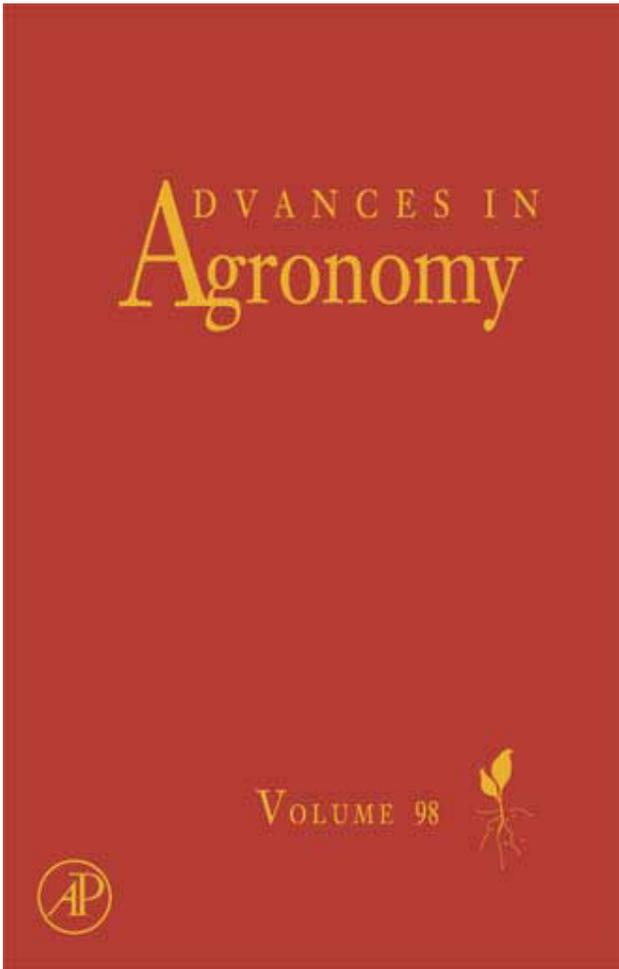


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SAMPLING AND MEASUREMENT OF AMMONIA AT ANIMAL FACILITIES

Ji-Qin Ni *and* Albert J. Heber

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Agricultural and Biological Engineering Department, Purdue University, West Lafayette, Indiana 47907

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Scientific understanding and technical control of ammonia (NH_3) at animal facilities, including animal buildings, feedlots, manure storages, and manure treatment plants, depend on reliable sampling and measurement techniques to ensure high quality data that are essential to the study and abatement of NH_3 emission. This chapter focuses on the methodology and technology of NH_3 sampling and measurement that has been tested or applied under field conditions since the 1960s. It draws a comprehensive and updated picture of the state of the art of NH_3 concentration measurement at animal facilities. Ammonia sampling requires selection of location, time, and/or control of sample volume. Three sampling methods, the closed, point, and open-path methods, are summarized. Thirty-one measurement instruments/sensors are identified. They are categorized in nine groups and evaluated according to their technical characteristics. Field studies or applications of these instruments/sensors are reviewed and summarized. Principles, procedures, advantages, and disadvantages of various sampling and measurement techniques are discussed. An overview of data and data quality is provided. Errors resulted from calibration, sampling, measurement, and data processing are discussed. Error reduction methods are presented. Recommendations are made for selection of sampling methods and measurement devices and for future needs including development of methodologies and standards.

ABBREVIATIONS

AQT, Ammonia Quick Test
CL, Chemiluminescence
DQIs, Data quality indicators
EC, Electrochemical
GMIS, Gas Manufacturers Intermediate Standards
IMEC, Inter-university Micro Electronic Center, Belgium
IR, Infrared
MPSS, Multi-point sampling system
NAEMS, National Air Emission Monitoring Study
NDIR, Non-dispersive infrared
NIST, National Institute of Standards and Technology
NTRM, NIST Traceable Reference Materials
OP-FTIR, open-path Fourier transform infrared
PAS, Photoacoustic spectrophotometer
PWA, Path-weighted average

QAQC, Quality assurance and quality control

TWA, Time-weighted average

U.S. EPA, United States Environmental Protection Agency

UV, Ultraviolet

UV-DOAS, Ultraviolet differential optical absorption spectrometer

1. INTRODUCTION

Ammonia (NH_3) is a common substance playing an important role in the nitrogen cycle. Since the 1980s, agricultural NH_3 emission has become one of the major worldwide air pollution concerns and has attracted more and more attention from the general public and government regulators.

It is believed by some researchers that excessive emissions of NH_3 from agriculture to the atmosphere have caused direct and indirect damage to the ecosystem in some regions with intensive animal production (Slanina, 1994; van Breemen *et al.*, 1982). Around 75% of European NH_3 emissions come from livestock production (Webb *et al.*, 2005). Most NH_3 emissions in Canada are from farm animals, and a 21% increase of NH_3 emission from animal husbandry in Canada from 1990 to 1995 was estimated (Kurvits and Marta, 1998). The agricultural sector in New Zealand is also the major contributor to NH_3 emissions to the atmosphere (Saggar *et al.*, 2004). The total NH_3 emission from agricultural fields in China in 1990 was estimated to be 1.80 Tg N, which accounted for 11% of the applied synthetic fertilizer N (Xing and Zhu, 2000). The European Parliament and the Council on National Emission Ceilings for certain pollutants (NEC Directive) set upper limits for each Member State for the total emissions in 2010 of four pollutants, which included NH_3 (Anonymous, 2001). Research in agricultural NH_3 in the United States has dramatically increased in recent years symbolized by large-scale and multi-institution projects, including the six-state research project funded by the U.S. Department of Agriculture (Heber *et al.*, 2006; Hoff *et al.*, 2006) and the ongoing world's largest study: the 14-million-dollar National Air Emission Monitoring Study (NAEMS) supervised by the U.S. Environmental Protection Agency (EPA).

High concentrations of NH_3 inside animal houses represent potential health hazards to humans and animals (Crook *et al.*, 1991; Kirkhorn and Garry, 2000; Portejoie *et al.*, 2002; Reece *et al.*, 1980). Chronic respiratory diseases of swine production facility workers have been attributed to dust and NH_3 (Donham *et al.*, 1995). The U.S. Occupational Safety and Health Administration (OSHA) has set a 15-min exposure limit for gaseous ammonia of 35 ppm by volume in the environmental air and an 8-h exposure limit

of 25 ppm by volume (ATSDR, 2004). There is a great need to evaluate health effects of exposures to air pollutants including toxic gases emitted into the general environment by confined animal feeding operations (Heederik *et al.*, 2007), and this depends on sufficient and high quality measurement data. However, reliable field data of NH_3 at animal facilities that include animal houses, feedlots, manure storages, and manure treatment plants are still a major need.

The understanding and control of NH_3 at animal facilities depend on sampling/measurement techniques, including devices, instruments, and procedures. Accurate and reliable techniques provide high quality data that are essential to research, emission abatement, and policy-making.

There are some publications that summarize techniques for measuring NH_3 at agricultural operations. Some of these articles provide detailed descriptions of specific measurement setups (Berckmans and Ni, 1993; Gates *et al.*, 2005; Heber *et al.*, 2001; van't Klooster and Heitlager, 1992) while others presented general overviews of the topic. The first comprehensive introduction of NH_3 measurement and monitoring techniques was published in 1979 (Kamin *et al.*, 1979). There have been new and advanced techniques developed and employed in agriculture since then. Van Ouwkerk (1993) reviewed various techniques of NH_3 emission measurement at animal houses. McGinn and Janzen (1998) presented techniques to determine the loss of NH_3 from manure-amended soils. Monteny and Erisman (1998) discussed NH_3 measurement in dairy cow buildings including naturally ventilated barns. Phillips *et al.* (2001) provided a comprehensive review of techniques for NH_3 emission measurement. Bolan *et al.* (2004) reviewed the sampling and measurement techniques applied at grazed pastures. Shah *et al.* (2006) presented the techniques for agricultural land and liquid surface measurement. Mosquera *et al.* (2005) and Losada (2007) studied NH_3 measurement methods in the Netherlands. Part of the overview by Bunton *et al.* (2007) focused on NH_3 measurement.

However, much of the useful information about the methodologies and technologies associated with field sampling and measurement is still scattered in the literature and needs more careful synthesis. A thorough and updated evaluation of NH_3 measurement techniques related to animal facilities will benefit users and researchers in selecting, employing, and developing such methods.

The objectives of this chapter were to (1) draw an accurate picture of the state of the art of NH_3 sampling/measurement methods/devices based on their tests and applications at animal facilities, (2) address technical and practical issues in their implementation, and (3) delineate future research needs in NH_3 measurement methodology.

2. A GENERAL VIEW OF AMMONIA DETERMINATION

Ammonia at animal facilities generally comes from open feedlots, confined animal buildings, manure storages (e.g., lagoons and storage tanks), and manure treatment sites (e.g., composts and anaerobic digesters). Confined animal buildings are typically either mechanically ventilated using fans or naturally ventilated without fans. Manure storages can be uncovered or have a physical cover to limit NH_3 emission into the atmosphere. Manure treatment sites can be indoors or outdoors. The design of animal housing and methods of manure storage and manure handling reflect large differences in climate and production objectives and affect the nitrogen flow and NH_3 release and emission (Sommer *et al.*, 2006). Although agricultural NH_3 emission is also related to manure application in the fields, it does not occur at animal facilities and is not within the scope of this chapter.

To obtain reliable information of NH_3 at animal facilities, suitable techniques must be adopted and one or more measurement variables must be chosen depending on measurement objectives. These variables include NH_3 concentration, air temperature, air pressure, and air exchange rate or air speed (Fig. 1).

To obtain atmospheric NH_3 concentrations at animal facilities for determining human and animal exposure, measurement of concentrations at required locations is indispensable while all the other variables are optional, because they are relatively less important. Comparison of animal facilities, management, and abatement techniques and their effects on NH_3 usually involves determining not only NH_3 concentrations but also its emissions (Heber *et al.*, 2000b). To obtain NH_3 emissions, whether for comparison or for baseline determination, from animal buildings or manure storages, the measurement of NH_3 concentration difference between the outgoing and

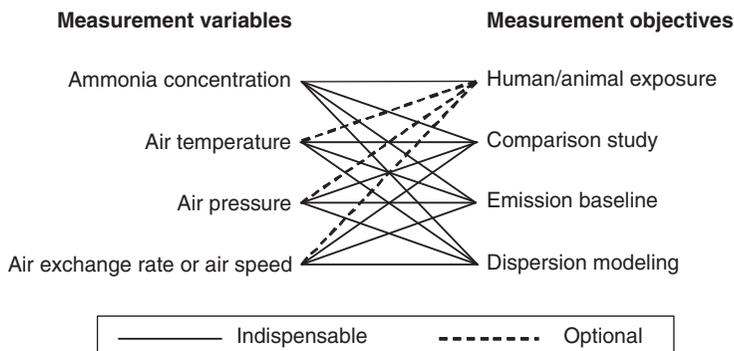


Figure 1 Determination of ammonia concentration and emission at animal facilities.

incoming air is essential along with the air temperature, air pressure, and air exchange rate (or ventilation rate). Techniques for measuring building air exchange rates were reviewed by Phillips *et al.* (2001). Measurements of NH_3 concentration, air temperature, air pressure, and air or wind speed are necessary for modeling NH_3 dispersion because it requires quantitative information of NH_3 mass at the source and at the sink.

