A Review on the Sampling and Analytical Methods for Ammonia in Air

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Abstract: The quantification of ammonia concentrations has received a lot of scientific attention. Numerous devices for the quantification of NH_3 in the ambient air have been developed to provide more technical possibilities for research in abating NH_3 emission from various source processes. For the proper quantification of NH_3, a number of sampling methods have been discussed by grouping them into different categories based on the principle of functioning. In general, active samplers employ pumps to draw air in, while passive samplers are exposed to air over a certain period of time to obtain integrated signature of NH_3. In case of the former, impingers and absorption flasks can be employed simultaneously with suitable absorbents to capture NH_3 passing through them. The methods of analysis include both in-situ and laboratory determination. In the laboratory, colorimetric or ion chromatographic methods are generally used for its quantification. In the field, a number of real time analyzers have been proven to be useful. These real time analyzers can be grouped according to their principle of operation. These analyzers may use the principle of spectroscopy (e.g. DOAS), photoacousticics (e.g. photoacoustic monitor) or Chemiluminescence (NO_x analyzer). The automated annular denuder sampling system with on-line analyzer is also suitable for continuous monitoring of ammonia in air.

Keywords: ammonia emission, sampling, analysis, real time analyzers

Introduction

Being one of the most abundant trace gases in the atmosphere, ammonia ranks the third after nitrogen and nitrous oxide among the nitrogen containing species (Roelle and Aneja, 2002, Yang et al., 2003, Mount et al., 2002). In the atmosphere, it serves as the principal neutralizing agent for atmospheric acids (Yang et al., 2003). Ammonia is protonated in the presence of acidic compounds such as different acids of nitrogen oxides and sulfur oxides, thereby affecting the acidity of cloud water and aerosols (Heeb et al., 2006, Roelle and Aneja, 2002). Ammonium aerosol, comprising mainly of ammonium sulphate and ammonium nitrate (major constituents of $PM_{2.5}$), can induce the reduction of atmospheric visibility (Rumburg et al., 2006). Ammonia is thus expected to exert significant effects on the different ecosystems and on tropospheric chemistry.

The main mechanism for removal of gaseous NH_3 and aerosol ammonium is wet and dry deposition which can in turn lead to eutrophication of aqueous ecosystems and/or soil acidification (Heeb et al., 2006, Yang et al., 2003). Through nitrification, soil deposited ammonia can be converted into nitrate by the soil microorganisms which then release hydrogen ion to promote acidification of the soil layer (Roelle and Aneja, 2002, Lee and Park, 2002, Mosquera et al., 2005). This phenomenon can lead to a deficiency in the availability of important plant nutrients such as potassium and magnesium. The NO_3-N formed through such process can be easily lost from the negatively charged soils, percolating into the groundwater (Mosquera et al., 2005, Santibáñez et al., 2007).

Animal manure, synthetic fertilizer, and agricultural crops, while being the primary sources of atmospheric ammonia, cumulatively contribute to about 64% of the global emissions (Walker et al., 2006). Soil and plant emissions account for anywhere between 10-15 Tg N yr^{-1} (Roelle and Aneja, 2002). Road traffic is also considered to be another important source emitting 0.2 Tg N yr^{-1} (Heeb et al., 2006, Roelle and Aneja,

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2002). With increasing concern over the potential environmental damage caused by atmospheric transport and subsequent deposition of NH_3, it is very vital to have reliable methods and instrumentation to accurately monitor its pollution level and emission pattern. Such information will then be used effectively to develop potential abatement strategies for NH_3. A variety of ammonia analyzers and measurement techniques have been developed over the past years. In this review article, we attempted to describe the various analytical methods available for sampling and analysis of ammonia. The advantages and limitations of various methodological approaches for the measurements of NH_3 have been evaluated and discussed in the present article.

