

Ammonia Monitoring using various Techniques in Environmental Applications

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Introduction

Ammonia emissions are of particular interest due to a variety of environmental impacts. As the primary atmospheric base, ammonia plays a crucial role in determining the acid-neutralizing capacity of tropospheric air masses [1]. Airborne sulfuric and nitric acid can react with gaseous NH_3 to form fine particulates, such as ammonium sulfate or ammonium nitrate. Fine aerosol is of special concern because small particles are able to penetrate deeply into the lung and may lead to adverse health effects [2]. As compared to gas-phase NH_3 , secondary aerosols have a much slower removal rate in the atmosphere and, thus, a higher chance for long-range transport [3, 4]. Dry and wet deposition of gaseous ammonia and ammonium aerosol contributes to both acidification and eutrophication, which may cause damage to sensitive ecosystems such as forests, heathlands and bogs [3]. In Switzerland, the deposition of nitrogen (from NO_x and NH_3) is above the critical loads for forests in about 90% of the forest land [5], and long-term measurements of NO_2 and NH_3 fluxes have shown that rates of NH_3 deposition typically exceed those of NO_2 , sometimes by an order of magnitude [6].

The major sources for atmospheric NH_3 are agricultural activities and animal feedlot operations, followed by biomass burning (including forest fires) and to a lesser extent fossil fuel combustion [7]. Industrial sources, although minor with respect to global considerations, may be very important locally [8]. The contribution of road traffic to the non-agricultural ammonia emissions has been considered to be rather small. However, recent studies indicate that NH_3 emission rates from automobiles may be higher than previously estimated, and that traffic might be an important source of ammonia in urban areas [9].

Ammonia measurements are challenging for a number of reasons. While NH_3 is a gas with a boiling point of $-33.4\text{ }^\circ\text{C}$, it readily reacts with acids to form ammonium aerosols. In industrial processes this form can dominate and behave like small particulates, which has large implications on sampling and measurement strategies, as well as on legal regulations. The absorption of ammonia - and to some extent of ammonium aerosols - in diluted acid, followed by analysis of NH_4^+ is the classical approach, which has been published in various countries for both emission [10] and ambient air [11] measurements. Continuous emission monitoring systems (CEMS) can be based on a variety of analytical concepts: chemiluminescence, UV-absorption, NDIR, or FTIR to name the most important ones [12]. However, reliable calibration is challenging because NH_3 reference gases tend to be unstable, and sampling is difficult due to the strong tendency of ammonia to adsorb to surfaces such as sampling line and measurement cell [13-15].

The following paper is based on three case studies that include a wide variety of sampling and measurement strategies in the field of ammonia measurements. We will start with the concepts of the reference method which is included in the Swiss regulations for measurements at stationary sources. Further examples are a large method validation study at a highway tunnel, and ambient air measurements at very low concentrations using a novel instrument based on photoacoustic laser

spectroscopy. The last example also illustrates how excellent ambient air measurement data might be used to validate and complement classical emission data.

Case study 1 Swiss emission regulation

The Swiss Ordinance on Air Pollution Control (OAPC) provides emission limits for the sum of ammonia and ammonium containing compounds. The values shall be given as ammonium equivalents and must not exceed 30 mg m^{-3} for mass flows above 300 g h^{-1} . For waste incinerators, an emission limit of 5 mg m^{-3} at 11 % O_2 must be met. The corresponding regulation on emission measurements [16] provides a method for the determination of basic nitrogen compounds seizable by absorption in sulphuric acid.

A significant fraction of ammonia and ammonium compounds may be emitted as particulates. Therefore, sampling has to fulfil typical requirements for both gases [17] and particulates [18]. This normally means isokinetic sampling at a number of selected points in a cross-section and heated sampling. Ammonia must then be analyzed on the filter, the connecting tubing and the gas washing bottles (Figure 1). Alternatively, the filter can be omitted when a standard impinger is used. This option is assuming that the impinger retains both the particulate and the gaseous fraction (Figure 2).

