Effect of moisture on the adsorption of ammonia

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Abstract. The effect of moisture on the adsorption of ammonia was systematically studied using different surface materials and humidity levels. The experimental water amount fractions varied between 6 and 18000 µmol mol^{-1} and the ammonia amount fraction was 400 nmol mol^{-1}. The investigated materials included plain 316L stainless steel and stainless steel cured with Dursan, SilcoNert 2000 and halocarbon wax coatings. Furthermore, Teflon (PTFE) and polyvinylidene difluoride (PVDF) polymer surfaces were studied. Dynamically diluted ammonia, test tubes prepared with the investigated materials, a commercial ammonia analyzer based on cavity ringdown spectroscopy and a commercial dew point transmitter were employed. The adsorption was assessed quantitatively using continuous flow conditions and real-time monitoring of the adsorption process. The ammonia adsorption was found to increase substantially in dry conditions for all the studied materials except PVDF. The increase was largest for plain stainless steel which was the most adsorbing material. The coatings applied on stainless steel decreased the adsorption significantly in dry conditions. Polymers PVDF and PTFE were the least adsorbing materials. In water amount fractions between 1000 and 10000 µmol mol^{-1}, the ammonia adsorption was at its lowest. The adsorption increased again above one percent humidity levels.

1 Introduction

Ammonia (NH_3) is a ubiquitous gaseous compound present at variable trace concentrations in the environment [1]. Quantification of the prevailing NH_3 levels at normal atmospheric concentrations requires sensitive methods [2, 3]. Traceable real-time quantification of NH_3 is challenging due to the molecule's high reactivity. This causes strong adsorption and desorption effects on the surfaces of the sampling system and the detection instrumentation [4]. These effects are observed as a negative or positive time-dependent bias limiting the time-resolution of the quantitative ammonia measurements.

Stainless steel (SS) is an alloy which is composed of several elements [5]. The main constituents of stainless steel are iron, chromium and nickel. These and other elements are present in various concentrations depending on the type of the steel. For example, austenitic SS 316L contains at least hundreds of parts-per-million of carbon, manganese, phosphorus, sulphur, silicon, molybdenum and nitrogen. These constitute a surface structure which is chemically complex and highly non-uniform. Additionally, there are mechanical defects and other imperfections in the morphological surface structure.

When stainless steel is exposed to water (H_2O), dissociative adsorption occurs, and a hydroxyl (OH) layer is formed as the first monolayer on the surface [6]. This has been corroborated by experimental and computational studies on iron oxide (Fe_2O_3) and chromium oxide (Cr_2O_3) surfaces [7, 8]. The underlying stainless steel surface becomes enriched in Cr_2O_3 in the case of liquid water exposure and in Fe_2O_3 in the case of air (containing some water) exposure, respectively [6]. In dry conditions (in this article, "dry" equals to $\sim 20\ \mu mol\ mol^{-1}$ or less water; all other amount fractions are designed as "wet"), the water adsorption layer contains about half a monolayer of OH and a small fraction of molecular H_2O [7]. When the relative humidity reaches about 60 %, there is a full monolayer of OH and additional 2-5 layers of molecular water on the surface [7, 9]. Thus, the adsorption of water is, at first, chemisorptive in nature. This is in contrast to the bonding of NH_3 which can be described as physisorption via van der Waals forces at the conditions of the experiments presented in this article. Moreover, water is arranged as clusters of various sizes depending on the anomalies of the surface [10]. When the arrangement described above comes in contact with trace levels of ammonia, several additional processes may occur. These include adsorption of ammonia on the surface, desorption of water from the surface, dissolution of ammonia into adsorbed water and dissociation of ammonia in water and on the surface.

Some work on the adsorption of ammonia on stainless steel and other surface materials has been performed earlier. A short introduction to some studies is presented in Ref. . [11]. A general outcome of these studies is that a plain SS surface adsorbs more ammonia than SS prepared with, e.g., silicon-based surface coatings. The adsorption can be reduced by a factor of up to 20 by means of such

coatings [4, 11]. The ammonia adsorption has also been modelled using different approaches [11--14]. All the models lack inclusion of water which may compromise their usefulness at normal atmospheric conditions.

The role of water in the adsorption process of ammonia has not been studied extensively. Usually no information is given about the water content of the experiment, except a phrase "dry" or "zero-gas". The exact information is *obligatory* in order to properly assess the adsorptivity or to compare different materials measured in different moisture conditions. Humidity differences may explain a major part of the apparent discrepancies present in literature.

