further and more detailed studies of this phenomenon.

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References

[EEA2011] European Environment Agency, *Ammonia (NH3) Emissions* (www.eea.europa.eu/data-and-maps/indicators/eea-32-ammonia-nh3-emissions-1/assessment-1)

[Korhonen1999] Korhonen P, Kulmala M, Laaksonen A, Viisanen Y, McGraw R and Seinfeld J H 1999 Ternary nucleation of H2SO4, NH3 and H2O in the atmosphere *J. Geophys. Res.* **104** 26349-53

[Whitehead2007] Whitehead J D, Longley I D and Gallagher M W 2007 Seasonal and diurnal variaitionon atmospheric ammonia in an urban environment measured using a quantum cascade laser absorption spectrometer *Water Air Soil. Pollut.* **183** 317-29

[vanderHoek1998] van der Hoek K W 1998 Estimating Ammonia emission factors in Europe: Summary of the work of the UNECE ammonia expert panel *Atmos. Environ.* **32** 315-6

[Sutton2000] Sutton M A, Dragosits U, Tang Y S and Fowler D 2000 Ammonia emissions from non-agricultural sources in the UK *Atmos. Environ.* **34** 855-69

[Järnström2008] Järnstöm H, Saarela K, Kalliokoski P and Pasanen A-L 2008 The impact of emissions from structures on indoor air concventrations in newly finishjed building – predicted and on-site measured levels *Indoor Built Environ.* **17** 303-22

[Schmidt2013] Schmidt F M Vaittinen O Metsälä M Lehto M Forsblom C Groop P-H and Halonen L 2013 *J. Breath Res.* accepted

[Directive2001] *Directive 2001/81/EC of the European Parliament and of the Council of 23 October 2001on national atmospheric ceilings for certain atmospheric pollutants* (eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2001:309:0022:0030:EN:PDF)

[Shah2006a] Shah S B Westerman P W and Arogo J 2006 Measuring ammonia concentrations and emissions from agricultural land and liquid surfaces: a review *J. Air Waste Manage. Assoc.* **56** 945-60

[Timmer2005] Timmer B Olthuis W and van der Berg A 2005 Ammonia sensors and their applications – a review *Sensors and Actuators* B **107** 666-77

[vonBobrutzki2010] von Bobrutzki *et al* 2010 Field intercomparison of eleven atmospheric ammonia measurement techniques *Atmos. Meas. Tech.* **3** 91-112

[Schwab2007] Schwab J J Li Y Bae M-S Demerjian K L Hou J Zhou X Jensen B and Pryor S C 2007 A laboratory intercomparison of real-time gaseous ammonia measurement methods *Environ. Sci. Technol.* **41** 8412-9

[Hennigsen1997] Henningsen J and Melander N 1997 Sensitive measurement of adsorption dynamics with nonresonant gas phase photoacoustics *Appl. Opt.* **36** 7037-45

[Melander1999] Melander N and Henningsen J 1999 A photoacoustic study of adsorption *Photoacoustic and Photothermal Phenomena: 10th International Conference* CP463 ed F. Scudieri and M. Bertolotti (New York: American Institute of Physics) pp 78-80)

[Schmol2001] Schmol A Miklos A and Hess P 2001 Effects of adsorption-desorption processes on the response time and accuracy of photoacoustic detection of ammonia *Appl. Opt.* **40** 2571-7

[Ellis2010] Ellis R A, Murphy J G Pattey E von Haarlem R O'Brien J M and Herndon S C 2010 Characterizing a quantum cascade tunable infrared laser differential absorption spectrometer (QC-TILDAS) for measurements of atmospheric ammonia *Atmos. Meas. Tech.* **3** 397-406

[Whitehead2008] Whitehead J D Twigg M Famulari D Nemitz E Sutton M A Gallagher M W and Fowler D 2008 Evaluation of laser absorption spectroscopic techniques for eddy covariance flux measurements of ammonia *Environ. Sci. Technol.* **42** 2041-6

[Shah2006b] Shah S B Grabow G L and Westerman P W 2006 Ammonia adsorption in five types of flexible tubing materials *Appl. Eng. Agric.* **22** 919-23

[Mukhtar2003] Mukhtar S Rose A J Capareda S C Boriack C N Lacey R E Shaw B W and Parnell Jr C B 2003 Assessment of ammonia adsorption onto Teflon and LDPE tubing used in pollutant stream conveyance *CIGR Journal* **5**

[Romanini1997] Romanini D Kachanov A A Sadeghi N and Stoeckel F 1997 CW cavity ring down spectroscopy *Chem. Phys. Lett.* **264** 316-322

[Berden2009] Berden G Engeln R ed 2009 *Cavity Ring-Down Spectroscopy: Techniques and Applications* (Chippenham:Wiley-Blackwell)