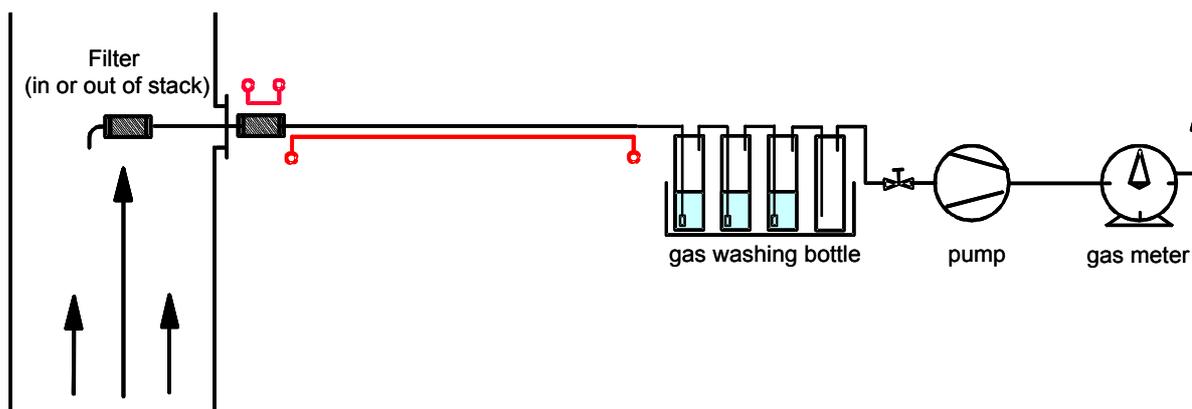


Figure 1
Schematic representation of the sampling setup filter for particulate matter and gas washing bottle for gaseous fraction.

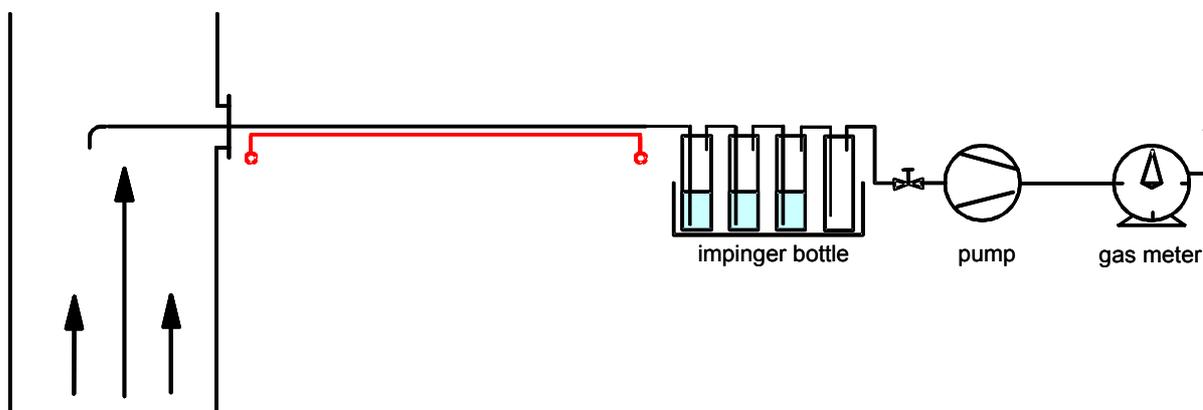


Figure 2
Schematic representation of the sampling setup Impinger bottle for particulate matter and gaseous fraction

Analysis of ammonium in the sulfuric acid solution can be done by photometry, ion selective electrodes or ion chromatography. An important simplification is allowed if the dust concentration is significantly lower than the gaseous ammonium concentration. Then, the conditions for particulate

matter sampling can be neglected, and simple extractive samples into sulfuric acid are sufficient. Many stationary sources can, therefore, be measured using a Teflon or steel probe, followed by gas washing bottles or impingers. If an unheated probe is preferred, then extraction of the sample line is readily done due to the excellent solubility of ammonia and ammonium salts in diluted acid.