In this study, we have systematically quantified the adsorption of ammonia on plain and coated stainless steel surfaces in the presence of water. The studied surface coatings have been untreated stainless steel 316L, stainless steel coated with SilcoNert 2000, Dursan and halocarbon wax (polychlorotrifluoroethylene, PCTFE) coatings. SilcoNert 2000 and Dursan are commercial coatings available from SilcoTek Corporations. SilcoNert 2000 has two layers: a hydrogenated amorphous silicon (a-Si) layer on a plain SS substrate and an extra alkyl layer on the top of the a-Si layer for capping the remaining active adsorption sites. No information is available from the manufacturer about the composition of the Dursan coating. These coating are applied on cleaned non-electropolished stainless steel 316L surfaces. In addition, we have also measured the adsorption of ammonia on two different types of polymer tubings. The studied polymers were polytetrafluoroethylene (PTFE, Teflon) and polyvinylidene difluoride (PVDF). The performance of the coatings was assessed by exposing so-called "test tubes" (TT) coated with the aforementioned surface materials to a fixed amount of ammonia (400 ppb = 400 nmol mol^{-1} $\approx$ 285 µg m^{-3} ammonia at 295 K and 1013 mbar (1013 hPa)) at water amount fractions corresponding to dry (~ 6 ppm = 6 µmol mol^{-1} $\approx$ 4.5 mg m^{-3} water at 295 K and 1013 mbar) and wet (~ 6400 ppm $\approx$ 4.7 g m^{-3} water at 295 K and 1013 mbar corresponding to relative humidity (RH) of 24 %) conditions. To further study the effect of water amount on adsorption in more detail, the water amount fraction was varied from ~ 6 ppm to ~ 18000 ppm ($\approx$ 13 g m^{-3} water at 295 K and 1013 mbar $\approx$ 67 % RH). Real-time cavity ring-down spectroscopy was applied as the ammonia quantification method.

2 Measurement method

2.1 Measurement setup

The measurement setup is presented in Fig. 1. We used a commercial Picarro G2103 Ammonia Analyzer to quantify the NH_3 amount fractions in the gas phase. Evenly spaced data provided at the data rate of the analyzer at 5 second interval were used [15]. The precision of the analyzer is ~ 1.2 ppb (three times standard deviation, 3σ) at 400 ppb amount fraction. The H_2O amount fraction was measured with a Vaisala DRYCAP DMT143 Dewpoint Transmitter at humidity levels of one percent (by volume) or less. The dew point transmitter was confirmed to operate satisfactorily down to ~ 1 ppm H_2O amount fractions with the help of an accurate dew point mirror. The Picarro analyzer was used to quantify the water content above one percent H_2O amount fractions. The analyzer was calibrated against the dew point transmitter for those humidity measurements by using their common operating range from about 100 to 10 000 ppm.

The desired NH_3 gas phase amount fraction (400 ppb $\pm$ 1 %, the percentual deviation refers to minimum and maximum values; this also applies to other values given later in this article using the same notation) was generated by dynamic dilution of a bottled NH_3 standard in nitrogen (AGA). The certified NH_3 amount fraction of the standard was 9 ppm $\pm$ 10 %, which was confirmed with the ammonia analyzer. Instrument nitrogen (N_2) (H_2O content < 2 ppm quantified by the dew point transmitter and NH_3 content of < 2 ppb quantified by the ammonia analyzer) (AGA) was used for dilution. Required humidity levels were generated by passing the N_2 gas flow over a stainless steel container partly filled with water or by bubbling the gas through water. Most of the measurements were performed either in dry conditions corresponding to ~ 5.6 ppm $\pm$ 30 % or in wet conditions corresponding to ~ 6430 ppm $\pm$ 3 % of water. Mass flow controllers (MKS Inc.) were used to generate appropriate NH_3 and H_2O amount fractions for the measurements.

The tubing and connections to the NH_3 analyzer were made of PTFE. Some connectors, valves and the dew point transmitter measurement cell (through which the measured gas was flowing continuously) were made of stainless steel. The mass flow controller seals were nitrile rubber (Buna-N) coated.

2.2 Measurement protocol

The applied measurement protocol was a refined version of the one described in more detail in [11]. The main modifications in the protocol arose because the commercial analyzer was used instead of the home-built one in [11]. Another major alteration was the addition of the dew point transmitter for water amount fraction quantification.

The measurements consisted of three successive stages: 1. cleaning of the test tube (TT), 2. exposure of the experimental setup (except the TT) to 400 ppb of NH_3 and 3. quantification of the NH_3

adsorption by exposing the prepared TT to gas stream containing 400 ppb NH_3 with a certain H_2O amount fraction. Details of the stages relevant to the current study are given below. More details are given in Ref. [11].

1. The test tube was flushed with indoor air until a certain NH_3 amount fraction corresponding to the indoor air level (~ 10 ppb) was achieved. This procedure is necessary to remove NH_3 due to earlier exposures from the TT (by H_2O molecules of the indoor air). In the case of dry measurements, the TT was flushed with pure nitrogen gas for about an hour to remove excess H_2O. After this, the NH_3 amount fraction in the gas stream was ~ 1 ppb and the H_2O content was ~ 6 ppm. It should be noted that although the NH_3 amount fraction *in the gas stream* drops from 10 ppb to 1 ppb during the N_2 flushing procedure, the amount of NH_3 *on the TT surface* (and elsewhere in the system) does not drop *vis-à-vis* to that ratio, if practically at all. This happens because nitrogen gas is not effective in removing NH_3 from the surfaces. In the case of wet measurements, the TT was flushed with N_2 containing the same amount of H_2O as was used in the measurement stage. At the end of this stage, the gas stream was switched to flow through a by-pass line (see Fig. 1) instead of the TT using electronic 3-way valves (Bio-Chem Valve 105T212-125). After this stage, the TT contained (possibly humidified) N_2 gas at a pressure of about 1017 mbar ± 2 %. A slight overpressure (few mbars) as compared to ambient pressure was used in the measurements. During the next stage, H_2O was slowly released from the TT surface and it accumulated into gas phase within the TT (in the case of dry measurements) or was adsorbed on the TT surface (in the case of wet measurements). These processes were not accounted for in the adsorption quantification since they are not considered to be significant.