[Schmidt2010] Schmidt F M, Vaittinen O Metsälä M Kraus P Halonen L 2010 Direct detection of acetylene in air by continuous wave cavity ring-down spectroscopy *Appl. Phys.* B **101** 671-82

[Lehmann2009] Lehmann K K Berden G Engeln R 2009 *Cavity Ring-Down Spectroscopy: Techniques and Applications* ed G Berden and R Engeln (Chippenham:Wiley-Blackwell) p 9

[Webber2001 Webber M E Baer D S and Hanson R K 2001 Ammonia monitoring near 1.5 µm with diode-laser absorption sensors *Appl. Opt.* **40** 2031-42

[Fityk] The FITYK software (www.unipress.waw.pl/fityk)

[Macko2004] Macko P Romanini D Mikhailenko S N Naumenko O V Kassi S Jenouvrier A Tyuterev V G and Campargue A 2004 High sensitivity CW-cavity ring down spectroscopy of water in the region of the 1.5 µm atmospheric window *J Mol. Spectrosc.* **227** 90-108

[SilcoTek] SilcoTek Corporation (http://www.silcotek.com/)

[Barone] G. Barone, SilcoTek Corporation, personal communication

[U.S. Patent] U.S. Patent No.: 6,444,326 B1, 2002

[Hansen2001] Hansen C M and Just L 2001 Water transport and condensation in fluoropolymer films *Prog. Org. Coat.* **42** 167-178

[Langmuir1918] Langmuir I 1918 The adsorption of gases on plane surfaces of glass, mica and platinum *J. Am. Chem. Soc.* **40** 1361-1403

[Freundlich1909] Freundlich H 1926 *Kapillarchemie*, (Leipzig:Academische Bibliotek)

[Sips1948] Sips R 1948 Combined form of Langmuir and Freundlich equations *J. Chem. Phys.* **16** 490-5

[Jeppu2012] Jeppu G P and Prabhakar Clement T A 2012 Modified Langmuir-Freundlich isotherm model for simulating pH-dependent adsorption effects, *J. Contam. Hydrol.* **129-130**, 46-53

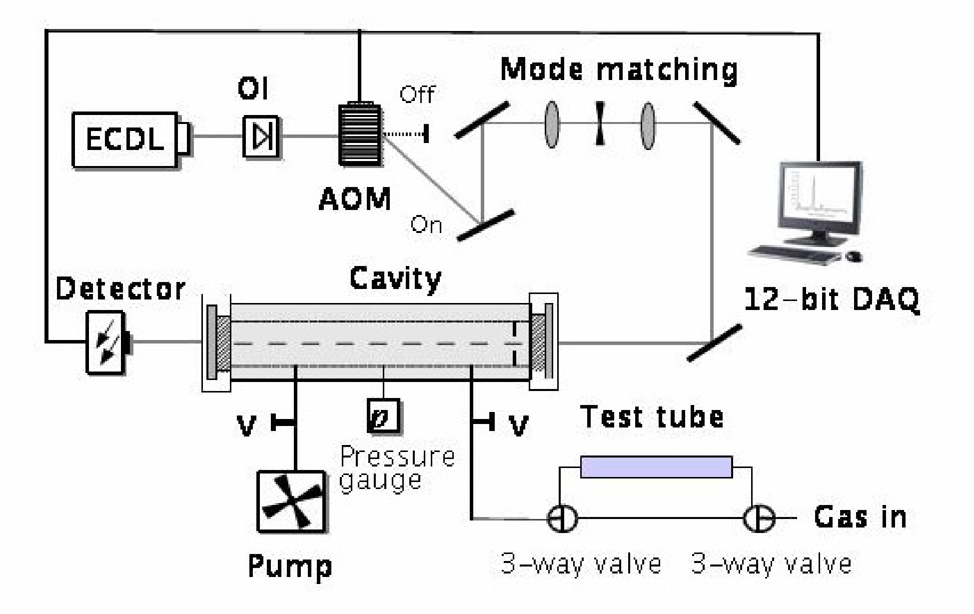

Figure 1. The measurement set-up. ECDL = external cavity diode laser, OI = optical isolator, AOM = acousto-optic modulator, DAQ = data acquisition card, V = valve.