Approaches

This review article has been written with respect to the following two basic aspects - sampling and analysis of NH_3. In the sampling section, we reviewed the different methods of sampling in terms of their efficiencies for collecting NH_3. The limitations involved in the application of such techniques are also discussed. Research papers covering the subjects of sampling methods in different environments (such as from animal houses and agricultural fields) have been collected and analyzed. The objectives of the present study had been to consider and to evaluate novel methods for sampling and analysis. In the next section, we attempted to give a brief outline about the selection of various instrumental systems available for NH_3 analysis. The diverse NH_3 analyzers are able to give direct 'on-the-spot' estimates for the content of NH_3 present at the sampling site, whereas subsequent laboratory analysis has to be made for less portable instrumental set-ups. We attempted to describe the fundamental aspects of each of these analytical methods.

Discussion

Sampling of NH_3 in air

Most sampling procedures in air pollution studies

are carried out with some types of vacuum instrumentation. The vacuum device or sampling pump can be used to draw air samples through a specific absorbing media, a filter package system, or a specific analyzer (Demmers et al., 1999; Erduran and Tuncel., 2001). As sampling pumps with a simple manifold configuration allows easy implementation, it is advantageous to the deployment of routine analysis. In order to make a quantitative test, the exact quantity of air volume drawn by such pumping system has to be determined in an accurate manner. A flowmeter with an adjustable flow device can be used to preset the vacuum pump to sample at a known flow rate. As one of the most important components of air sampling train, the vacuum pump must meet certain criteria. Being fully portable, the sampling pump should possess a device to regulate sampling rates at a constant phase for a desirable amount of time.

There is a pressing need for establishing reliable sampling methods for NH_3 to improve our understanding of its environmental behavior. In Table 1, various techniques available for the collection of NH_3 have been summarized. There are basically two types of methods for the collection of gaseous samples. The first one is grab sampling, where an actual sample of air is taken in a flask, bottle, bag, or some other types of suitable container. The other one is called integrated or continuous sampling in which the target gas is removed (or preconcentrated) from the air by passing through a solid (or liquid) sorbent over a measured time period. Grab sampling is usually done, when the occurrence of instantaneous emission is sought or when concentrations are relatively constant. However, grab sampling can yield questionable value, if there are contaminants or strong temporal variations of target analyte. In the latter case, a time weighted average exposure needs to be considered. During an integrated sampling, the collection of gas is made from air by liquid-phase absorption into a solid adsorbent. Integrated sampling can also be achieved either actively by the use of a sampling pump or passively by the use of diffusive samplers.

Absorption flasks have been demonstrated to be

Table 1. Sampling methods of NH_3 in air

Method No.	Method	Reference	Brief description	Sampling duration	Advantages	Disadvantages
A1	Absorption flasks	Weerden and Jarvis, 1997	Drawing air through the absorption flasks containing orthophosphoric acid	7 days sampling with the flasks being changed every 24 hrs	Inexpensive, simple & can be used for a wide conc range	The absorbing solvent may evaporate
A2	Filterpack System	Aas et al., 2007	Whatman 40 filter impregnated with oxalic acid to collect NH_3	Weekly sampling	Inexpensive, simple & requires no power	Labour intensive, time averaged concentration measurements are done difficulty in estimating required exposure times
A3	Annular Denuder System	McCulloh et al., 1998	A cyclone & two denuder tubes. The second tube is used to collect NH_3; it is coated with 2% citric acid in a 50% mixture of methanol and distilled water	12-24 hrs at flow-rate 10 lmin^{-1} (McCulloh et al., 1998)	Reactive gases and aerosols can be measured	Some filter materials may retain NH_3 when the concentration of the gas is not too high
A4	Mist Chamber Technique	Cofer et al., 1985 Talbot et al., 1990 Parmar et al., 2001	Passing air through Teflon filters and then through a fine spray of H_2SO_4	Flow rate was 12 LPM for 3 hrs (Cofer et al., 1985)		the sampling process may lead to random errors due to uncertainty in the flow rate through the mist chamber
A5	Passive samplers	Sommer et al., 2004 Sacoby and Serre, 2007	Samplers were coated with 1% v/v H_2SO_4 to capture NH_3	5 days 8 months	Direct measurement of flux, no power requirement.	The cost is high for some samplers, time averaged flux measurement is obtained.
A6	Active sampling tubes	Stowell and Foster, 2000 Stowell et al., 2000	Samplers attached to pumps which allows air to flow through them generating color which is evaluated		Operational and functional simplicity	The performance of the tubes deteriorates at low NH_3 concentration.
A7	Sampling pump or by-pass pump	Demmers et al., 1999	Continuous sampling via a 20-channel multiplexer using either a sampling pump or a by-pass pump	24 hours	The device is portable hence very useful for air sampling	