Most NH_3 concentration measuring devices provide volumetric concentrations directly. However, mass concentrations are required to calculate NH_3 emissions. The volume of gas depends on both temperature and pressure and is therefore generally not constant. When converting to mass concentration, the volumetric concentration is multiplied by the molecular weight and the pressure, and divided by the gas constant and the temperature. Temperature and pressure therefore needs to be known. However, although measurement of air temperature was often reported in published works, air pressure measurements are seldom found. Atmosphere pressure varies between 980 and 1040 mbar, a 6% variation, or $\pm 3\%$ from standard atmosphere, which was often assumed. The measurements of temperature and air pressure are relatively easy with few technical challenges. Reported sampling and measurement methodologies applied at animal facilities are summarized in Fig. 2. Details of these techniques are discussed in the following sections.

3. AMMONIA SAMPLING

Because of the large volume of air flowing through animal facilities, it is impossible to capture all the air for gas concentration determination. Therefore, air must be sampled in order to perform gas concentration measurement. The technical term “sampling” has different definitions in different research fields. In the case of gases at animal facilities, we define “sampling” as:

The technique and procedure that specifies the locations where air samples are taken, controls the time, interval, frequency, and duration of sample taking, and regulates the volume or mass of the sample air to be measured.

This definition includes three elements: location, time, and volume/mass. However, inclusion of all three factors is not always necessary depending on sampling and measurement techniques that are used. For example, in open-path sampling (Section 3.4.3), volume/mass does not need to be known because there is no need to draw air from the sampling space. Another example, in which volume/mass may not be needed, is when using passive diffusion sampling devices, such as pH test paper (Section 5.1.2) and diffusion gas tubes (Sections 5.2.2) for NH_3 sampling and concentration determination.

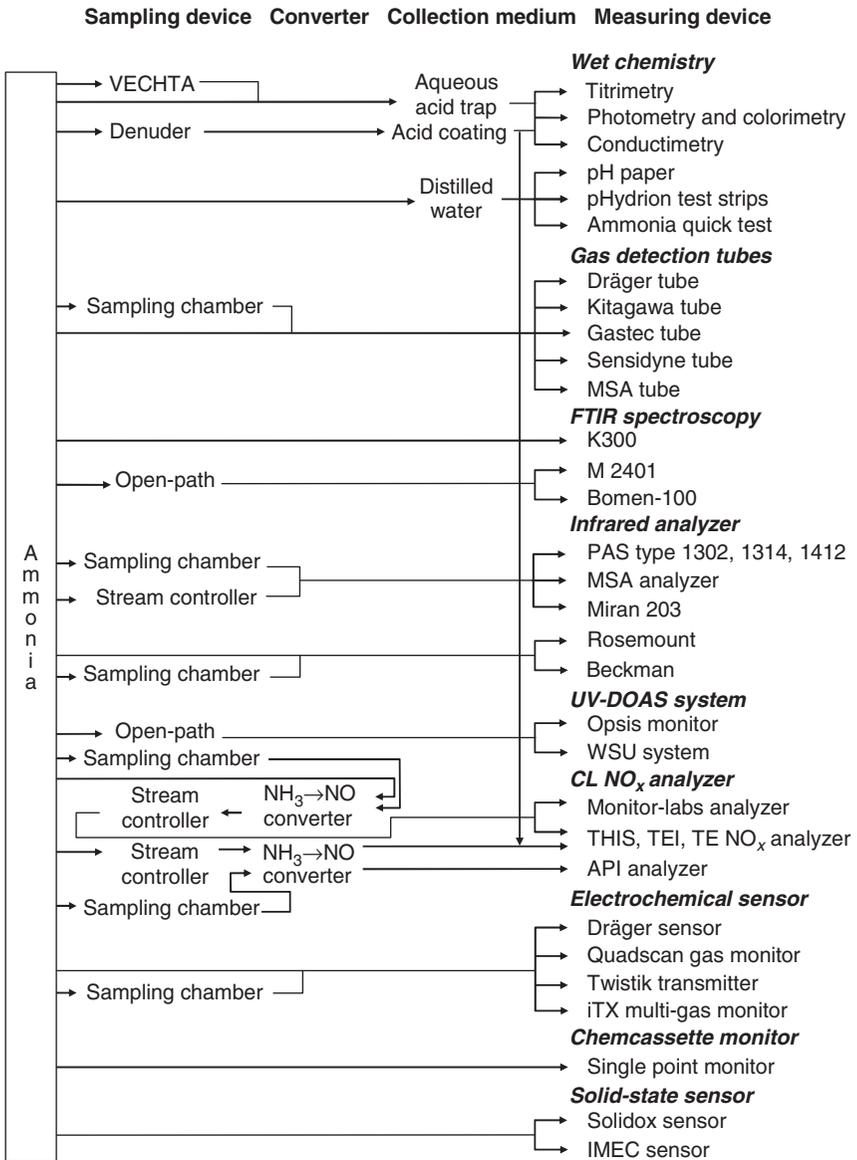


Figure 2 An overview of techniques applied to sample and measure ammonia at animal facilities.

Specific devices are often required during NH₃ sampling. Integrated systems that regulate the time and volume of air intake inside measurement instruments are not within the scope of this chapter.

3.1. Sampling location

Spatial variations of NH_3 concentration that exist at animal facilities make the selection of sampling location very important. An animal building is a ventilated but imperfectly mixed air space with nonuniform sources, resulting in temperature and concentration gradients. Although ventilation in the building creates air mixing, it can also increase the spatial concentration variations in situations when it dilutes NH_3 at some locations more than at others. At uncovered manure storages and lagoons, in addition to the less than uniform source across the surface, localized NH_3 concentrations depend to a great extent on weather conditions especially the wind speed, wind direction, and temperature. Large concentration gradients exist at these areas when there is a poor dispersion due to slow air movement. Consequently, different sampling locations may result in wide variations in measurement data because of spatial NH_3 differences.

Sampling at particular locations is needed if the NH_3 concentrations at these locations are to be obtained. The number of sampling locations determines the spatial resolution of the NH_3 concentration profile. The more the sampling locations are, the better the spatial resolution of the data. Unfortunately, in practical situations, the ideal number of sampling locations is often compromised due to the limitation of budget, equipment, time, and manpower. Many recent long-term emission research projects at large animal buildings with continuous measurement equipment can only afford about a dozen shared sampling locations at a farm. Therefore, choosing the most representative sampling locations has great statistical importance.

Selection of sampling locations depends on the measurement objectives. If the study is to determine human or animal exposure to NH_3 , the sampling locations should be at the human or animal breathing zones. If the primary objective of sampling is to determine emissions, the sampling locations should be located to represent not only the ventilation exhaust air but also the incoming air to account for background concentrations. The sampling locations were at the building air inlets and ventilation fan exhausts for mechanically ventilated livestock buildings (Hartung *et al.*, 1997; Heber *et al.*, 2001), at the ridge exhaust of a naturally ventilated dairy buildings (Monteny *et al.*, 2002; Snell *et al.*, 2003), and upwind and downwind of an uncovered manure storage (Sommer *et al.*, 2004a). Sampling at both inlet/upwind and exhaust/downwind is to subtract background NH_3 concentrations and obtain the net emission or generation from these facilities. For NH_3 dispersion modeling, sufficient samples should be taken to represent a large area downwind as well as the NH_3 generation sources.

3.2. Sampling time

Temporal variation of NH_3 concentration at animal facilities is the reason that time of sampling is critical for obtaining dependable data. Results of NH_3 concentrations acquired at specific times usually are only valid for that

time. Extended reference of these concentrations could introduce errors. For example, NH_3 concentrations in animal buildings measured in winter are not suitable to represent those in summer because of seasonal differences.

Seasonal temperature change is the most important factor influencing seasonal NH_3 concentration variations. The difference between summer and winter daily mean temperatures can be significant in agricultural regions. Temperature plays an important role in NH_3 release from liquid manure because it determines the convective mass transfer coefficient (Ni, 1999). In open animal feedlots and manure storages/lagoons, higher temperature means faster NH_3 release from liquid manure and hence higher NH_3 concentrations above the manure surface. In confined animal buildings, higher ambient temperature in summer requires more ventilation to reduce animal heat stress. Daily mean ventilation rates in summer can be more than 20 times than those in winter in mechanically ventilated animal buildings. Seasonal variations of temperature and ventilation at animal houses change not only the NH_3 concentrations but also the NH_3 emission rates (Harper *et al.*, 2004).

Seasonal wind velocity and direction changes have greater effects on NH_3 concentration in open facilities than in buildings. In addition, precipitation and solar radiation can quickly change the solid content in manure in open fields, consequently changing the NH_3 release rate from manure.

Diurnal variations of NH_3 concentration at animal facilities are also caused by weather conditions. In fair weather, the recorded diurnal temperature varied as much as 15°C on a swine farm in Midwest, USA, and the temperature-based ventilation in the afternoon was about 5 times as high as in early morning (Fig. 3). The diurnal NH_3 concentrations in the same

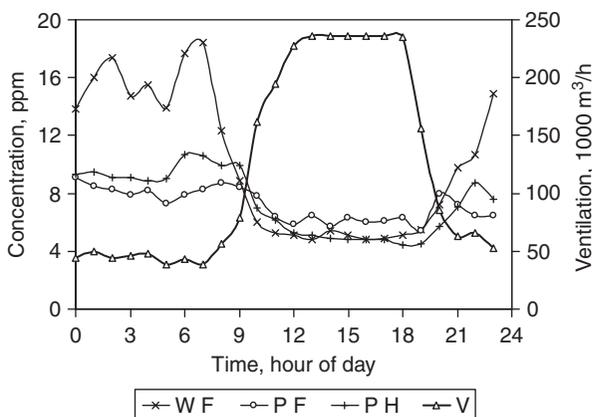


Figure 3 A 24-h record of temporal and spatial variations of ammonia concentrations at wall fans (WF), pit fans (PF), pit headspace (PH), and ventilation rate (V) in a 66 m (L) \times 13 m (W) mechanically ventilated swine finish building. Source: Ni *et al.* (2000b).

study closely followed the diurnal variation of ventilation rates (Ni *et al.*, 2000b). Moreover, certain daily animal activities affected the NH_3 concentrations, for example, pig urination was followed by NH_3 concentration peaks (Aarnink *et al.*, 1993a).