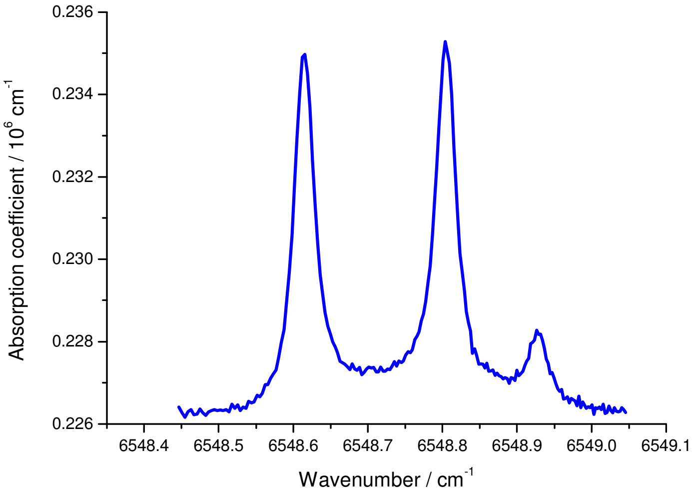

Figure 2. The spectrum of ammonia (91 ppbv) around 6548.8 cm^{-1}.

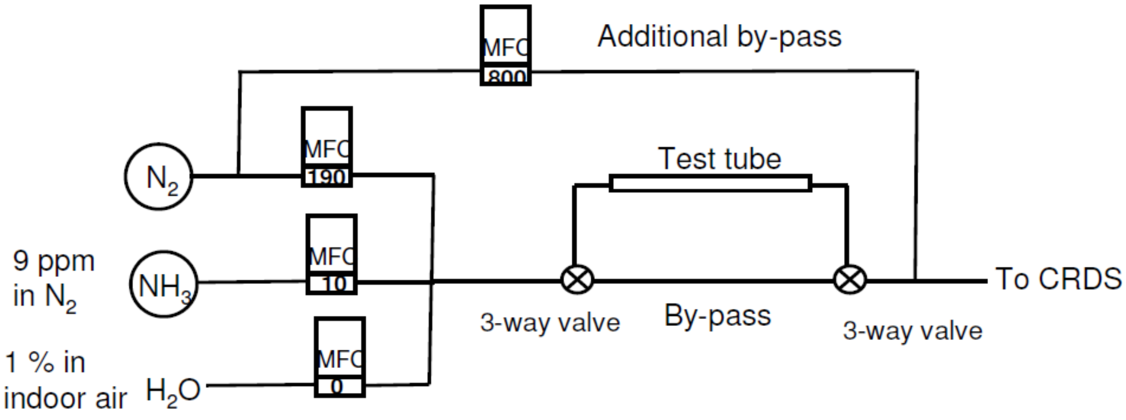

Figure 3. The gas generation and test tube set-up. The additional by-pass was used in test measurements.

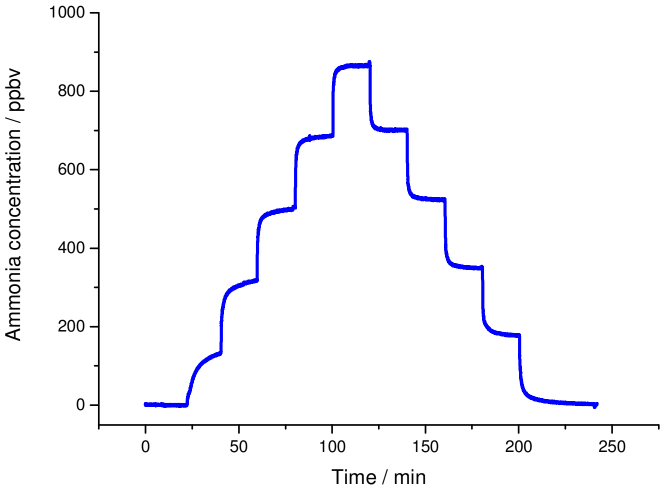

Figure 4. Step-wise increase and decrease of dynamically diluted gas phase ammonia (in indoor air; water content ~ 0.6%) concentration.