robust samplers for ammonia over a wide range of concentrations and air flow rates. In the study of Weerden and Jarvis (1997), absorption flasks were used to collect NH_3 coming out of the wind tunnel in the experimental field. Orthophosphoric acid has been used as the absorbent. The absorbed NH_3 was then analyzed using colorimetric procedures. It is possible that some adsorption of NH_3 can take place on the tubing part connecting the absorption flask and the chamber from which NH_3 are introduced or released. Hence, flasks can give an underestimation of NH_3 concentrations, compared to passive samplers (Misselbrook et al., 2005). The use of absorption flask is simple and inexpensive, while applicable to a wide range of concentrations. A filterpack system (with a multistage filter assembly) can also serve as a tool for sampling the main air components. Whatman filter paper impregnated with oxalic acid (or any other suitable adsorbent) can be used to collect atmospheric ammonia in the filterpack system (Aas et al., 2007). In the lab, the HNO_3 extract of this filter paper can be analyzed for ammonium ions by ion chromatography. Although this method is labor intensive, it is simple and inexpensive without requiring power consumptions for the operation. Nonetheless, filter-based measurement approaches can be problematic in accurate determination of NH_3 and its semi volatile aerosol components, because it can be exposed to various sources of both positive and negative sampling artifacts (Appel 1993, Yu et al., 2006). The former artifacts arise from uptake of the sampled gas by the collected particles or the filter medium itself. The negative artifacts on the other hand arise from the volatilization of the collected particles from the surface of the filter pack (Yu et al., 2006).

Annular Denuder System (ADS) is another device for sampling atmospheric pollutants like hydrogen chloride, nitrous acid, nitric acid, sulfur dioxide, ammonia, and volatile chloride, nitrate, sulfate and ammonium in fine aerosol (McCulloch et al., 1998; Chang et al., 2002). The denuder tubes collect gases of interest, while the filter pack collects aerosols. The denuder tubes are coated with suitable adsorbents like

citric acid or phosphorus acid for collecting gaseous ammonia. The mechanism of sampling is the diffusion of atmospheric gases onto the denuder walls coated with reactive substances. The ADS generally consists of one cyclone, two tubes, and a filter pack. The cyclone is operated to remove coarse aerosol fractions (>2.5 μm). Mass-flow controllers with electronic timers coupled with the ADS control the sampling flow rates and/ or sampling intervals. After sampling, the tubes are washed with deionized water for extraction. Ammonium is then analyzed by ion chromatography or colorimetric flow injection analysis. Despite the fact that the denuder has advantages of allowing high sampling velocities with large sampling capacities, significant artifacts can be introduced during sampling (Chang et al., 2002). As the gaseous pollutants are absorbed onto the denuder walls, the equilibrium between the gas phase and the aerosol can be disturbed. If it occurs, the evaporation of aerosols and the release of additional gaseous pollutant can be accompanied. This additional amount of gaseous pollutant results in surplus sampling. This phenomenon may be particularly true for volatile aerosols like NH_4NO_3 and NH_4Cl and their associated gases. Furthermore, additional gaseous pollutants may be introduced by the diffusional deposition of aerosols containing compounds similar to the sampling gases (Chang et al., 2002).

In the mist chamber technique, air is initially passed through a Teflon filter to remove aerosol particles and then into a fine spray of the appropriate absorbing media (such as H_2SO_4). The sampling flow rate is recorded by a calibrated rotameter attached to the sampling assembly (e.g., Parmar et al., 2001). The NH_3 absorbed in acid solution is then analyzed by indophenol blue method (Weatherburn, 1967). Because evaporative losses of the absorbing solution may occur in the mist-chamber, such process has to be monitored and compensated by the addition of the solution. This sampling process can result in random errors, because of the uncertainty in the flow rate through the mist chamber.