It is clear that low frequency sampling results in poor representation of the true NH_3 fluctuation patterns and therefore unreliable mean NH_3 concentrations. Measurements of varying concentrations that cover excessively short periods may produce data with serious temporal limitations. To depict an accurate picture of NH_3 at animal facilities, its temporal variations should be resolved by selecting sufficiently high sampling frequency. The higher the sampling frequency is, the better the data resolution and the more accurate the mean value. According to the Nyquist Theorem, the sampling frequency should be at least twice the maximum frequency of the signal that is being sampled (Finkelstein and Grattan, 1994). However, high frequency sampling is subject to some technical restrictions especially the response time of the measuring device.

The temporal variations of NH_3 concentrations shown in Fig. 3 demonstrate that it is important to select proper sampling time. Sampling time should be arranged to cover peak and valley concentrations during the day, especially when there are significant temperature and airflow rate fluctuations, to obtain daily mean concentration, whether short-duration sampling (e.g., active gas detection tube) or long-duration sampling (e.g., passive gas tube or wet chemistry) techniques are used.

Based on the same principle, sampling should be designed to cover the low concentration season (usually summer) and high concentration season (usually winter) if an annual mean concentration or emission rate is to be obtained.

3.3. Sample volume

Accurate control of air sample volume is indispensable for some measurement techniques such as active gas tubes and wet chemistry with acid traps, in which the chemical reaction depends on the total mass of NH_3 in the sample. In order to get volume-specific concentration, the volume of the air sample in the chemical reaction must be accurately known.

A special sampling/control device is often needed to control sample volume. For active gas tubes, a handheld pump provided by the gas tube manufacturer is employed (Section 5.2.1). For wet chemistry, several different air volume control devices with different sample volumes and sampling durations were reported in the literature. Pfeiffer *et al.* (1993) and Krieger *et al.* (1993) adopted an air collection system called VECHTA to control sampling volume. The system continuously provided 1.0 l/min of sample air to an acid collection medium. In Guiziou and Beline (2005), 5 l/min sampling air was flown through acid trap for 2–3 days.

3.4. Sampling methods and devices

Three main sampling methods are currently applied in field tests. They are closed, point, and open-path methods (Fig. 4). The differences among the three methods are the spatial coverage by the sampling devices. The closed method collects samples from an enclosed surface area. The point method and the open-path method target air at certain points and in a narrow optical path within a three-dimensional zone, respectively. Depending on the sampling devices, the point sampling method can also be divided as two sub-methods: the passive exposure method and the active extraction method, which can be localized or centralized.

3.4.1. Closed sampling

The closed sampling method involves a physical enclosure or chamber to create a limited headspace over a selected piece of NH_3 release surface. The “static” chamber (Sommer *et al.*, 2004b) does not have air exchange between the outside and inside of the chamber and has thus far only been used in investigations of NH_3 release from soil. The sampling chambers discussed in this chapter are all “dynamic.” They have an open bottom and are equipped with one or more air inlets and one or more outlets. The chamber is placed on the floors of animal buildings or on the surfaces of liquid or solid manure that releases NH_3 thus isolating the release surface from its surroundings. The samples are drawn from the inlet and outlet of the chamber (Fig. 5).

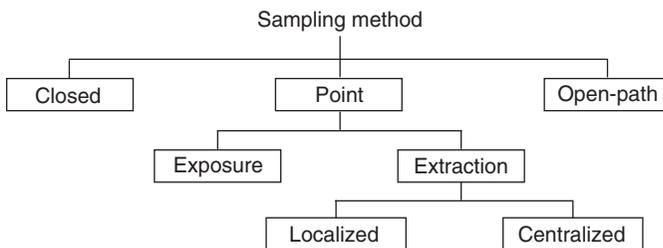


Figure 4 Ammonia sampling methods at animal facilities.

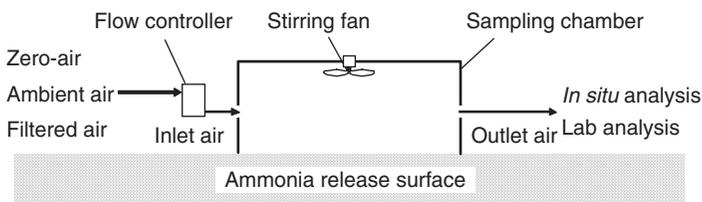


Figure 5 Schematic of a closed method for ammonia sampling.

Sampling chambers have been given various names, for example, Lindvall box (Scholtens, 1990), dynamic chamber (Elwinger and Svensson, 1996; Loyon *et al.*, 2007), wind tunnel (Misselbrook *et al.*, 1998), flux chamber (Heber *et al.*, 2000a), measuring chamber (Andersson, 1996), floating chamber (Willers *et al.*, 1996), and emission hood (Chadwick, 2005). The earliest sampling chamber was the Lindvall Box ($1.5 \times 1.0 \times 0.4 \text{ m}^3$) developed in Sweden for odor analysis, during which cleaned air was blown through the box and brought back to a mobile laboratory for measurement (Lindvall *et al.*, 1974). The Lindvall Box was later used for NH_3 sampling in animal building by Scholtens (1990), Kant *et al.* (1992), Elzing and Swierstra (1993), and Kroodsma *et al.* (1993).

The volumes of the sampling chambers were between 0.02 and 108 m^3 , and most of them had box-like shapes. The largest chamber covering area was 160 m^2 in a pig house converted from manure culverts (Andersson, 1995). A special design, a movable sampling chamber attached to a steel trolley that could be rolled back and forth along a steel runner system was reported by Chadwick (2005) to sample NH_3 from beef cattle farmyard manure.

Airflow through the chamber was supplied by a fan (installed in the inlet or outlet) or a compressed air cylinder, hence sometimes emphasized as “dynamic.” Most tests involved blowing ambient air, filtered (Heber *et al.*, 2000a) or unfiltered (Svensson *et al.*, 1997), through the chamber. A few tests blew compressed zero-air (Aneja *et al.*, 2000). In one study, the fan was in the chamber air exhaust (Jeppsson, 1999). Some projects used stirring fans inside the chamber to mix air (Aneja *et al.*, 2000; Ferguson *et al.*, 1997; Jeppsson, 1999; Svensson *et al.*, 1997). A comparison of 14 reported sampling chambers is given in Table 1.

Many of these sampling chambers were used in animal houses. Elwinger and Svensson (1996) described a battery-powered chamber, developed by Svensson and Ferm (1993), in an experimental broiler house. Ferguson *et al.* (1997) developed an isolated 19-liter container laid over a portion of the litter in a broiler room. Brewer and Costello (1999) used a Plexiglas chamber to cover the litter in a commercial broiler house. Misselbrook *et al.* (1998) conducted sampling on concrete floors in a commercial dairy yard. In a study by Blanes-Vidal *et al.* (2007), a 30-cm diameter stainless steel chamber was constructed with circulation air delivered via nine inlet holes into the chamber for dairy manure emission in an experimental test room. The NH_3 concentration was measured with an Innova Gas Monitor.

Sampling chambers were also used in manure composting sites. Amon *et al.* (1997) described two large-scale chambers developed in Austria to collect emission data from aerobically composted and anaerobically stored solid manure. Osada and Fukumoto (2001) developed a 13-m^3 chamber for monitoring a composting mixture.

Table 1 Summary of sampling chambers

Chamber name	Shape	Dimension	Incoming air	Emission source	Stir fan	Note
Lindvall box	Box	$1.5 \times 1.0 \times 0.4 \text{ m}^3$	Cleaned	Animal houses	No	Elzing and Swierstra (1993) , Kant <i>et al.</i> (1992) , Kroodsmas <i>et al.</i> (1993) , Scholtens (1990)
Dynamic chamber	Box	$0.40 \times 0.30 \times 0.18 \text{ m}^3$	Ambient	Broiler house	No	Elwinger and Svensson (1996)
Chamber	Box	Length 5.4 m	Ambient	Pig house	No	Andersson (1995)
Container	Not specified	Volume 19 liter	None	Broiler litter	Yes	Ferguson <i>et al.</i> (1997) . Shape of the chamber was not described
Chamber	Box	$1.22 \times 0.76 \times 0.41 \text{ m}^3$	Ambient (0.2 m/s)	Broiler litter	No	Brewer and Costello (1999)
Dynamic chamber	Box	Bottom 0.25 m^2	Ambient	Pig house	Yes	Svensson <i>et al.</i> (1997)
Open dynamic chamber	Box	$6 \times 3 \times 2 \text{ m}^3$ and $9 \times 6 \times 2 \text{ m}^3$	Ambient (1–11 m ³ /h)	Treated manure	No	Amon <i>et al.</i> (1997)
Wind tunnel	Not specified	$2 \times 0.5 \text{ m}^2$	Ambient (1.0 m/s)	Concrete floor	No	Misselbrook <i>et al.</i> (1998) . Shape and height of the wind tunnel was not given by the authors

(continued)

Table 1 (continued)

Chamber name	Shape	Dimension	Incoming air	Emission source	Stir fan	Note
Hood	Box	Open face: 0.9 m ²	Filtered (1.0 m/s)	Dairy farm	No	Misselbrook <i>et al.</i> (1998)
Buoyant convective flux chamber	Box	1.22 × 0.61 × 0.25 m ³	Filtered (1.1 m/s)	Lagoon	No	Heber <i>et al.</i> (2000a)
Dynamic chamber	Cylinder	0.27 m (d) × 0.42 m (h)	Zero-air (2.4– 4.7 l/min)	Lagoon	Yes	Aneja <i>et al.</i> (2000)
Emission hood	Not specified	1.15 m (h), volume 7 m ³	Not specified (130 l/s)	Farmyard manure	No	Chadwick (2005)
Flux chamber	Cylinder	30 cm	Circulation air	Dairy farm	No	Blanes-Vidal <i>et al.</i> (2007) . Only partial cylinder dimension was provided
Dynamic chamber	Box	0.4 × 0.4 × 0.6 m ³	Clean air (1.5 m ³ /h)	Manure treatment	No	Loyon <i>et al.</i> (2007)

The buoyant sampling chamber was a tool for NH₃ monitoring in lagoons. Heber *et al.* (2000a) and Lim *et al.* (2003) developed and employed a buoyant chamber using 1.0 m/s air speed in the chamber. It floated ~0.17 m above the water and covered 0.74 m² of swine lagoon surface. Aneja *et al.* (2000) and Bajwa *et al.* (2006) obtained NH₃ data from lagoons using a cylinder (27-cm diameter, 42-cm height) with a Teflon-coated wall and a stirring fan.