2. The entire experimental setup except the test tube was exposed to 400 ppb NH_3 utilizing the by-pass line. At least three hours were required for the measured gas phase NH_3 amount fraction signal to adequately stabilize to the used NH_3 amount fraction. This time is necessary for all the surfaces of the measurement system to be saturated with NH_3 at the prevalent amount fraction. As the measured NH_3 amount fraction increases, the H_2O amount fraction simultaneously slowly decreases, as NH_3 molecules replace H_2O on the surfaces and a new equilibrium is reached (Fig. 2).

3. The actual time-resolved adsorption measurement took place at this stage (see Fig. 3 for the time-evolution of the adsorption signal). The NH_3 flow was switched to pass through the TT with the help of the 3-way valves. An instantaneous sharp drop in the NH_3 gas phase amount fraction signal is observed because the space inside the TT, at this stage emptied of ammonia molecules, becomes occupied (gas exchange, a minor component) and because NH_3 adsorption takes place on the surface of the TT (a major component). The gas exchange occurs within a few seconds and naturally depends on the length of the test tube. After the initial drop, the NH_3 amount fraction signal recovered slowly and finally reached the original level of 400 ppb. This stage took 15 to 90 minutes depending on the

strength of the adsorption. It is worthwhile to note that the length of this process does not necessarily reflect the rapidity of the adsorption occurring inside the TT but more likely the sorption processes occurring within the whole measurement setup. Fortunately, these processes do not affect the net amount of adsorbed molecules (see Sect. 2.3). The entire measurement protocol took one full working day.

The measurement conditions are compiled in Table 1. The measurement protocol was repeated using different surface materials which are listed in Table 2. The same test tube was used for three repeated measurements in dry conditions and for three measurements in wet conditions. In some cases, the first exposure of a pristine TT produced significantly stronger adsorption than the subsequent measurements. In those cases, the first exposure was omitted. In the case of PTFE, PVDF and halocarbon wax, the increased TT length was necessary to observe the adsorption phenomenon with an adequate signal-to-noise ratio.

Table 1. The measurement conditions.

Variable	Unit	Value	Max. deviation from value
Pressure	mbar	1017	32
Temperature	K	295	2
Flow rate	ml min^{-1}	1265	3
NH$_3$ amount fraction	ppb	400	4
H$_2$O amount fraction (dry)	ppm	5.6[a]	1.5
H$_2$O amount fraction (wet)	ppm	6430	210
H$_2$O amount fraction (max.)	ppm	18000	n/a

[a]In the case of PVDF, dry condition equals to ~ 21 ppm of water.

Table 2. The studied materials.

Material/coating	Manufacturer	Test tube length (cm)
Stainless steel 316L	Unknown	30
SilcoNert 2000	SilcoTek Corporation	30
Dursan	SilcoTek Corporation	30

Halocarbon wax	Halocarbon Wax Corporation	160
PTFE	Oy Fluorplast Ab	170
PVDF	Oy Fluorplast Ab	1000

2.3 Important measurement method features

The time evolution of the observed NH_3 amount fraction signal after the adsorption event is strongly influenced by two filters located immediately upstream of the measurement cell within the Picarro analyzer. This creates a potential problem in the quantification of the adsorption strength. There is a dynamic interaction between the TT, the filters, the tubing and the measurement cell of the spectrometer. The filters are major players in the interaction due to their large effective surface area. When the TT is exposed to ammonia, due to adsorption, there are less NH_3 molecules in the gas stream approaching the filters. This induces desorption of NH_3 molecules from the (previously in stage 2 of Sect. 2.2) saturated filters into the gas stream. Consequently, the measured gas phase NH_3 amount fraction is increased. After a new equilibrium is reached in about 10 seconds at a lower NH_3 gas phase amount fraction, the ammonia molecules begin to re-adsorb (net effect) to the filters (and elsewhere in the system). This leads to a reduced gas phase NH_3 amount fraction and a dampening effect of the adsorption signal is observed. Presence of water complicates the situation even further as there is a continuous competitive adsorption between these two species. The shape of the time dependent signal is therefore dictated by the adsorption-desorption processes occurring in the filters. This means that the stronger the original adsorption is, the longer it takes to return to the original saturated NH_3 amount fraction due to the measurement system's "memory effect". The observed time-evolution is thus largely a reflection of the sorption effects caused by the filters and other surfaces outside the TT. Luckily, this complicated interaction does not affect the total measured number of adsorbed NH_3 molecules because the same number of molecules is re-adsorbed to the filters that has initially been desorbed. This applies as long as the H_2O amount fraction remains constant over the entire measurement as was the case in this study. The adsorption-desorption effects were extensively tested in [11] using slow flow rates within the test tube and fast flow rates elsewhere in the system.

The water amount fraction referred in Sect. 2.1 was defined as an average of the water amount fraction immediately before stage 3 and at the end of stage 3 of the protocol. It was impossible to fully control the water amount fraction in the test tubes in dry conditions as shown by the large maximum variation in Table 1. Furthermore, the water amount fraction measurement occurred about 30 cm downstream

from the test tube, and therefore the water amount fraction *inside* the TT was not accurately known. In all the measurements except one (PVDF), the recorded water amount fraction was between 4.5 and 7.1 ppm in dry conditions (see Sect. 3.1).