Passive samplers are an efficient sampling device

that can be deployed in massive quantities over a wide spatial scale to characterize dispersion and fate of gases released from various sources (Wilson and Serre, 2007). Different passive samplers can have different frames. For instance, they can be assembled using two stainless grids that act as a support for an acidic absorbent, e.g., 5% H_2SO_4. The grids are placed into a colored polyethylene cap which is fitted into a PTFE diffusion tube (Sutton et al., 2001; Walker et al., 2006). At the top of the diffusion tube, a porous filter paper is placed to act as a turbulence barrier. Upon retrieval, the samplers are washed with deionized water and analyzed for ammonium ions by Ion Chromatography using methanesulfonic acid as eluent (Wilson and Serre., 2007) or by the indophenol blue colorimetric method (Sommer et al., 2004). The passive diffusion tubes, while not requiring electric power, are also inexpensive, easy to handle, while being capable of detecting gases at relatively low levels with excellent spatial coverage. Nevertheless, Sutton et al. (2001) found that many uncertainties arise from the use of passive samplers at very low concentration levels (<3 ppb). This method is possibly less reliable and inaccurate at fairly low concentrations.

Along with the passive samplers, active sampling tubes are also available for sampling NH_3 at varying measurement ranges (Ni and Heber, 2001). Both ends of the tube are sealed when manufactured and are cut open just before the actual measurement. For sampling, the tube must be tightly connected to the pump connector, which delivers air through the tube. The extent of coloring is determined by the level of the NH_3 concentration. For example, Dräger tube is an example of an active sampling method for the collection of NH_3 in exhaust air from animal houses (Garry et al., 2007, Hayes et al., 2004). A hand operated pump draws air through the tube at one stroke, during which the air contained in the pump chamber escapes through the exhaust valve. If NH_3 is present, the reagent reacts to result in color change from yellow to blue. The tubes have a measurement range of NH_3 between 0-30 ppm. These tubes are simple to operate designed for on spot measurement of NH_3.

Analysis of NH_3 in air

In this section, the instrumental approaches used for detecting and quantifying NH_3 after the completion of sampling are discussed. The operation of some on-spot analyzers developed for the simultaneous sampling and analysis of gaseous NH_3 is also discussed. Table 2 summarizes various types of the analytical approaches applicable to NH_3 analysis at present time.

The widely used Indophenol method involves the reaction of ammonium ion with hypochlorous acid and salicylate ions in the presence of nitroferricyanide ions to form the salicylic acid analog of indophenol blue (Weatherburn, 1967). The optimum pH for the formation of this chromophore is about 13.4. The concentration of ammonium is determined spectro-photometrically at about 630 nm. Tartrate ions are added to the highly alkaline medium to prevent the precipitation of Ca (or Mg) ions which might otherwise occur. Such application can be modified by inducing reactions between NH_3, NaOCl, and phenol. The concentration range of this method can be controlled by adjusting the sample volume introduced, gain of the spectrophotometer, the flow cell path length, or all of the above three. For example, a high working concentration range can be obtained, when the pump is operated at a high flow rate. Because this method is highly sensitive, sample preparation should be made cautiously to avoid contamination by ammonia present in the laboratory atmosphere.

Potentiometric determination by flow injection analysis (FIA) system consists of a gas diffusion unit and a potentiometric detecter. The solution from which ammonium concentration has to be determined is injected in the FIA system by which ammonium is converted into ammonia. NH_3 diffuses through a gas-permeable membrane to a buffer accepter stream so that the gas can be separated from the rest of the sample (Lima et al., 1999). Once in contact with the buffer solution, NH_3 becomes reconverted to ammonium and is finally led to an ion-selective electrode. A wide linear response range of the potentiometric detector allows the injection of samples with a wide range of ammonium concentrations. This is an advantage over