3.4.2. Point sampling

Point sampling is the method in which samples are taken at a selected single point or at multiple points at animal facilities. Unlike closed sampling, the sampling location of this method can be at different heights from the NH₃ release surface or at the air inlet/exhaust of a building. It can also be used to sample upwind or downwind ambient air around the facility.

There are two different ways of point sampling: exposure and extraction. Exposure sampling uses passive sampling devices or sensors and therefore does not require sampling pumps. It can be a simple procedure when using measuring devices, such as detection tubes, where sample air is diffused to passive NH₃ samplers/sensors for obtaining a small number of time weighted average (TWA) concentration data.

The micrometeorological technique is a point-sampling method and has been used to determine NH₃ concentrations at lagoons (Zahn *et al.*, 2001), on animal farms (Cassel *et al.*, 2005a,b), and at a manure storage (Sommer *et al.*, 2004a). In micrometeorological sampling, multiple passive samplers are set up at different height in towers or poles located upwind and downwind of the source. The samplers provide TWA NH₃ concentrations. This method is usually applied to large area sources.

Extraction sampling employs a pump or pumps to pull air from sample locations. Localized extraction uses a pump and sampler at the sampling location, for example, sucking air with a handheld pump to a gas tube (Section 5.2.1), or with an electrical pump to an acid trap (Section 5.1.1). It does not engage transporting the sample air long distances to a measurement location.

Centralized extraction is a more complex method for multi-point sampling. It extracts and transports sample air from different points to a single set of measurement devices, which can be as far as several hundred meters away from the sampling points. Sample air is transported continuously via tubing, usually Teflon[®] tubing (Ogink and Kroodsmas, 1996). The tubing may require insulation or heating to avoid condensation inside the tubing when it passes through zone that is cooler than the dew point of the sample location (Heber *et al.*, 2006; Ogink and Kroodsmas, 1996). The instruments used in the system measure the NH₃ concentration in the sample air from one sampling point for a certain duration, for example, 10 min, before switching to air from another point. A multi-point sampling system

(MPSS), usually computer controlled, is needed to regulate the time and location of sampling.

Figure 6 presents schematics of three commonly used MPSSs. The system on top of the figure is a negative pressure system. It has a vacuum sampling pump that applies vacuum pressure to a stream controller and tubing network. Sample air is withdrawn into the pump and then delivered to the gas measurement instrument. This system requires that the stream controller and the tubing network must be airtight. It was first reported in Europe in the early 1990s. An air stream controller placed between several $\text{NH}_3 \rightarrow \text{NO}$ converters and an NO_x analyzer was described by van Ouwerkerk (1993). Berckmans and Ni (1993) employed a similar system that regulated air sample streams, 2 min for each of six converters. This system requires multiple converters, one at each sampling point, but has fast response because it avoids the transportation of the “sticky” NH_3 in the long tubing between the converter and the analyzer. In the study by Ogink and Kroodsmma (1996), air samples of each sampling location were analyzed over 1 min at intervals of 5 min.

The system shown in the middle of Fig. 6 is also a negative pressure system. It was used in the United States (Heber *et al.*, 2001). Heber *et al.* (2006) described a gas sampling system, which included a set of solenoids,

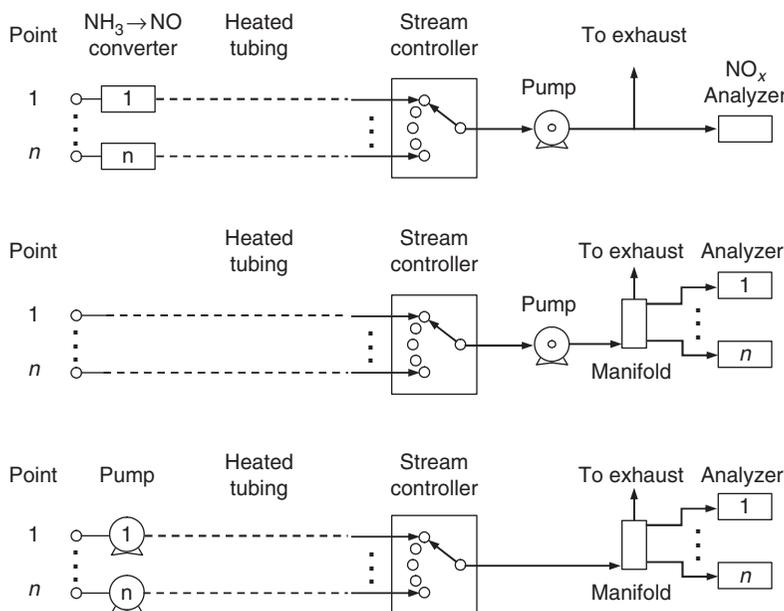


Figure 6 Schematics of three MPSS. Top, negative pressure system with multiple $\text{NH}_3 \rightarrow \text{NO}$ converters and single NO_x analyzer. Middle, negative pressure system with multiple analyzers. Bottom, positive pressure system with multiple analyzers.

manifolds, pumps, mass flow meter, and vacuum pressure transducer in a semi-enclosure. It was used to sample and regulate air streams from multiple sampling locations, each lasting for 10 min, to a set of analytical instruments, including a single $\text{NH}_3 \rightarrow \text{NO}$ converter that was followed by an NH_3 analyzer and other gas analyzers for hydrogen sulfide (H_2S) and carbon dioxide (CO_2) measurement.

The system at the bottom of Fig. 6 is a positive pressure system that uses one air compressor at each sampling location to pump air to the measurement instrument (Hoff, 2005; Zhang *et al.*, 2005). This system avoids most of the air leakage problem but requires multiple air pumps.

3.4.3. Open-path sampling

Open-path sampling uses optical detection devices, which consist of an emitter telescope and a receiver/detector. The source light from the emitter, ultraviolet (UV) or infrared (IR), is beamed in one direction over a certain distance (hence an open path), which contains gaseous NH_3 , to the receiver/detector (Fig. 7). The open-path technique provides path-weighted average (PWA) gas concentrations of samples taken in a one-dimensional path within a three-dimensional zone.

Depending on the technology, the length of the open path between the light source and receiver can be 100–150 m (Secrest, 2001a), 500 m (Amon *et al.*, 1997), and up to 750 m (Mount *et al.*, 2001). The source and the receiver can be at two ends of the open path. The detection path is between the source and the receiver. They can also be at the same end with a reflection mirror at the other end of the open path. In this case, the light source beamed to the distant mirror reflects back to the receiver. The path is between the mirror and the source/receiver.

Open-path sampling for NH_3 concentration was conducted downwind of an animal facility for assessment of neighbor exposure to NH_3 concentrations. Secrest (2001a) oriented the monitoring paths east–west when the prevailing winds were from the south at 0.8 km north of a cluster of eight swine barns in Missouri using an ultraviolet differential optical absorption

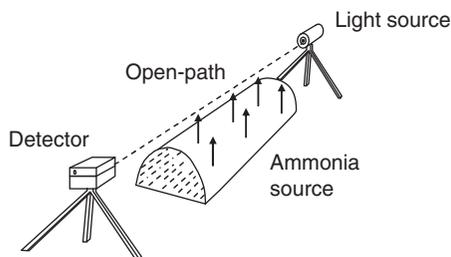


Figure 7 Schematic of open-path sampling. According to Amon *et al.* (1997).

spectrometer (UV-DOAS) and a Fourier transform interferometer. [Harris *et al.* \(2001\)](#) employed a single-beam open-path Fourier transform infrared (OP-FTIR) system along several paths to measure all the exhaust plumes from nine finishing swine barns in North Carolina. The OP-FTIR beam passed through the fan plumes 1 m from the fan outlets. This technique was also used to measure anaerobic lagoon NH_3 emissions by [Shores *et al.* \(2005\)](#).

3.5. Selection of sampling method

The selection of a sampling method depends on several factors, including cost, sampling objective, and technical pros and cons of the method.

Financial resource is always one of the most important factors in choosing a sampling method. Sampling methods differ in initial cost, which includes equipment cost, setup cost, and operation cost. Cost of sampling equipment and setup can vary greatly depending on the scale of the study. To reduce the equipment and setup cost, many research institutions tend to take advantage of existing equipment, laboratory facilities, and technical expertise. The cost per sample depends on the measurement method. Wet chemistry ([Section 5.1](#)) and gas tubes ([Section 5.2](#)) can have high cost per sample although their initial sampling cost is relatively low compared with some other measurement devices, for example, chemiluminescence (CL) gas analyzers ([Section 5.6](#)), which offer continuous measurement hence large numbers of sample concentration data.

Sampling objectives may vary from defining NH_3 exposure to human and animals, determining NH_3 emission rate, comparing facilities or abatement techniques, to modeling NH_3 dispersion. Some studies may need only a few samples to get a quick and preliminary result. Others may require large number of samples taken at different locations and cover a long period of time to fulfill the objective.

Technical characteristics of the methods are reflected in their intrusiveness, controllability, source isolation, sampling area, measurement instrument sharing, and automation. Intrusion of the sampling equipment may alter airflow patterns and gas concentration gradients that would naturally occur at the sampling location. Controllable sampling allows simulation of the animal facility to sample NH_3 concentrations at different physical conditions, for example, air speed ([Lim *et al.*, 2003](#)) and manure temperature ([Andersson, 1996](#)). Animal facilities differ in size and complexity. Many modern animal facilities include multiple large animal buildings, manure storages, and processing plants. Some research institution- or university-owned experimental facilities and traditional family farms are relatively small. Large size complexes have multiple NH_3 sources that are difficult to isolate if only some components are of research interest. Sampling area refers to the size of area at the animal facility for which the method is

suitable to use. Measurement instrument sharing allows a single set of instruments to measure NH_3 concentrations sampled at multiple locations. It reduces the cost of instruments as well as the errors among the instruments if multiple instruments are used. Automation is necessary for comprehensive projects to obtain large number of samples over long periods.

Table 2 compares various aspects of the three sampling methods. The cost of each method in the table is relative to each other and is split into equipment and setup. The per-sample cost is not listed because it does not only depend on the sampling method.

The equipment and setup costs of the closed method are low (<US\$1000). This method provides a small-scale cut-off space under field conditions and therefore enables easily controllable studies. For example, airflow through and temperature in the chamber can be measured and adjusted to investigate their effects on NH_3 concentration. This method is also very good for source isolation. However, a sampling chamber is intrusive and alters the facility's natural conditions and gas concentration profile. Thus, there can be a significant difference between controlled and natural airflow patterns and gas concentration gradients above the NH_3 release surface. Shah *et al.* (2006) concluded that this method is suitable only for comparing treatments. Moreover, closed sampling is limited to small NH_3 release surfaces.