The effect of water amount fraction on the adsorption of ammonia was studied more in detail for stainless steel 316L and SilcoNert 2000 surfaces. The measurements were performed at 11 different water amount fractions from 7 to 18000 ppm for stainless steel 316L and at 6 different amount fractions from 5 to 17000 ppm for SilcoNert 2000. The other conditions were the same as presented in Table 1.

3 Results and discussion

3.1 Ammonia adsorption on different surface materials

The procedure for the NH_3 adsorption calculation is presented in Ref. [11]. First, the total number of lost molecules is obtained by integration over duration of the adsorption process (Fig. 3). Second, the number of molecules that were missing in the initially ammonia-depleted test tube (gas exchange) is subtracted from the obtained value. Third, the total adsorption is attained in the units of molecules per cubic centimeter by taking the surface area of the TT into account. It should be noted that the concept of "total adsorption" may also include ammonia molecules lost due to other processes such as dissolution into water. The results are presented in Table 3.

Table 3. Total adsorption of ammonia N_s (10^{12} molecules cm^{-2}) on different surfaces in dry and wet conditions.

Material/coating	Dry adsorption		Wet adsorption		Dry/wet
	N_s	σ^a	N_s	σ^a	
SS316L	492	63	52	7	9.5
Dursan	153	11	52	1	2.9
SilcoNert 2000	77.5	3.3	22.3	1.4	3.5
Halocarbon wax	48.4	6.0	9.1	0.3	5.3
PTFE	21.4	2.5	8.2	0.9	2.6
PVDF	4.5	1.7	7.3	0.9	0.7

[a] The symbol σ is the standard deviation of N_s for three consecutive measurements.

The results show that the adsorption of ammonia is significantly reduced in wet conditions when compared to dry conditions with the exception of PVDF. In general, larger is the dry adsorption of the material, larger is the ratio of dry and wet adsorption. Halocarbon wax is possibly an exception to that trend. In the case of PVDF, the values corresponding to dry and wet conditions are within the experimental uncertainty.

The rank order of the materials remains the same for both dry and wet conditions. The materials can thus be classified in two separate groups: treated or non-treated stainless steel and polymer surfaces. Halocarbon wax is positioned between these groups in this classification – justly so, as it represents both classes being a polymer coating on stainless steel surface. The adsorption on polymer surfaces is lower than on coated and non-coated SS surfaces. The coating significantly reduces the adsorptivity of stainless steel, in the case of SilcoNert 2000 by a factor of over 6.

All the investigated surface materials, except for halocarbon wax, have been studied earlier in dry conditions [11]. The reference includes a comparison to other literature values which is not repeated here. Although the two investigations (2014 and current) in Helsinki were performed in different conditions, the current results qualitatively validate the earlier results obtained at the H_2O amount fraction of $\sim$ 20 ppm. There are, however, some quantitative differences between the studies that require further clarification. In the 2014 study, the ratio of adsorption SS316L/SilcoNert 2000 was about 24. In the current study, the ratio was only 6.3. Although the uncertainty of the measurements may explain most of the difference, the other possible reasons remain unknown. In any case, the surface smoothness (effective surface area), possible contamination, treatment prior to coating and coating procedure all play a critical role. The same surface materials were studied at METAS in Bern where a ratio of about 11 was obtained for *electro-polished* SS and SilcoNert 2000 applied on *electro-polished* SS [4].

The authors consider the current results more trustworthy than those of [11] for the following two reasons: First, the water amount fractions of the current experiment were measured in real-time which was not the case for the earlier study where these were only estimated on the basis of a limited number of measurements performed off-line. Second, the flushing (cleaning) and stabilization times in the current investigation were considerably longer which results in higher probability that ammonia from earlier exposures was effectively removed. These factors ensure that the driest and cleanest possible conditions were achieved. The obtained results in [11] were claimed in the article to be minimum values for total adsorption. This means that the relative error is the highest for the smallest total adsorption values possibly leading to an overestimation of the ratios of adsorption between SS316L and SilcoNert 2000.

The same piece of 316L stainless steel test tube was used in the current as well as for the 2014 study [11]. The NH_3 adsorption for SS 316L was 492×10^{12} molecule cm^{-2} in this study and 138×10^{12} molecule cm^{-2} in the 2014 study. This gives a ratio of 3.6 between the studies. The NH_3 mass concentration in this study was $286\ \mu g\ m^{-3}$, and in the 2014 study it was $49\ \mu g\ m^{-3}$. This gives a factor of 5.8. The H_2O mass concentrations of the studies were 4 and 3 mg m^{-3}, respectively, making the experiments comparable in that sense although the other conditions differ considerably. In the light of this fact, and considering the non-linearity of the adsorption isotherm in the NH_3 mass concentrations in question, the obtained ratio of 3.6 appears realistic.

The measurements on polymer surfaces also qualitatively agree between the above-mentioned two studies. However, the obtained absolute adsorptivities are difficult to explain. The mass concentrations used in the earlier study were higher by a factor of 2.5 meaning that the adsorptivities in the earlier study should also be higher. However, in both polymer cases (PTFE and PVDF), they were smaller than what was obtained in this study. The reason for this is unknown. On top of what has been discussed above, other possible reasons may arise because there were at least 10-fold differences in the NH_3 amount fractions (8750 vs. 400 ppb) and measurement pressures (119 vs. 1017 mbar) between the studies. The low adsorptivity of the polymers means that the relative uncertainty is the highest for these materials, which may partly explain the discrepancy.