Table 2. Analytical methods of determining NH$_3$ in air

Method No.	Instrument	Reference	Brief description	Advantages	Disadvantages	Specifications
B1	Spectrophotometer	Sommer et al., 2004 Weatherburn, 1967 Parmar et al., 2001 Yang et al., 2003	NH$_4^+$ reacts with hypochlorous acid and salicylate ions in the presence of nitroferricyanideions resulting in deep blue method color (Indophenol blue)	Highly sensitive	Br$^-$ ions present in the solution can result in lower readings	DL 0.36 ppb with precision of 10%. (Parmar et al., 2001)
B2	LPFTIR spectroscope	Galle et al., 2000	IR light from a source is transmitted through a gas and then spectrally analyzed	Simultaneous detection of different gases	Good for relatively high emssions due to DL problems.	DL and precision of around 8 8 ppbv for concentrations corresponding to fluxes of 0.5gNH$_3$ m^{-2}s^{-1} for fluxes from 20 min measurements
B3	Colorimetric flow injection analysis	McCulloch et al., 1998	NH$_4^+$ reacts with color reagent thereby producing a response in the detector	Simple, accurate, fast & precise method using low cost equipment	Because of high axial diffusion, it is difficult to apply it to slow reactions	DL 0.05mg L^{-1} (http://groups.ucanr.org /danranlab/water_and_ waste_water) accessed on 2.4.07
B4	Ion chromatography Column switching Ion chromatography	Aas W et al., 2007 Kirchner et al., 1999 Kai et al., 2007 Huang et al., 2000	Uses a specific column e.g Dionex 80 with guard column. Analysis was performed with elution using methanesulfonic acid and H2SO4 in case of column column switching IC	The precision, accuracy, versatility and ease of operation makes IC very useful to environmental analysis.	Sodium and potassium interfere with the analysis when present at conc reater than 0.1 mass%	DL in case of column switching IC is 12.8 µg l^{-1} (Huang et al., 2000)
B5	Chemiluminescence NO$_x$-analyser	Demmers et al., 1999 Roelle and Aneja, 2002	NH$_3$ concentration determined after conversion to NO	Useful for measuring NH$_3$ when high concentrations are expected	It severely suffers from NH$_4^+$ interferences which causes unacceptable deviations at low NH$_3$ concentrations	Accuracy 1% repeatability 0.2% (Roelle and Aneja, 2002)
B6	Photoacoustic Multi-gas Monitor	Webber et al., 2005	NH$_3$ concentration is determined by the absorption of light energy by the gas molecules and its conversion into acoustic signals which is detected by microphone.	Meets the desired criteria for size, weight, power consumption, ruggedness, portability and suitability for dusty environments.	Problem may arise with the stability of the instrument and interference of water at high relative humidities.	Accuracy 10%, precision 1-2% sensitivity 120 ppb or better some can sense at sub-ppb level also.
B7	Differential optical Absorption Spectroscopy	Mennen et al., 1996 Rumburg et al., 2006 Mount et al., 2002	Averaged spectra were analysed based on known reference spectra of components absorbing in the measured spectral region.	Useful for measuring several trace species simultaneously, the method is self callibrating.	Frequent attention has to be paid to allign the receiver with the light path, high noise	DL 1 ppb (Mount et al., 2002)

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Method No.	Instrument	Reference	Brief description	Advantages	Disadvantages	Specifications
B8 Contd.	Gradient Ammonia-High Accuracy-Monitor (GRAHAM)	Kruit et al., 2007	The GRAHAM is basically a wet denuder system equipped with a conductivity detector which gives an indication of NH$_3$	Has low detection limit, high precision & accuracy and high time resolution		
B9	AMANDA	Horvath et al., 2005 Scholtens et al., 2004 Neirynck et al., 2005 Erisman et al., 2001	Air is drawn through a rotating annular wet denuder continually coated with NaHSO$_4$. The solution is then processed an passed through a conductivity detector.		Flow rates are determined manually at service visits which deteriorates the precision and accuracy of the instrument.	Accuracy 5% and precision 2% (Scholtens et al., 2004) DL 0.01g m^{-3} (Erisman et al., 2001)
B10	AirSentry ion mobility spectrometer	Myles et al., 2006	Operates on time-of-flight principle, which equated molecular movement through a drift region to species concentration.	IMS provides in-situ measurements and have the capability to quantify over a broad range of concentrations		DL 0.10 ppb range 0-100 ppb NH$_3$
B11	AiRRmonia	Erisman et al., 2001	This instrument uses a membrane to select the ammonia from the airflow into de-mineralised water flow. The NH$_4^+$ concentration is determined conductometrically	Needs less support, less liquids and power and uses a much less airflow which makes it suitable for all applications	The instrument cannot measure the absolute ammonia concentration	DL 0.01g m^{-3} Accuracy 3%