The cost of point sampling varies greatly because this method has different variations. The exposure method can have very low equipment and setup cost due to its simplicity. However, it can also be very high if a complicated micrometeorological sampling system is involved. The exposure method uses diffusion samplers and is suitable for small number of samples. Therefore, its per-sample cost can be high. The equipment and setup cost for the centralized extraction method is the highest among different methods. A complete 14-point negative pressure sampling system at two large animal buildings described by Heber *et al.* (2006) could cost around US\$20,000.

Point sampling can be used for different study objectives. Samplers and sampling probes can be easily located at the animal and human breath zones. Samples can also be obtained for baseline emission determination, comparison studies, and emission/dispersion model development. The method is flexible for different sizes of studies, ranging from a small emission source to an entire commercial animal farm. One special technical advantage of the centralized extraction method is that it allows sharing measurement instrumentation. Because the size of the point-sampling device exposed at the sampling locations is very small compared with the sampling zone that it represents, this method is basically nonintrusive and does not disturb the NH_3 source and its surroundings. It is the most widely used sampling method in animal buildings.

Table 2 Comparison of different ammonia sampling methods

	Closed sampling	Point sampling	Open-path sampling
Cost			
Equipment	Low	Very low for exposure method. Medium for localized extraction method. High for centralized extraction method.	Medium to very high
Setup	Medium	Very low to high for exposure and localized extraction methods. Very high for centralized extraction method.	Low to medium
Technical aspect			
Study objective	Treatment comparison and surface release	Animal and human exposure, baseline emission, treatment comparison, and dispersion modeling	Human ambient exposure, baseline emission, treatment comparison, and dispersion modeling
Size of sampling area	Small release surface	Flexible	Large
Intrusiveness	Intrusive	Little intrusive	Nonintrusive
Controllability	Controllable for airflow at release surface	Controllable for sampling flow	Not controllable
Source isolation	Best	Better	Poor
Instrument sharing	Yes	Yes in centralized extraction method	Yes for scanning system

Open-path sampling has a relatively shorter history than point sampling for agricultural NH_3 study. Its sampling equipment and setup cost can be from low to medium depending on the complexity of the research objectives. An obvious advantage of this method is that it is not intrusive to the system being measured. There is also no adsorption of NH_3 on sample transporting system (e.g., tubing and fitting). Large areas can be investigated and the detection limit is very low. Disadvantages of the method lie in the determination of emission rates by the inverse dispersion models. Weather conditions must be known during the measurement period. Different emission sources lying close to each other cannot be distinguished from each other (Amon *et al.*, 1997). It is also not easy to use for animal exposure study inside the barns.

4. AMMONIA CONCENTRATION MEASUREMENT

4.1. Characteristics of measurement techniques

The first reported measurements of NH_3 concentrations at animal facilities were in the 1960s using wet chemistry (Moum *et al.*, 1969; Valentine, 1964). With the advancement of sensor and analytical technology, more and more techniques were developed. Thus far, nine groups of technologies have been introduced and used at animal facilities. They are summarized in Fig. 2, which also illustrates the sampling methods that these measurement devices were reportedly used with. The devices and setups were chosen to meet various objectives, different technical requirements, and budget constraints based on their characteristics, which are categorized in Table 3 and discussed below.

4.1.1. Wet or dry

According to Kamin *et al.* (1979), analytical methods of NH_3 can be categorized as “wet methods,” which use aqueous media, and “dry methods,” which is a direct analysis of NH_3 in the gas phase.

4.1.2. Active or passive

An active measurement device needs a pump, whether hand or electric powered, to provide controlled sample air flowing to the device. A passive measurement device does not require a pump. It allows air to diffuse into the sensor. Passive measurement devices need to be placed right at the sampling location during measurement. Passive techniques that depend on diffusion take longer to finish a measurement. Because of this, it can provide TWA concentration with a single point measurement. Some active methods (e.g., wet chemistry) only provide TWA concentrations.

Table 3 Characteristics of some reviewed ammonia measurement devices and methods

Method	Wet or dry	Active or passive ^a	Sensitivity ^b	Readout	Sensor life ^c	Response time ^d	Cost ^e
Standardized wet chemistry	Wet	A	0.01–1 mg/l	Indirect	S	h	L ^f
pH paper/test strip	Wet	P	ppm	Direct	S	s	VL
Denuder and wet chemistry	Wet	P	ppb	Indirect	S	h	L
Active gas tubes	Dry	A	0.5 ppm	Direct	S	m	L
Passive gas tubes	Dry	P	ppm	Direct	S	h	L
Chemcassette	Dry	A	ppm	Direct	S	s	H
EC sensors	Dry	A; P	ppm	Direct	M	m	H
NO _x analyzers	Dry	A	1 ppb	Direct	M	m	VH
FTIR spectroscopy	Dry	P	ppb	Direct	M	m	VH
Rosemount NDIR ^g	Dry	A	ppm	Direct	M	s	H–VH
PAS ^h	Dry	A	0.01–1 ppm	Direct	M	s–m ⁱ	VH
Chillgard MSA analyzer	Dry	A	1 ppm	Direct	M	m	H
UV-DOAS	Dry	P	ppb	Direct	M	s	H
Solid-state sensor	Dry	P	ppm	Direct	M	s	M

^a A, active, P, passive.

^b Expressed in concentration level.

^c S, single use, M, multiple use.

^d Response time in the ranges of: h = hours, m = minutes, s = seconds.

^e Costs are approximate and may vary depending on time and location of purchase, providers, and accessories. Equipment cost only, not including maintenance and operation. VL, very low (<US\$1/sample); L, low (US\$1–10/sample); M, medium (<US\$5000/device); H, high (US\$5000–15,000/device); and VH, very high (>US\$15,000/device).

^f Analytical instrument used to analyze the collection medium is not counted.

^g Rosemount® nondispersive infrared analyzer.

^h Brüel & Kjær PAS and Innova photoacoustic gas monitor.

ⁱ Depending on the number of gases to measure and the instrument configuration.

EC, electrochemical; FTIR, Fourier transform infrared; MSA, Mine Safety Appliances; NDIR, nondispersive infrared; PAS, photoacoustic spectrophotometer; UV-DOAS, ultraviolet differential optical absorption spectrometer.

4.1.3. Sensitivity

Sensitivity is the capability of a measuring device to discriminate between measurement responses representing different levels of a variable of interest. Sensitivity is determined from the value of the standard deviation at the concentration level of interest. It represents the minimum difference in concentration that can be distinguished between two samples with a high degree of confidence (USEPA, 1998).

Some techniques were reported to be highly sensitive, for example, the method of converting NH_3 to NO followed by NO_x analysis has lower detectable limit of 1 ppb NH_3 . Others provide sensitivity at ppm reading, for example, NH_3 detection tubes. Sometimes high sensitivity techniques are called analytical techniques, which provide quantitative data, and low sensitivity ones are called detection techniques, which provide qualitative or semi-quantitative data.

4.1.4. Readout

Direct readout is an important feature, especially for field measurements. Techniques with direct readouts provide an immediate visual display of NH_3 concentration right after the measurement is completed. Most of the techniques reviewed in this study provide direct readout. Some of them are followed by automatic data retrieving and calculation.

Techniques with indirect readouts require a chain of procedures and devices, for example, trapping NH_3 in acid collection medium followed by laboratory analysis of the medium with wet chemistry methods. Compared with the direct readout, the indirect readout method takes more time to obtain results and is less suitable for large numbers of measurements.

4.1.5. Sensor life

The sensor in an NH_3 measuring device is the material or part that undergoes a physical or chemical change when exposed to sample air.

Single measurement techniques adopt disposable sensor materials that cannot be reused. The gas detection tube is a typical single use sensor. In wet chemistry methods, the NH_3 collection medium is used only once. Continuous measurement techniques can provide many concentration readings over time, usually in the form of electronic signals that can be easily recorded and processed. Sensor materials for these devices usually do not need to be replaced, with the exception of EC sensors (e.g., Dräger unit that has a sensor life of 18 months). The cassette in the Chemcassette gas monitor is a single-use sensor material, although one cassette can provide multiple readings.

4.1.6. Response

Response is a measure to evaluate how quickly or slowly a measuring system can react to NH_3 and present correct concentration readings. Manufacturers use response time, time needed for an instrument to reach from

0 to 90% (t_{90}) at zero to span difference in gas concentrations, to describe the instrument specifications. The response of passive diffusion sampling can be as long as 8–24 h.

4.1.7. Cost

Costs of the reviewed techniques vary widely and also differ with time and geographical locations. The lowest cost of single measurement is <US\$0.10 (e.g., pH paper test strips) if only sensor material is counted. A gas detection tube may cost about US\$8.00.

The most expensive measuring device with a multiuse sensor can cost more than US\$35,000 (e.g., a photo-acoustic multi-gas analyzer). Cost may also be much different for accessories (e.g., calibration kit, stream controller) and maintenance parts (e.g., NH_3 scrubbers).

4.2. Selection of measurement techniques

Selection of measurement techniques should be based on research objectives, coupled with the capabilities of the research institution and the research budget constraints. Cost of the techniques is one of the most important factors to be considered in almost all research projects. Thus, capital and operating costs may need to be assessed with the performance of the technique.

Standard wet chemistry requires analytical instruments that may already exist at many institutions. When the capital investment of analytical instruments does not need to be considered, wet chemistry methods are inexpensive and affordable. They are especially useful for small numbers of samples. The pH-paper-based test kits are appropriate for obtaining mere indications of in-building NH_3 concentrations when accuracy is not a high priority.

However, small numbers of samples and short-term measurements cannot satisfy the quality requirements in many field investigations. Techniques that produce large amounts of data should therefore be considered. The cost per sample using high-priced instruments with multiuse sensors may be less expensive than using low-price single-use sensors. Nevertheless, some expensive instruments, like IR analyzers and NH_3 analyzers, are usually only used at institutions conducting intensive research on agricultural NH_3 .

Applications of high and low sensitivity measuring devices are generally related to indoor and outdoor NH_3 measurements, respectively. Indoor NH_3 concentrations at animal facilities are usually at least several ppm, and almost all the techniques reviewed in this study are compatible. Because outdoor NH_3 may be at ppb level, some sensors, for example, gas detection tubes, are not appropriate due to their low sensitivity and high minimum detection limit.

Measuring devices with quick responses, for example, having a t_{90} less than 2 min, are required to properly study the dynamic behavior and diurnal

variations of NH_3 concentrations. Sensors with long response times, for example, passive gas tubes, are good only when TWA data are needed.