Case study 2 Comparative NH₃ measurements in a road tunnel study

Ammonia formation in internal combustion engines is primarily due to a series of reactions that occur over the catalyst. A number of studies indicate that they strongly depend on driving mode, and that NH₃ is primarily generated after catalyst light-off and during acceleration events [19-21]. Because of wide variations between individual cars, tunnel studies are especially suited to derive emission factors that are representative for a whole fleet. During such studies, ammonia concentrations are measured at the entrance and exit of a road tunnel. Additional parameters, such as traffic density, traffic composition, ventilation rate and vehicle speed are then used to determine averaged emission factors.

Validated methods for continuous ammonia measurements are not readily available in the wide concentration range needed for tunnel studies. Therefore, a field-based intercomparison study was conducted to evaluate the performance of seven analytical methods for the measurement of ammonia. This method validation included sulfuric acid impinger and citric acid denuder followed by ion chromatography, differential optical absorption spectroscopy (DOAS), Fourier transform infrared spectroscopy (FTIR), Photoacoustic spectroscopy (PAS), and continuous aqueous extraction followed by measurement of conductivity (Airrmonia). Measurements were done at the entrance and the exit of the Gubrist highway tunnel near Zürich, Switzerland. 24-h mean values were compared using the impinger method as a reference.

At the tunnel exit, the average of all 24-h samples agreed within 13%. At the tunnel entrance, the maximal difference of 23 % was found between impinger and denuder. Continuous data of all methods agreed well at the tunnel exit. At the entrance, some limitation occurred due to restrictions in the measurement range, both for high NH₃ concentrations (Airrmonia), as well as near the detection limit (DOAS). Ammonia emission factors were calculated based on 4 weeks of continuous measurements with the Airrmonia. Evaluation as a function of traffic composition yielded specific emission factors of 33 mg·km⁻¹ for light-duty vehicles and 16 mg·km⁻¹ for heavy-duty vehicles [22].

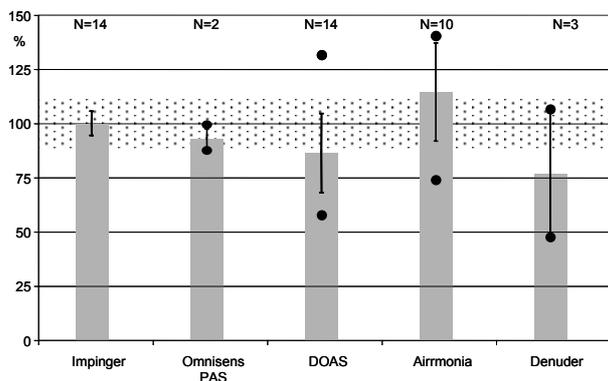


Figure 3
24-h average, tunnel entrance. All data is given as a fraction of impinger results. Columns are the average of N 24-h mean values, circles correspond to the maximum and minimum, and error bars give the standard deviation of all normalized 24-h means. The horizontal bar is the 95% confidence interval determined from parallel measurements by impinger

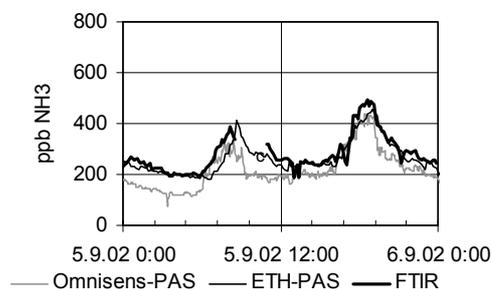


Figure 4
Continuous measurements at the tunnel exit represent the typical traffic density on a week-day.