the colorimetric detection in which the small linearity of the detector requires the adjustment of the FIA parameters to consider the absolute content of NH_4^+ in each sample. The principle of a colorimetric flow injection analysis involves the reaction of NH_3 with salicylate and hypochlorite in an alkaline phosphate buffer. The presence of EDTA prevents precipitation of calcium and magnesium. Sodium nitroprusside is added to enhance the sensitivity of the reaction. At the absorbance maximum (near 630 nm), the signal strength is proportional to the original ammonia concentration. The detection limit of this method is $0.05 \, mg \, L^{-1} \, NH_4^+$ and the results are reproducible within a range of 7% (http://groups.uncar.org/danlab/water_and_waste_water). Although this method is fast and precise, it is difficult to apply to slow reactions because of high axial diffusion (Aminot et al., 2001). Using Ion chromatography with sequential FIA, quantization of multiple ions can be done (Karmakar, 1999). This system is equipped with a regenerable suppressor. A sample is injected, while leaving the suppressor off-line. Ammonium elutes in the void volume of an anion-exchange column. The unsuppressed column effluent exiting the conductivity flow cell is used for FIA determination of NH_3. This novel method of using IC with sequential FIA enables precise and accurate analyses of samples with ammonium ions along with other anions in a single injection.

Another popular method for measuring ammonium ions in the laboratory is ion chromatography (IC) which allows the separation of ions and polar molecules based on the charge properties of the molecules. Kai et al (2007) used a Dionex 80 column as stationary phase and methanesulfonic acid (MSA) as the eluent for ammonium analysis. Although IC can separate ammonium ions from other cations and is sensitive at microgram level, the technique is not feasible for samples with high sodium content (e.g., in seawater). Since ammonium and sodium ions have similar selectiveness for the stationary phase, they elute in close proximity to each other which makes the ammonium quantification difficult (Huang et al., 2000). The application of the IC technique is not cost-justified for samples in which the ammonium ion has to be determined only (Karmakar et al., 1999).

NH_3 concentrations can be measured by on-spot measuring devices which operate without the intervention of any collecting media. Chemiluminescence analyzers consist of an indirect measurement of NH_3 by converting NH_3 to NO which is then analyzed by Chemiluminescence method (Ni and Heber, 2001). By heating stainless steel converter to ~750°C, both the oxides of nitrogen (NO_y) and NH_3 are converted to NO. NH_3 concentrations are obtained by subtracting the NO_x signals obtained by passing the sample through a molybdenum converter heated to ~325°C from the total signal (Roelle and Aneja, 2002). A multipoint calibration has to be made prior to the measurement. Zero and span checks have to be done on each day basis. The advantages of this technique include high sensitivity (1 ppb), high precision (±0.5 ppb), linearity (±1% full scale), and automation. The disadvantages include highly priced parts (e.g., internal gas scrubbers), relatively large initial investment, and complicated maintenance.

Photoacoustic technique is well known for its application to ammonia detection. Being an optical technique, it involves absorption of the laser radiation at a wavelength that overlaps the absorption feature of the target species, followed by deactivation of the excited molecule via collisions. During this collision, the absorbed radiation energy is converted into periodic local heating at the modulation frequency, thereby inducing acoustic waves that can be monitored with a low-noise microphone (Webber et al., 2005). A portable photoacoustic monitor is useful for detecting trace concentrations of ambient ammonia in agricultural settings with infra-red diode lasers and fibre amplifiers. The accuracy of the instrument is within 10% except for very low (near 0 ppm) NH_3 concentration (Webber et al., 2005). The replicate precision varies between 1-2% of the measured value. The sensitivity of a typical photoacoustic NH_3 sensor is 120 ppb or better (Webber et al., 2005). The instrument is known to exhibit 99.99% linearity for a range of 1-100 ppm. The detection sensitivity of photoacoustic sensor based

on CO_2-lasers is sub-ppb ammonia (Pushkarshy et al., 2003). Most of the sensors are ideally suited for monitoring emissions in agricultural sites, satisfying the desired criteria for size, weight, power consumption, ruggedness, portability, and suitability for dusty environments. Nonetheless, these sensors are relatively expensive and are subject to interference by water at high relative humidity (Ni and Heber, 2001).