The authors are unaware of any previous quantitative ammonia adsorption measurements on halocarbon wax surface. It has been reported that halocarbon wax coated steel had similar passing efficiency (this is an effect of adsorption) for ammonia than Teflon at room temperature [16]. Halocarbon wax consists of polychlorotrifluoroethylene (PCTFE) which is easily applicable on a stainless steel surface. The wax is dissolved in acetone and the solution is let to affect overnight on the metal surface to be treated. According to our investigations, the coating reduces the NH_3 adsorption by a factor of 10 as compared to uncoated stainless steel. A possible shortcoming of the coating is that it melts already at 132 °C [17] and its quality may deteriorate already at lower temperatures.

The average coefficient of variation for all 36 measurements was 11 %. This demonstrates a surprisingly high reproducibility for such measurements which are supposed to be inherently sensitive to prevailing conditions. The accuracy of the investigations was not always as good as the coefficient of variation implies. The calculation of the total adsorption included a subjective element where the final NH_3 amount fraction (the background amount fraction against which the loss of molecules was integrated, see Fig. 3) was determined visually. If we suppose that the error in the NH_3 amount fraction is 0.5 ppb (the precision of the amount fraction determination), this factor alone would induce, at worst, a 30 % error in the total adsorption value. This introduces a possibility for a

systematic error of that magnitude for the measurements possessing the lowest signal-to-noise ratios. In the case of PVDF, it was impossible to obtain a water amount fraction below 21 ppm. The reason for this behavior could be the difficulty of removing the adsorbed (or *absorbed*) water in reasonable time *within* the studied tube and/or permeation of water *through* the tube from indoor air. Both of these effects stem from the large surface area of the 1000 cm long PVDF test tube in this case. The low adsorptivity of this material causes additional uncertainty in the total adsorption integration. According to this study, the gas exchange within the PVDF test tube corresponds to up to 25 % of the observed loss of molecules which emphasizes the susceptibility of the measurements. The above-mentioned factors increase the observed relative error in the PVDF adsorption quantification as shown in Table 3.

3.2 Effect of humidity on ammonia adsorption

The results of the measurements performed at different water amount fractions for stainless steel 316L and SilcoNert 2000 surfaces are presented in Fig. 4. There are three qualitatively similar features in both adsorption curves. The number of adsorbed NH_3 molecules decreases slowly and monotonously from about 50 to 10000 ppm (one percent) humidity. Below H_2O amount fractions of 10 ppm, there is a sharp increase in adsorption, conspicuous especially in the case of the SS 316L surface. It would have been interesting to explicitly quantify the adsorption at water amount fractions between 15 and 50 ppm where there is supposed to be a sharp decline in adsorption. Regrettably, the available ranges of the available mass flow controllers did not allow for dilution to such H_2O amount fractions. Above one percent humidity, there is a distinctive but smaller (as compared to adsorption below 10 ppm) intensification of the adsorptivity for both SilcoNert 2000 and stainless steel 316L.

A simple calculation yields the amount of 600×10^{12} molecule cm^{-2} for the full ammonia monolayer coverage [18]. Although the monolayer concept is not necessarily appropriate in this context, it is intriguing to notice the similarity of the calculated value with respect to the measured total adsorption value of $\sim 500 \times 10^{12}$ molecule cm^{-2} for non-treated SS in dry conditions. Even though the condition is labelled as "dry" in this article, there are still ten times more water molecules than ammonia molecules present in the system. At those moisture conditions, according to Ref. [7], the water coverage is also close to the same figure (corresponding to a little over half a monolayer of water). This raises two questions: 1) Does ammonia largely replace water on the stainless steel surface? 2) Does ammonia form a more densely packed layer than water? For SilcoNert 2000 coating, the NH_3 coverage is obviously less dense even at dry conditions.

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For both plain 316L and SilcoNert 2000 surfaces, the apparent total adsorption increases at high water vapour levels. The observed increase has approximately the same magnitude for both within the experimental uncertainty. The most likely explanation for such a behavior is the dissolution of ammonia into the multiple water layers present on the surface. It should be considered that, by using the current experimental setup, not only adsorption but the integrated loss of ammonia molecules from the gas stream to anywhere inside the TT is quantified. The measurement does not reveal the exact fate of the lost molecules, be it adsorption or other processes.

The ratio of ammonia adsorption 316L/SilcoNert 2000 at different water amount fractions is presented in Fig. 5. The plot was obtained simply by dividing the 316L adsorption values by the SilcoNert 2000 values at certain common humidity levels. Because it was impossible to fully control the experimental water amount fraction, there were small differences in the obtained humidity levels, which was not taken into account in the calculation above. This does not introduce problems because the experimental uncertainty is nevertheless the limiting factor. It is obvious from Fig. 5 that the adsorption ratio diminishes monotonously as the water amount fraction increases. This is not surprising, since, as the water amount fraction in the gas stream increases, the surface becomes more densely covered by water molecules and the surface loses its original character. As a result, the adsorbing ammonia molecules experience more water-like surface. Eventually, at highest water amount fractions, the plotted ratio approaches unity as ammonia molecules almost exclusively encounter only water. Unfortunately, it was impossible to study this effect beyond 1.8 percent humidity levels, since water started to condense to the measurement setup surfaces at higher amount fractions.