There appears to be an increasing use of dry methods with direct read-outs in recent years. Some of these methods can handle large numbers of measurements with immediate results, provide high frequency and high precision measurements, and enable computer-aided data logging. The successful application of these techniques advanced the characterization, quantification, and modeling of agricultural NH_3 emission significantly, for example, by establishing NH_3 emission factors for different sources and by revealing dynamic behaviors of NH_3 release from various components of animal production systems.

5. MEASUREMENT METHODS AND DEVICES

5.1. Wet methods

5.1.1. Standardized wet methods

Most wet methods are standardized methods (Table 4) that rely on collecting gaseous NH_3 into a suitable acid solution (acid trap or scrubber) and then performing concentration determination in the laboratory (Fig. 8). Wet methods can be active or passive. In the active method, air is pumped through the acid solution during sampling and the volume of air passing through the solution is recorded (Nicholson *et al.*, 2004). The NH_3 concentration in the air is calculated based on the volume. This method has a long history in NH_3 measurement at animal facilities started in the 1960s (Valentine, 1964) and is still in use (Guiziou and Beline, 2005; Loyon *et al.*, 2007; Shah *et al.*, 2006). In the passive method, NH_3 in air is diffused into the acid and no pump is required.

The most commonly used acid traps for measuring NH_3 at animal facilities include boric acid (Curtis *et al.*, 1975), orthophosphoric acid (Kay and Lee, 1997; Misselbrook *et al.*, 1998; Nicholson *et al.*, 2004), nitric acid (Willers *et al.*, 1996), and sulfuric acid (Guingand, 1997, #1681; Guiziou, 2005, #2272; Jiang and Sands, 2000; Krieger *et al.*, 1993; Loyon *et al.*, 2007; Pfeiffer *et al.*, 1993; Valli *et al.*, 1991).

Three general methods of colorimetric techniques have accounted for the majority of the determinations of NH_3 concentration in the acid trap solutions. They are Nessler, indophenol, and pyridine-pyrazolone techniques; each of them has modifications and adaptations. However, only the first two, the Nessler and indophenol techniques, have been applied to the NH_3 measurement at animal facilities.

Photometry constitutes one of the most important methods in air analysis. The air samples must be converted into colored compounds that are then determined. There are specific and very sensitive color reactions

Table 4 Standardized wet methods used for measuring ammonia in acid traps

Methods	Sensitivity	Comments	References
Colorimetry- Nessler	0.02 mg/l	Traditional method, widely used in past; numerous interferences by other compounds, including aldehydes, sulfur dioxide, amines, and metals; pre-purification by distillation often recommended	Hashimoto (1972), Kamin <i>et al.</i> (1979), Kay <i>et al.</i> (1992), Valentine (1964), Valli <i>et al.</i> (1991)
Colorimetry- indophenol	0.01 mg/l	Widely used; adapted for automated analysis; less sensitive to interference than Nessler method; pH dependent	Kamin <i>et al.</i> (1979), Hesse (1994), Hoy <i>et al.</i> (1994)
Photometry	NA	Relatively simple but cannot handle large amounts of samples	Leithe (1971), Schmidt-Van Riel (1991), Wang <i>et al.</i> (1991)
Photometry- Nessler	NA	NA	Jiang and Sands (2000)
Conductimetry	0.1 mg/l	Potential interference from other redox species	Kamin <i>et al.</i> (1979), Mannebeck and Oldenburg (1991)
Titrimetry	1 mg/l	All acids and bases interfere	Curtis <i>et al.</i> (1975), Kamin <i>et al.</i> (1979), Verstegen <i>et al.</i> (1976)

Notes: Some references cited in this table provided technical information of the methods but did not report NH₃ measurement in animal houses. NA: not available from the cited references.

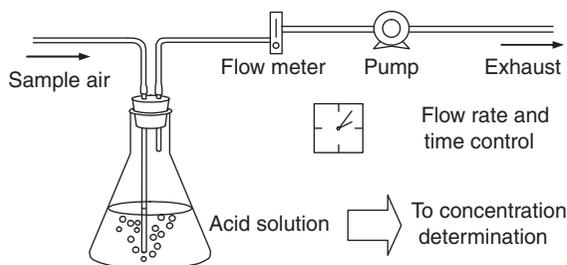


Figure 8 Schematic of sampling and analysis with wet chemistry.

available and the time required to perform a comparatively accurate measurement is short. Jiang and Sands (2000) analyzed NH_3 concentration in broiler buildings using the Nessler method and a spectrophotometer.

Noncolorimetric wet-chemistry techniques used at animal houses include acid conductimetry (Mannebeck and Oldenburg, 1991) and titrimetry (Curtis *et al.*, 1975; Versteegen *et al.*, 1976). Generally these techniques tend to be less sensitive than the colorimetric method and are subject to a host of interferences (Kamin *et al.*, 1979).

5.1.2. pH test paper

The method of pH test paper is based on the fact that NH_3 is readily dissolvable in water and converted into the ammonium cation (NH_4^+) thus changes the pH of the water. It is so far the simplest and least expensive way to obtain discrete ammonia measurements.

Moum *et al.* (1969) developed a very simple method by employing pH test paper and neutral distilled water as an NH_3 trap. The measuring range was 0–100 ppm and the resolution was ± 5 ppm. One follow-up use was tested by Seltzer *et al.* (1969). The method was inexpensive and provided direct *in situ* readout. However, it had low sensitivity and precision.

Using a commercialized version of this method, Dewey *et al.* (2000) tested pHydrionTM NH_3 test strips (Micro Essential Laboratory, Brooklyn, NY) in a swine unit in 1994. The pHydrion cost only US\$0.06 per test. It involved placing a drop of distilled water on a paper test strip, waving the strip in the air for one minute, and estimating NH_3 concentrations by matching the color change with a calibrated color chart.

A similar product, Ammonia Quick Test (AQT), distributed by Vineland Laboratories (Vineland, NJ), has a measurement range of 0–100 ppm NH_3 . An inch of the strip is tore off a roll of the test paper, wetted with 1 or 2 drops of distilled water, shaken off of excess water, and exposed for 15 s in sampling air. The paper strip changes color and is compared with the color chart to get the concentration reading. Skewes and Harmon (1995) tested the AQT in eight commercial broiler houses and concluded that it estimated NH_3 levels accurately in the 20–25 ppm range.

5.1.3. Denuder

The denuder is a device used to separate gases and aerosols over a given diameter based upon the difference in diffusion velocity between gases and aerosol particles. It is usually a tube containing a selective internal wall coating that removes the gaseous compounds at the wall.

Two different denuder systems are available for sampling and determination of gaseous NH_3 . The first procedure uses simple cylindrical tubes, sometimes called Ferm tube, as introduced by Ferm (1979). The second procedure uses so-called annular denuders, where the air is passed through the annular space between two concentric cylinders. This arrangement allows the airflow rate to be increased, and makes the subsequent chemical analyses somewhat less demanding (EMEP, 2001).

Preparation of denuders involves a careful laboratory procedure of coating an acid solution (usually citric acid, oxalic acid, or phosphorous acid) on the denuder internal wall and evaporating the liquid film. The NH_3 collected in the denuder is extracted with a chemical solution and analyzed in the laboratory, for example, using colorimetry (McCulloch *et al.*, 1998; Sommer *et al.*, 2004a).

Sampling can be passive using a diffusion denuder as described by Fitz *et al.* (2003) for evaluating NH_3 emissions from a dairy lagoon. A revised passive "Ferm tube" was reported by Phillips *et al.* (2000). The essential feature of this device was that a precision orifice in a disc of very thin material was installed in the mid-section of the tube so that the air flowing through the tube was proportional to the wind speed. A similar device, passive flux sampler, was described by Scholtens *et al.* (2003, 2004) and Mosquera *et al.* (2005) for NH_3 sampling and measurement at mechanically and naturally ventilated animal houses. It contains an orifice and collects NH_3 at a rate proportional to the air velocity of the air stream passing it without a pump. The passive flux samplers were also reported by Rodhe and Karlsson (2002) in a micrometeorological mass balance setup for NH_3 emission at a broiler manure storage. Ferm *et al.* (2005) presented a passive sampler consisting of two glass tubes internally coated with an acid. One end has a probe with a thin (0.05 mm) stainless steel disc with a 1-mm diameter hole. The average airflow in two opposite directed samplers is proportional to the wind speed vector component along the tubes.

Sampling with a denuder can be active with a sampling pump as outlined by EMEP (2001). Denuders can also be combined with NO_x monitors for continuous sampling/measurement (Mennen *et al.*, 1996).

5.2. Gas detection tubes

Gas detection tubes are based on adsorption of target air pollutants on solid surfaces accompanied by a color reaction. There are two types of disposable tubes: active and passive. Tubes with different measurement ranges are

available. Some have suitable measurement ranges for NH_3 in animal buildings. Usually, the sensitivities of the tubes are too low for measuring outdoor NH_3 concentrations.

The most obvious advantage of the gas detection tube is its operational and functional simplicity. Therefore, it was widely used in agricultural NH_3 measurements. Meyer and Bundy (1991) measured NH_3 concentrations in 200 farrowing pig houses with gas detection tubes.

Gas tubes are relatively low cost, usually US\$5–10 per tube and US\$300–500 for a hand pump. Dewey *et al.* (2000) reported US\$306 for the hand pump (Dräger Accuro Pump, Dräger Safety Inc., Pittsburgh, PA) and US\$4.12 for each tube.

Leithe (1971) stated that the standard deviation of the results of Dräger gas detection tubes is ~6–8% in favorable and 10–20% in less favorable cases. Skewes and Harmon (1995) found that the passive tubes (Gastec Passive Dosimeter Tube No. 3D) estimated average NH_3 levels accurately at low levels of NH_3 as compared with the Gastec Low Range Ammonia Detector Tube No. 3La. Liu *et al.* (1993) concluded that the accuracy of NH_3 detector tubes from the Mine Safety Appliance Company in Pennsylvania was ± 1 ppm. According to Scholtens (1993), Dräger tubes Type 2A and Kitagawa tubes Type 105SD for NH_3 measurement both had precision (coefficient of variation) less than 5% and an inaccuracy (systematic error) less than 10%. The precision of Dräger gas detector tubes (Type 5A) was ~10% and the inaccuracy was ~15%. Both precision and inaccuracy of Kitagawa tube (Type 105SC) were ~2%. The precision and inaccuracy of the gas tubes became worse at lower NH_3 concentration levels.