Differential optical absorption spectroscopy (DOAS) technique averages spectroscopic absorption from various molecular species in the atmosphere over a path length ranging from a few tens of meters to several kilometers. The DOAS generally consists of a broad and bright ultraviolet (UV) light source, a telescope, a mirror system, a receiver telescope system, a spectral line source, a multi-element multi-plexing digital detector, and a data analysis system (Mount et al., 2002). For inter-comparison, spectra in the range of 200-300 nm are measured at a frequency of 100 Hz averaged over a certain time period. Such information is then analyzed based on known reference spectra of components absorbed in the measured spectral region. NH_3 has its main absorption peaks between 200 and 235 nm (Rumburg et al., 2006). The sensitivity of the DOAS instrument is about 1 ppbv in 1 s integration time (Mount et al., 2002). A detection limit ~4 ppbv (3 μg m^{-3}) can be reached by the DOAS system for an optical path length of 75 m and an averaging time of 3 min. A longer path length and averaging time would decrease the detection limit even further (Sommer et al., 1995). The DOAS system has numerous advantages. It does not suffer from ammonia adhering to inlet walls of the instrument. Real time measurements can be done without the intervention of any collection device. As the DOAS system can automate the calibration, it has the ability to measure several trace species simultaneously. The instrument has very high signal-to-noise ratios allowing high-precision measurements as fast as every second (Rumburg et al., 2007). However, in spite of the numerous advantages, the DOAS technique is limited to only a few atmospheric gases, mainly because of the limited information in the spectral analysis. (The total number of trace gases

whose spectral identity is reliable for DOAS application is yet confined to only a few species.) In addition, because of the fact that the DOAS relies on the retrieval of light beams released by an artificial light source, changes in meteorological conditions can influence its analytical performance to a certain extent due to changes in light transmissivity (Kim et al., 2001).

In a long-path Fourier Transform Infrared (LP-FTIR) spectroscopy, IR-light from a source is transmitted through a gas and then analyzed spectrally in FTIR spectrometer for the absorption spectra of the gas (Galle et al., 2000). Due to their spectral dissimilarity, different gases may be simultaneously but uniquely determined. To improve the detection limits, a long optical path length may be obtained by the use of multiple reflection optics. If the LP-FTIR is combined with powerful retrieval algorithms, quantitative analysis can be made for NH_3 as well as a number of gases (like N_2O, CO, CO_2, CH_4, and H_2O) with high precision. Griffith and Galle (2000) achieved a detection limit of about 8 ppbv for NH_3; if this system is applied to flux measurements, such DL value corresponds to a flux value of 0.5 μg (NH_3) m^{-2}s^{-1} for 20 min flux measurements. A significant advantage of the FTIR technique is that there is no requirement of corrections for air density (e.g., due to heat), because the air is brought to a common temperature before measurement. FTIR Spectroscopy allows ideal measurement of NH_3 because of strong spectra relatively clear from absorptions other than isolated H_2O lines (Griffith and Galle, 2000).

AMANDA (ammonia measurement by annular denuder sampling with on-line analyses) is another reliable equipment suitable for continuous monitoring of ammonia concentration (Erisman et al., 2001, Horẏath et al., 2005, Schlosten et al., 2004, Neirynck et al., 2005). Air is drawn through the AMANDA which consists of a rotating wet annular denuder coated continually with a liquid film of $NaHSO_4$-stripping solution. The solution flow is processed to pass through a conductivity detector. This conductivity measurement gives an indication of the captured NH_3

in terms of the ammonium ions (Scholtens et al., 2004). The temperature corrections have to be done to derive accurate NH_3 concentration, which occurs automatically. AMANDA has a resolution time of 2 mins, accuracy 2-5%, precision ±2%, and detection limit 0.01 µg m^{-3} (Erisman et al., 2001, Scholtens et al., 2004). AMANDA can give 1 min averages of near real-time NH_3 concentration. The calibration steps of AMANDA are quite complex, giving rise to sources of large uncertainties. Another monitoring instrument, the AiRRmonia, is an improved adaptation of the AMANDA (Erisman et al., 2001). AiRRmonia needs less support, requires less coating solution (90% less), and power. It also uses a much reduced air flow (Erisman et al., 2001). Although this instrument does not use a denuder, a membrane is used instead to select the NH_3 from the airflow into demineralized water flow. Because the detection system of the AiRRmonia is the same as the AMANDA, their performance is comparable. The detection limit of AiRRmonia is 0.1 µg m^{-3} with an accuracy of 2% and time resolution 5 mins (Erisman et al., 2001).