4 Conclusions

There is water present on almost any surface in the usual laboratory conditions (normal temperature, pressure and humidity). It is difficult to remove the last chemisorbed monolayer of water molecules without replacing them with other "sticky" molecules such as ammonia. This means that it is challenging to investigate the individual behavior of these molecules.

Water amount greatly affects the adsorption properties of the surface. At moderate humidity levels, water molecules cause an "active passivation" effect which significantly reduces the adsorption of ammonia onto the surface. Shorter stabilization times are thus required to eliminate the adsorption induced bias in measurements performed at those levels. At humidity levels above one percent, which correspond to normal atmospheric conditions, ammonia begins to dissolve into the multiple water

layers present on the surface. This increases the loss of ammonia molecules from the gas phase and generates effects similar to adsorption. The surface coating selection does not play a big role under such conditions as the differences between the coating materials almost disappear. The surface coating becomes vital in genuinely dry conditions where the water amount fraction approaches the prevalent ammonia amount fraction. Such conditions are met in e.g. the preparation of dry gas standards at low ammonia amount fractions. The least-adsorbing surface coatings, such as SilcoNert 2000 applied to surfaces of e.g. gas cylinders, considerably reduce the error in the ammonia amount fraction of such standards.

This article offers new insight into the role of water in the framework of ammonia adsorption on stainless steel and other surfaces. At the same time, the presented study provokes some compelling new questions. To which extent does ammonia replace water on the innermost monolayer on the surface? Does ammonia dissociate in this process? In which form is the ammonia molecule attached to the surface? Advanced theoretical and computational studies along with sophisticated experiments are required to answer these questions.