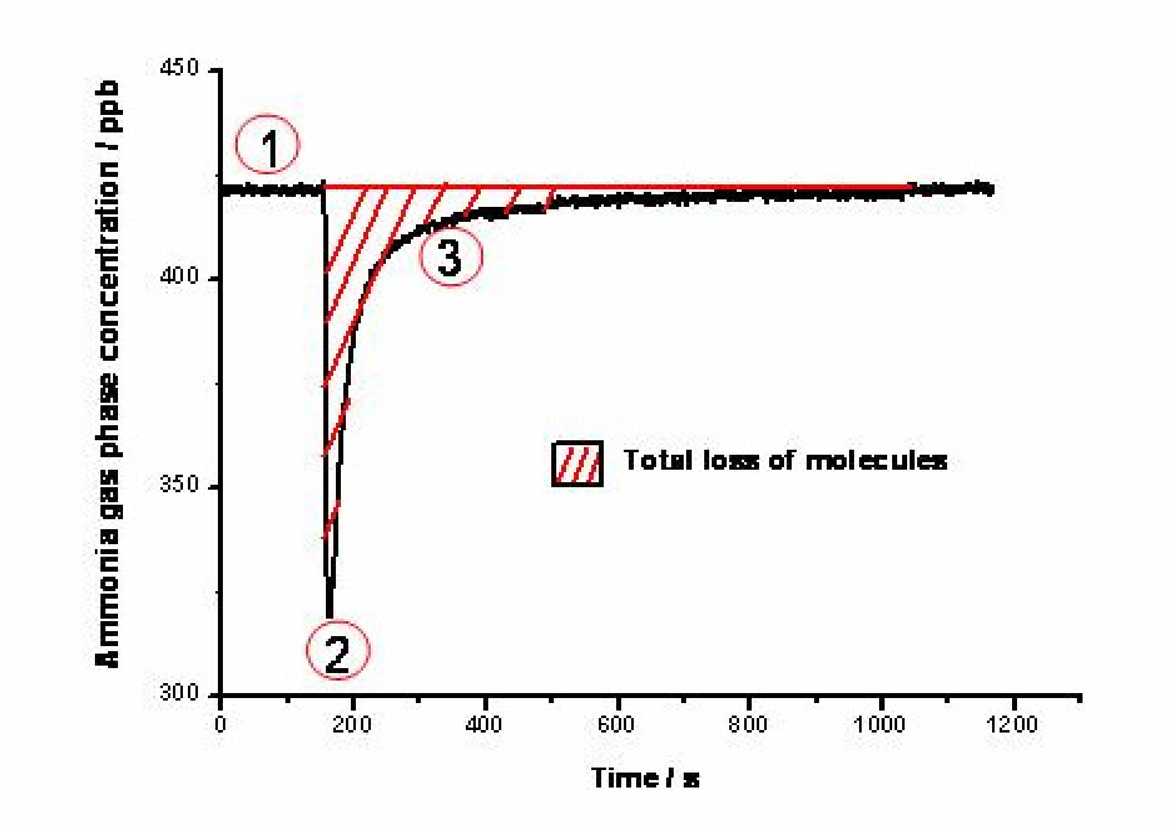

Figure 5. The total loss of ammonia molecules due to gas exchange and adsorption. 1 = stable NH_3 concentration before actual experiment, 2 = sharp decrease of NH_3 concentration due to gas exchange and fast component of adsorption, 3 = slow recovery of NH_3 concentration due to slow component of adsorption.

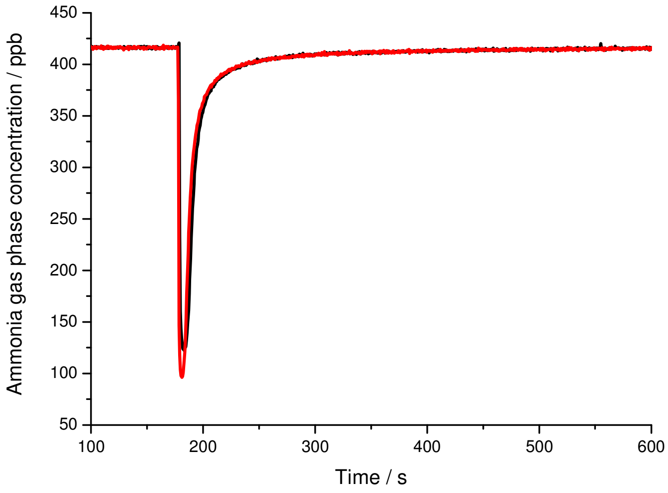

Figure 6. The reproducibility of the measurement is two successive recordings. The studied surface material was stainless steel 316L and the gas phase NH_3 concentration ~ 425 ppbv.

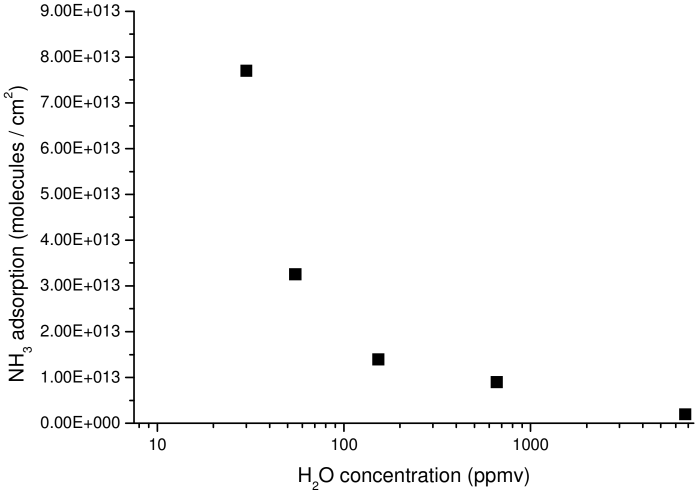

Figure 7. Ammonia adsorption as a function of water concentration. The studied surface was SS 316L in this case.