GRadient Ammonia-High Accuracy-Monitor (GRAHAM) is basically the same as the AMANDA but with several improvements (Kruit et al., 2007). Especially, continuous in-line air flow measurements were implemented to the system. The GRAHAM has high precision (by about 4%) which enables it to derive the fluxes and/or emission patterns more accurately than the AMANDA. The multi-channel peristaltic pump was replaced by two 3-channel syringe pumps to support a well-defined sample flow from the denuders. The conical structure of the inlet was also applied to the outlet which prevented the ammonium containing particles from impaction on wetted surfaces and from being a source of interference. The GRAHAM is ideally suited for micrometeorologial measurements because of its low detection limit, high precision, accuracy, and high time resolution (Kruit et al., 2007).

The Air Sentry ion mobility spectrometer (ASIMS), another device for quantifying ambient NH_3 operates on time of flight principle, which equates molecular movement through a drift region to species concentration

(King et al., 2004). Ambient air entering the ASIMS passes through a semi permeable membrane and is merged with the carrier gas composed of dimethyl methanphosphonate (DMMP) dopant molecules and instrument air (with a dew-point of −40°C). The merged sample and carrier gas were ionized to generate spectral signals with peaks proportional to the NH_3 concentration. The ASIMS had detection limit of 0.10 ppb NH_3 with a applicable range of 0-100 ppb NH_3 (Myles et al., 2006). The IMS technology is well suited to measure ambient NH_3 because of its capability to quantify NH_3 over a broad range of concentration. The ASIMS can provide quick response to NH_3 concentration changes, little maintenance time, and an easy interface for data acquisitions (Myles et al., 2006).

Conclusion

In this article, we reviewed the different approaches for sampling and analysis of ammonia which is one of the most abundant nitrogen containing trace gases in the atmosphere. In the first part, we attempted to illustrate the different means of sampling that are widely in use. Both active and diffuse sampling can be used to measure NH_3 levels in the air. The Annular denuder tubes coated with suitable absorbents, the filterpacks, or the absorption flasks rely on the application of vacuum pumping system to draw the air to capture NH_3. Passive diffusion tubes can also serve as efficient samplers accumulating NH_3 from the ambient air. In the second part of the article, we tried to offer some insights into the numerous ways of analyzing ammonia in the laboratory or in the field with the use of on-the-spot ammonia analyzers. In the lab, the most common method is the colorimetric determination of the ammonium ion. Potentiometric determination by sequential flow injection analysis is an excellent alternative over the colorimetric procedure. Employing ion chromatography with methanesulfonic acid as the eluent can lead to separation of ammonium ions, except for samples with high sodium concentration. The on-the-spot instruments are more applicable in

field monitoring studies. One such device, the Chemiluminescence NH_3 analyzer, which gives indirect measurement of NH_3, has high sensitivity. The portable photoacoustic multi gas monitor is useful for detecting trace concentrations of ambient ammonia in agricultural settings but is less sensitive and less accurate than the Chemiluminescence analyzer. Other NH_3 analyzers utilize the principle of spectroscopy - the DOAS or the LP-FTIR technique. A lower limit of detection can be achieved by the DOAS technique, although the system can be influenced by the changes in the meteorological conditions at the sampling site. A much lower detection limit and a broad range of measurement can be attained by the ASIMS, being the most suited for measuring ambient NH_3. The other on-the-spot devices i.e. the AMANDA, the AiRRmonia and the GRAHAM are basically the wet denuder systems modified suitably to show NH_3 concentrations in the field both accurately and precisely. Thus, prior to adapting any particular method to investigate ammonia concentration, scientific, practical, and economic considerations must be done.

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