Case study 3

Ambient air measurements near traffic related ammonia sources

To control the success of reduction measures, accurate and reliable measurement systems for the observation of ambient ammonia levels are required. It is necessary to have instruments available that fulfil the requirements for unattended long-term monitoring, i.e. they should enable user-friendly operation with long maintenance-free intervals, sufficient zero and span point stability, and automatic zero and span point calibrations.

Photoacoustic systems have the potential to fulfil these requirements. They are based on the photoacoustic effect, which consist in the generation of a sound wave in a medium irradiated by a modulated (laser) light beam. The generation of the signal can schematically be divided in four steps: (i) molecular absorption of photons, resulting in the excitation of absorbing molecules, (ii) release of the absorbed energy as heat, thus inducing the expansion of the gas, (iii) periodic pressure variation due to the use of a modulated laser intensity, and (iv) detection of the generated acoustic wave using a microphone. The signal can be strongly enhanced if the photoacoustic cell is designed to be an acoustic resonator and the laser is modulated at a resonance frequency of this cavity.

The Omnisens-PAS is a commercially available ammonia trace gas analyzer (TGA 300 series, Omnisens SA, Lausanne, Switzerland) for process control in the semiconductor industry or atmospheric pollution monitoring. Its laser source is a sealed-off RF-excited CO₂ laser. Single-mode emission and wavelength selection is granted by an intracavity grating. The photoacoustic cell is made of a central cylindrical resonator and two buffer volumes acting as acoustic filters. It is operated in the first radial mode of the resonator, occurring near 10.5 kHz. Cross-sensitivity to water vapour and CO₂ is minimized by careful selection of the wavelength and by the application of an empirical compensation for water vapour, determined by a precision hygrometer [23].

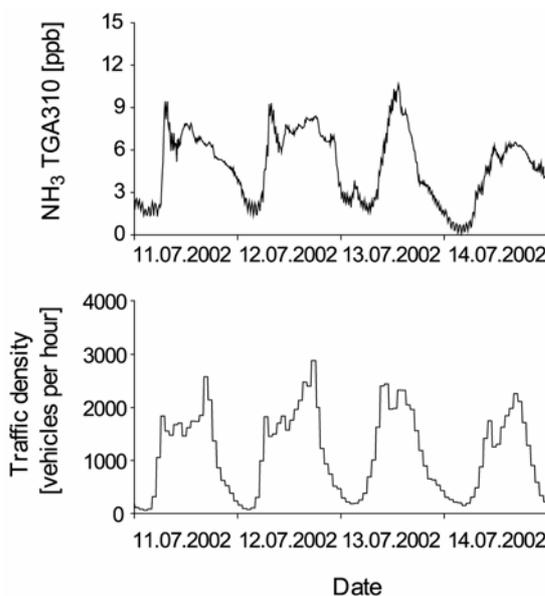


Figure 5

Four days (Thursday July 11, 2002 to Sunday July 14, 2002) of continuous ammonia measurements at the rural and traffic related site near Sion, Switzerland, obtained with the TGA310 (upper graph). The signal is clearly related to the traffic density on the nearby motorway (lower graph).

Field measurements have been performed at the rural and traffic related monitoring site in the Rhone valley near Sion, Switzerland. The site belongs to the Swiss national air quality monitoring network (NABEL). It is located within 50 meter distance to a motorway with a traffic density of about 20'000 vehicles per day. Figure 5 shows the TGA310's signal during four days in July 2002. The ammonia concentration has a distinct diurnal pattern that is clearly correlated with the traffic density on the

nearby motorway. These observations indicate that road traffic was the dominating emission source contributing to the ambient ammonia level at the monitoring site during the measuring period. In further studies we will attempt to include continuous, very precise CO₂ Measurements to use carbon dioxide as a tracer with a known emission factor to allow the determination of traffic related NH₃ emission factors.

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