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Figures
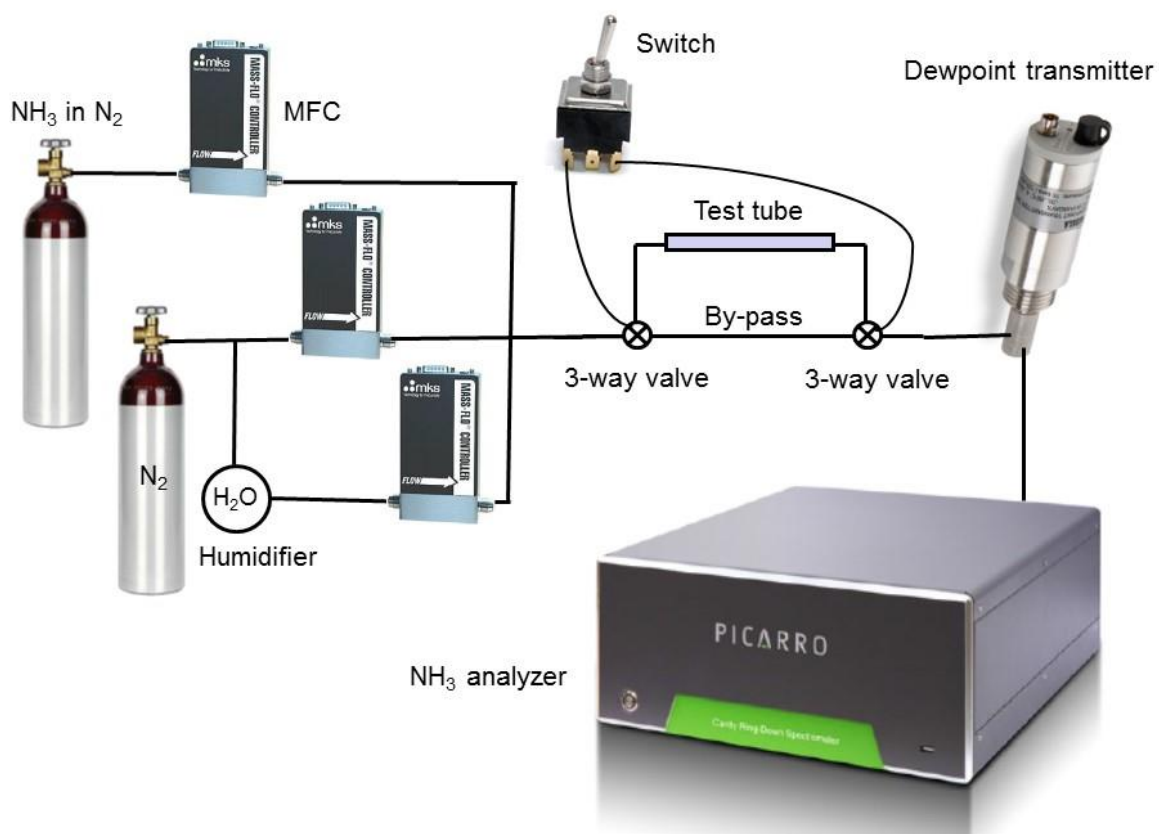
Figure 1. The measurement setup. MFC = mass flow controller.
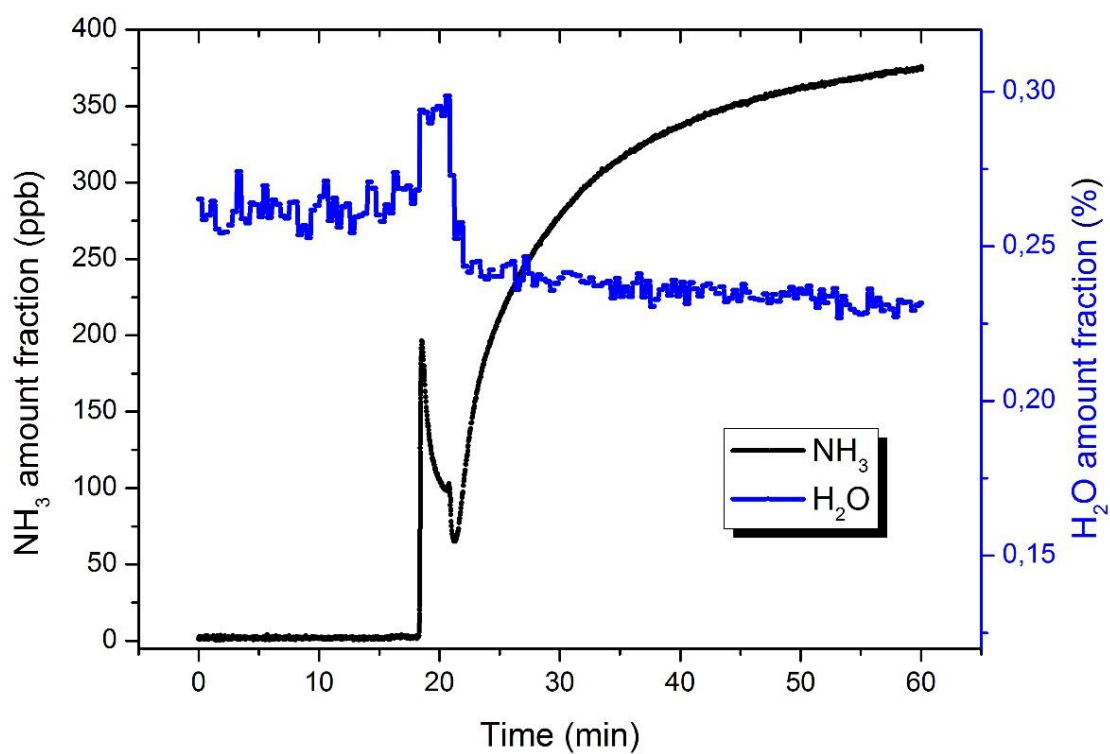
Figure 2. The interaction between ammonia and water. The ammonia flow is switched on at about 18 min. After initial sharp increase in both the ammonia and water amount fraction, the water amount fraction slowly decreases as ammonia amount fraction approaches the value (400 ppb) used in the measurements.
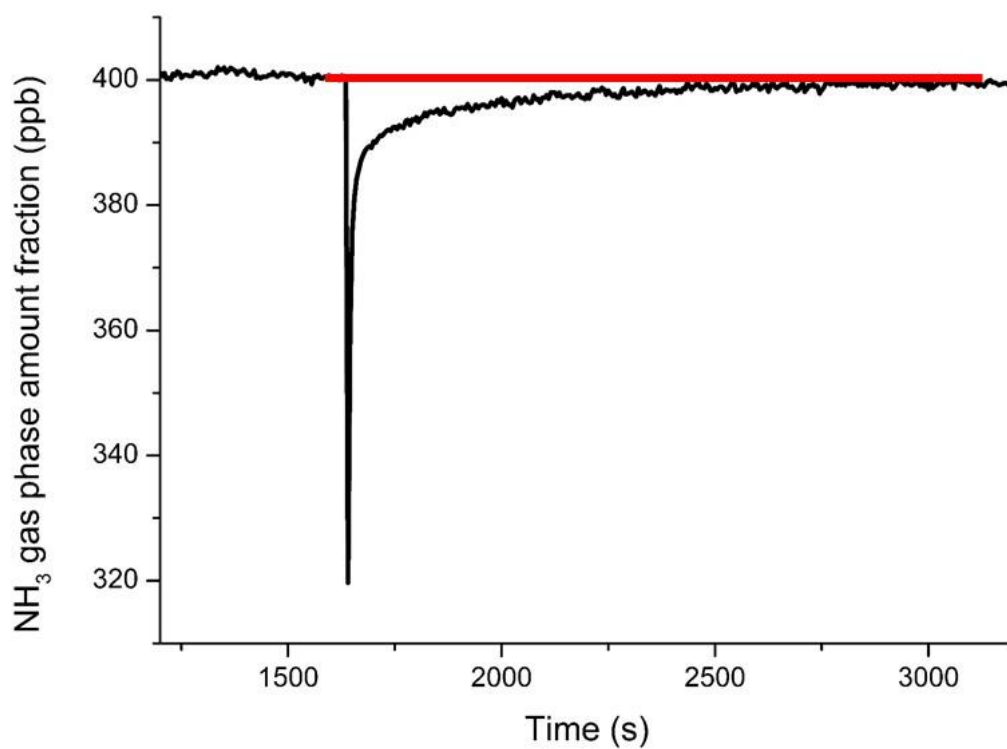