5.2.1. Active tubes

Active gas tubes require a hand-pump that sucks a predefined volume of air per stroke (Fig. 9). Both ends of the test tube are sealed when manufactured and are cut open just before measurement. The open-end tube is inserted tightly into the pump connector. By pumping the hand-pump, the air sample flows through the tube. The color that arises is evaluated to assess the NH_3 concentration. Active gas tubes from five different manufacturers have been used for NH_3 measurement at animal facilities.

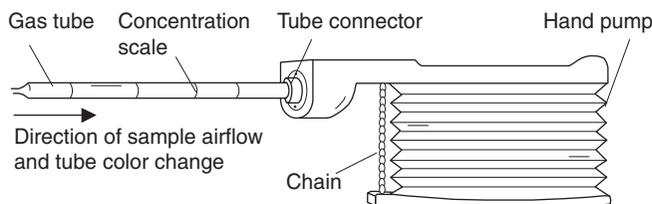


Figure 9 Dräger gas test tube and hand pump. Source: Ni (1998)

The Dräger tube is probably the most widely applied gas tube product in dairy cattle barns (Patni and Clarke, 1991), swine barns (Amon *et al.*, 1995; Hayes *et al.*, 2004; Stowell and Foster, 2000), and caged-layer barns (Patni and Clarke, 1991).

Other detection tubes used in animal houses include the Kitagawa[®] gas detector (De Praetere and van Der Biest, 1990; Jeppsson, 1999; Johnston *et al.*, 1981; Reece *et al.*, 1979; Scholtens, 1993; Svensson *et al.*, 1997), Gastec tubes (Jacobson *et al.*, 1992), Sensidyne detector tubes (Xin *et al.*, 1996), and Mine Safety Appliances (MSA) detector tubes with a Kwik-Draw[®] Pump (Mine Safety Appliances Company, Part number#487500) (Wheeler *et al.*, 1999).

5.2.2. Passive tubes

Like active tubes, passive sampling tubes are also sealed before using. However, only one sealed end of the tube is broken open to commence measurement. The opened tube is exposed at the selected sampling location for a specific time, usually several hours. The gas concentration indicated in the tube should be interpreted with the exposure time.

Passive NH₃ sampling tubes from different manufacturers have also been used at animal facilities. Patni and Clarke (1991) used Dräger tubes for TWA NH₃ concentrations in dairy, swine, and poultry barns. Busse (1993) used a passive Dräger system with a diffusion tube and a holder, in which the tube was inserted for 24-h measurements. Nicks *et al.* (1993) reported using 8-h diffusion tubes. Nicks *et al.* (1997), Choinière *et al.* (1997), and Wheeler *et al.* (1999) employed Gastec diffusion tubes. Pratt *et al.* (2000) used diffusion tubes in horse stalls in Kentucky, but did not indicate the tube manufacturer.

5.3. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy is a technique involving the interaction of IR electromagnetic radiation with the test sample. The technology has been called interferential spectroscopy, multiplex spectroscopy, Fourier spectroscopy, interferometric spectrophotometry, or Fourier transform spectroscopy through its development by physicists and manufacturers over the years. The acronym FTIR is almost universally used by chemists to refer to the technique (Johnston, 1991). The Fourier transformation is a mathematical manipulation that relates a signal, curve, or algebraic function to its frequency content.

In Fourier spectroscopy, the output signal is known as an interferogram and is produced by an interferometer (Fig. 10). Interferometers used in FTIR instruments manufactured in recent years are similar in design to the one built at the end of nineteenth century (White, 1990). As the movable mirror is gradually displaced, a cycle of maximum and minimum intensity recurs. It yields specific information about the chemical structure of organic and inorganic compounds based on the unique vibrational modes of

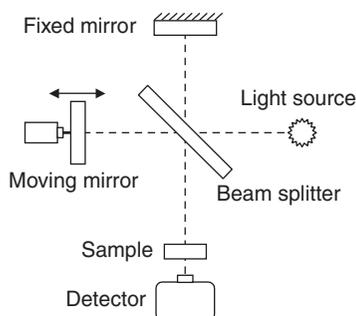


Figure 10 Schematic diagram of interferometer. Drawn according to [White \(1990\)](#) and [Johnston \(1991\)](#).

different chemical bonds. The FTIR spectrum is rich with information because each vibrational mode absorbs a specific wavelength of IR radiation. Each bond within a molecule may have several vibrational modes. The FTIR absorption spectrum is a “fingerprint” for a particular molecule that can be compared with reference spectra of known compounds, thereby aiding in the identification of unknowns and providing unambiguous confirmation of the identity of “known” materials.

A few of the many models of FTIR spectroscopy have been used for NH_3 measurement at animal facilities. An FTIR spectroscope K300 with a White-Cell was used in Germany ([Neser et al., 1997](#)). Air samples were pumped into or through a special optic cell (White-cell), which used a series of mirrors to create a lengthened light path of 8 m ([Amon et al., 1997](#)).

A Midac Model M2401 FTIR spectroscope was used in an outdoor open-path measurement of NH_3 emission from swine buildings in North Carolina ([Harris, 2001](#); [Harris et al., 2001](#)). An FTIR ETG w/ Bomen-100 interferometer and sterling cycle cooled detector was used in Missouri ([Secrest, 2001a,b](#)).

Other uses of FTIR spectroscopy included an NH_3 gas analyzer in the IR/VIS and UV spectral regions ([Keck et al., 1994](#)), an IR spectrometer, and a data logging system measuring NH_3 emission from pig and dairy barns in Germany ([Hartung et al., 1997](#); [Jungbluth and Büscher, 1996](#); [Jungbluth et al., 1997](#)), and two other reports by [Hauser and Fölsch \(1993\)](#) and [Gallmann and Hartung \(2000\)](#) without technical details.

5.4. Infrared gas analyzer

An infrared gas analyzer is an infrared spectroscope, a subset of spectroscopy that deals with the infrared region of the electromagnetic spectrum. Non-dispersive infrared (NDIR) analyzers measure the spectral absorption of a gas at one spectral band of the IR spectrum. The spectral dispersion of the absorption spectrum of the gas is not used ([Phillips et al., 2001](#)).

Osada *et al.* (1998) and Zhang *et al.* (2005) reported an Innova Type 1312 gas monitor (Ballerup, Denmark) and a multiplexer 1303 in a pig house and a dairy building, respectively, in Denmark. The 1312 is a newer version of the Type 1302. It costs between US\$28,000 and 35,000 depending on options (Einfeld and Billets, 1998).

The PAS has been used in the United States by Ferguson *et al.* (1997) in a broiler house and by Pratt *et al.* (2000) in horse stalls in Kentucky. The ongoing NAEMS project (PAAQL, 2007) has obtained 18 units of Model 1412 photoacoustic field gas monitors (Ballerup, Denmark) for multiple gas measurement, mainly NH₃, in animal barns and lagoons.

5.4.2. Chillgard Refrigerant Leak Detection System

The Chillgard Refrigerant Leak Detection System is a product of the Mine Safety Appliances Company (Pittsburgh, PA) and operates on the photoacoustic principle, allowing continuous measurement of NH₃ concentration. The Chillgard has two models. The IR model has an NH₃ detection range of 0–1000 ppm and the new RT model has selectable measurement ranges of 0–100 ppm and 0–1000 ppm. The instrument has a low detection limit of ± 1 ppm. The applications of this instrument in agricultural NH₃ emission study were reported in Canada (Cortus, 2006; Godbout *et al.*, 2000) and in the United States (Sun *et al.*, 2007). Although this instrument has low resolution, our field comparison study (unpublished data) demonstrates some of its advantages over other NH₃ analyzers, including stability, low cost, and low maintenance, when used in high NH₃ concentration situations.

5.4.3. Rosemount gas analyzer

According to Rosemount[®] Analytical (Orrville, OH), the Model 880A analyzer produces IR radiation from two separate energy sources. A chopper modulates this radiation into 5 Hz pulses. Depending on the application, the radiation may then pass through optical or gas filters to reduce background interference from other IR-absorbing components. Each IR beam passes through a separate cell. One cell contains a continuous flowing sample while the other cell is either sealed or contains a continuous flowing reference gas. A portion of the IR radiation is absorbed by the component of interest in the sample, with the quantity of IR radiation absorbed being proportional to the component concentration. The detector is a “gas microphone” based on the Luft principle. It converts the difference in energy between sample and reference cells to a change in capacitance (Fig. 12).

Brewer and Costello (1999) used a Rosemount Analytical Model 880A gas analyzer with a sampling chamber to measure NH₃ concentration in a broiler house in Arkansas. Hartung *et al.* (2001) described an IR gas analyzer Model BINOS[™]-IR-2 (Rosemount GmbH & Co.), but did not provide details.

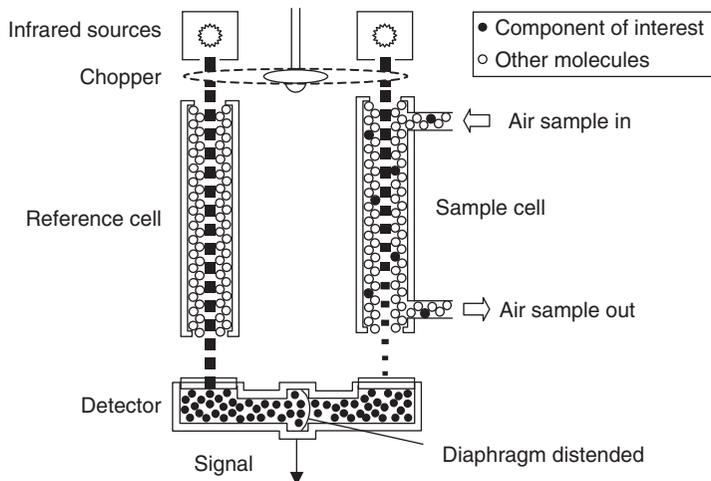


Figure 12 Schematic of operation principle of nondispersive infrared analyzer Model 880A. *Source:* Product Data Sheet PDS 103–880A.A01, Rosemount Analytical. Courtesy of Rosemount Analytical Inc.

5.4.4. Beckman Industrial models

Maghirang *et al.* (1991) and Maghirang and Manbeck (1993) used Beckman Industrial models 770 and 780 (Beckman Industrial Corporation, La Habra, CA) NDIR analyzers in a commercial egg laying house in Pennsylvania. The Beckman models have been discontinued.

5.4.5. Miran 203 infrared analyzer

The Miran 203 infrared analyzer (Foxboro Company, East Bridgewater, MA) is a portable analyzer designed primarily to promote safety in some areas of the hospital that can have high levels of toxic gases. It went to the gas analyzer market at the end of 1991.