Figure 3. The time-evolution of the adsorption signal. The straight thick line represents the background ammonia amount fraction against which the total loss of molecules is integrated. The studied surface material was halocarbon wax on wet conditions in this case.
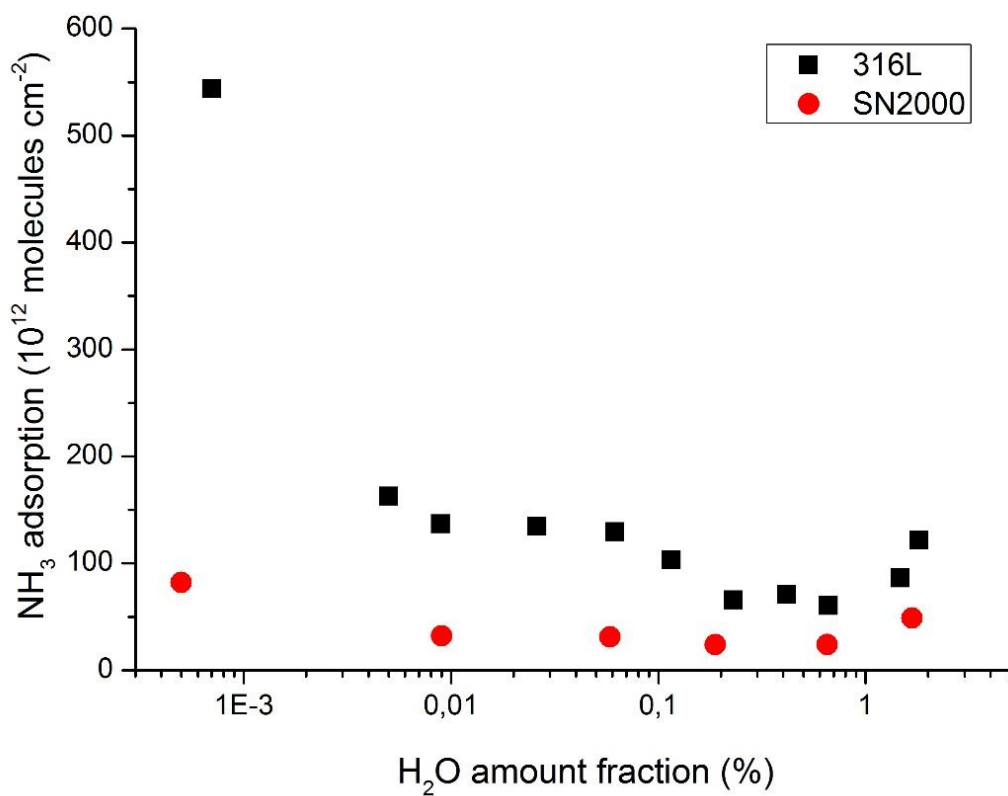
Figure 4. The adsorption of ammonia on stainless steel 316L and SilcoNert 2000 at different water amount fractions. A single measurement was performed at one water amount fraction. SN2000 = SilcoNert 2000.
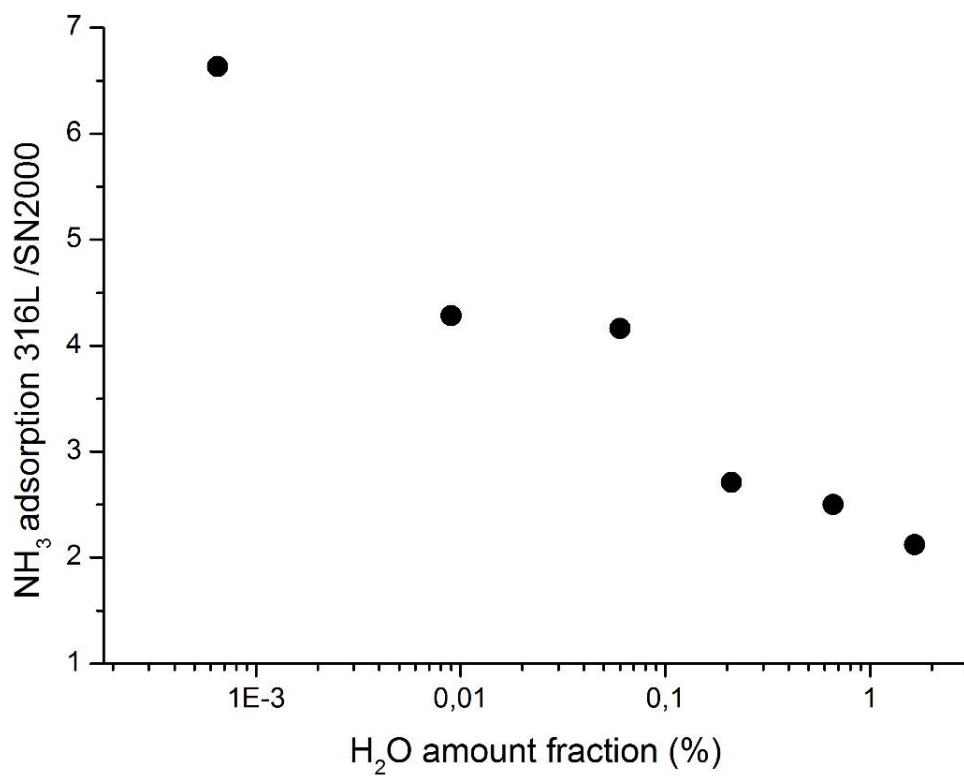
Figure 5. The ammonia adsorption ratio stainless steel 316L/SilcoNert 2000 at different water amount fractions. SN2000 = SilcoNert 2000.