This analyzer was only reported in Sweden for measurement of NH_3 in pig houses (Andersson, 1996, 1998; Jeppsson, 2002) and layer houses (Gustafsson and von Wachenfelt, 2005; Nimmermark and Gustafsson, 2005), but no details were provided. Miran infrared analyzers are currently products by Thermo Electron Corporation (Franklin, MA).

5.5. Ultraviolet differential optical absorption spectroscopy

In the ultraviolet differential optical absorption spectroscopy (UV-DOAS) method, an emitter–receiver set creates a light path in a detection zone. Light is generated by a xenon lamp in the emitter and projected to the receiver. Each gas in the detection path absorbs different parts of the light spectrum in a unique way. The absorption is recorded using a spectroscope.

5.5.1. Opsis AR-500 UV open-path monitor

The Opsis AR-500 open-path monitoring system consists of a light source emitter, a target gas cell, a receiver, a fiber optic cable, and an analyzer. The fiber optic cable connects the receiver and the analyzer (Fig. 13).

According to an environmental technology verification test (Myers *et al.*, 2000), the AR-500 had an NH_3 detection limit between 2.8 and 5.8 ppb with good linearity. Its relative accuracy was 3.3–11% over the range of 24–200 ppb.

Secrest (2001a,b) used a UV-DOAS Model AR-500 (Opsis AB, Furulund, Sweden) with a Czerny-Turner spectrometer and “ER-110” series (110 mm optics) telescopes to measure ambient NH_3 concentration on swine farms in Missouri and Maryland.

5.5.2. Washington State University system

An open-path measurement system was developed by Washington State University and has been used for over 10 years in challenging field conditions. Mount *et al.* (2001) described its use on a dairy farm, where NH_3 was measured in the UV bands near a wavelength of 210 nm at an integration time of several seconds to an accuracy of approximately $\pm 20\%$. The system was conceptually simple and consisted of (1) a UV light source, (2) a telescope to beam the UV light into the atmosphere, (3) a mirror system to reflect the light back toward the light source, (4) a receiver telescope to focus the light spectrally absorbed by the atmosphere onto a dispersing spectrograph, (5) a multielement multiplexing digital detector, and (6) a data analysis system. The path length ranged from a few meters to 750 m, and the sensitivity limit was 1 ppbv (parts per billion based on volume).

5.6. Chemiluminescence analyzer

Chemiluminescence (CL) NH_3 analyzers involve an indirect measurement of NH_3 based on converting NH_3 to nitric oxide (NO) and then performing NO analysis by the CL method. The NH_3 content is obtained by either chemical or mathematical subtraction of the background NO

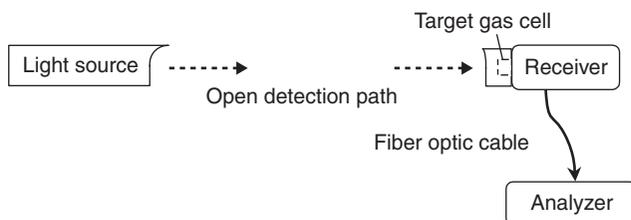
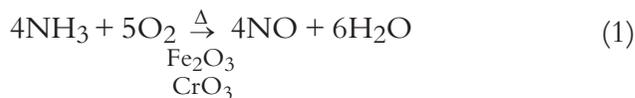


Figure 13 Schematic of Opsis monitoring system. Drawn according to Myers *et al.* (2000).

signal (Pranitis and Meyerhoff, 1987). This technique requires two instrument modules: an NH_3 converter and an NO_x analyzer.

The converter is kept at a temperature of 795°C , and stainless steel is usually used as the catalytic active metal. At this temperature, NH_3 is converted into NO by the following reaction (Aneja *et al.*, 1978):



The gas phase reaction of NO and ozone (O_3) produces NO_2 and a characteristic luminescence in the analyzer (Fig. 14). When electronically excited, NO_2 molecules decay to lower energy states and light emission occurs:



Pressure in the NO_2 detection chamber is kept at least 31 kPa below atmospheric pressure and temperature is kept at 50°C . Under these conditions, the NO concentration is directly proportional to the photon emission intensity. During transport of gas in tubes from the converter to the NO_x analyzer, some NO may oxidize to NO_2 . A molybdenum converter at 325°C converts NO_2 into NO prior to entering the reaction chamber of the NO_x analyzer (van't Klooster and Heitlager, 1992).

The advantages of this technique include high sensitivity (1 ppb), high precision (± 0.5 ppb), linearity ($\pm 1\%$ full scale), and automation. The disadvantages include highly priced parts (e.g., internal gas scrubbers) by

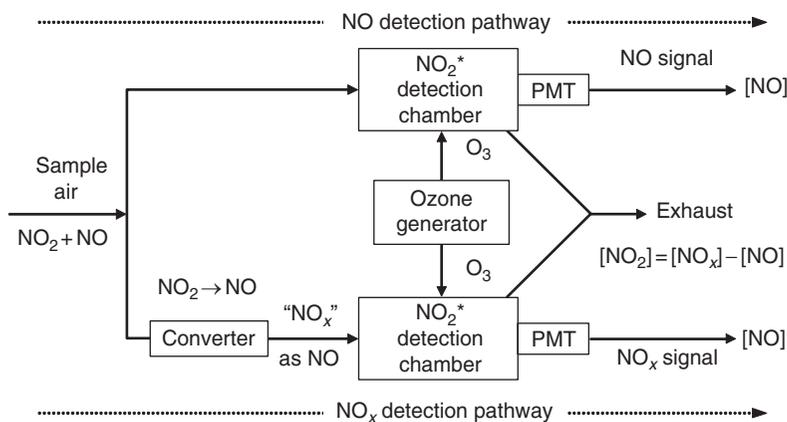


Figure 14 Schematic diagram of the general principle of chemiluminescent detector for nitrogen dioxide and nitric oxide. PMT, photo-multiplier tube. Source: Stern *et al.* (1984).

some manufacturers, and relatively large initial investment and complicated maintenance. The CL method has been used for NH_3 measurement at animal facilities in the Netherlands, UK, Belgium, and the United States.

5.6.1. Matthëus-IMAG converter and Monitor-Labs analyzer

van't Klooster and Heitlager (1992). (1992), Verdoes and Ogink (1997), and den Brok and Verdoes (1997) used $\text{NH}_3 \rightarrow \text{NO}$ converters type Matthëus-IMAG and a dual-channel NO_x analyzer (Monitor-Labs Model 8840) in the Research Institute for Pig Husbandry (RIPH), the Netherlands. Scholtens (1990), Aarnink *et al.* (1993b, 1995, 1996, 1997), Smits *et al.* (1995), Braam *et al.* (1997), Groenestein and Faassen (1996), Groenestein *et al.* (1997, 2003, 2006, 2007), and Swierstra *et al.* (1995) used an instrument of the same model in the Institute of Agricultural and Environmental Engineering, the Netherlands. Once a week, the monitor was calibrated with a gas of 40 ppm NO in N_2 and the flow of the different channels was checked. Dust filters were changed when necessary. The converter heated the sample air to 775 °C (Ogink and Kroodsmas, 1996). A similar system was reported by Demmers *et al.* (1999) in the UK.

5.6.2. Matthëus-IMAG converter and THIS NO_x analyzer

Berckmans and Ni (1993) and Ni *et al.* (1999, 2000d) described another system in Belgium that had five $\text{NH}_3 \rightarrow \text{NO}$ converters (Type Matthëus-IMAG) installed at five different sampling locations. Through some heated tubing and a stream selector, the converted air from all the converters was conducted to a single NO_x analyzer [Model 42-I, THIS (Thermal Instrument System, currently Thermo Electron Corporation), Franklin, MA]. The converters had conversion efficiencies between 95 and 99% at NH_3 concentrations below 30 ppm according to the manufacturer.

5.6.3. TEI converter and analyzer

Heber *et al.* (2001) reported that four NH_3 analyzers [Model 17C, TEI (Thermal Environmental Instruments, currently Thermo Electron Corporation), Inc., Franklin, MA]. were used in a comprehensive field study of gas emission measurement in Indiana and Illinois. Each NH_3 analyzer consisted of two separate modules, a converter module and an analyzer module. The difference between these systems and the systems in Europe is that only one converter was used with each analyzer. An air stream controller was installed before the converter to facilitate multi-point sampling (Fig. 6). Several papers on NH_3 emissions using these analyzers have been published (e.g., Heber *et al.*, 1997; Lim *et al.*, 2004; Ni *et al.*, 2000a,b).

Harris *et al.* (2001) and Walker (2001) reported using two TEI analyzers (Model 17C) in tunnel-ventilated swine finishing houses in North Carolina. At each house, one analyzer was dedicated to the primary exhaust fan and the other was periodically moved from fan to fan in order to ascertain

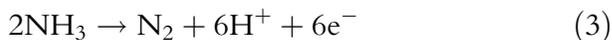
variability in exhaust NH₃ concentrations. McCulloch *et al.* (2000) tested three TEI Model 17C analyzers and found that two of them exhibited excellent system linearity across the 0–1000 ppb range. In a third analyzer, the converter efficiency varied from 54 to 77% at 12 and 46 ppb, respectively.

5.6.4. MT converter and API analyzer

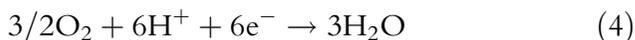
Aneja *et al.* (2000) transferred sampling air to a Measurement Technologies 1000N stainless steel NH₃ converter when measuring lagoon NH₃ emission in North Carolina. The sample flow from the converter was routed to a CL NO_x analyzer (Model 200, Advanced Pollution Instrumentation, San Diego, CA).

5.7. Electrochemical sensor

Electrochemical (EC) NH₃ sensors consist of two electrodes and detect NH₃ with the following EC reactions: on the measuring electrode,



and on the counter electrode,



EC sensors provide direct readout and continuous measurements. Several EC sensors have been tested or used at animal facilities.

5.7.1. Dräger sensor

The most frequently reported EC sensor was the Dräger sensor, including a Dräger apparatus for measuring NH₃ in a fattening pig house (Heinrichs and Oldenburg, 1993), a Dräger Polytron 2 used in broiler houses (Wheeler *et al.*, 2000a), and a Dräger Pac III for testing in dairy cow and pig housing systems (Kavolelis, 2006).

The Dräger Polytron 2 (Dräger Safety, Inc., Pittsburgh, PA) was battery powered. Its scale was 0–300 ppm and its precision was ±3% or ±9 ppm. The unit consisted of a multi-gas body (Polytron 2) and a sensing unit. The multi-gas body can combine with specific sensor units to measure over 60 toxic gases including NH₃. The expected life of an NH₃ sensor is equal to or longer than 18 months.

Xin *et al.* (2002) developed a portable and relatively low-cost unit for continuous measurement of NH₃ at animal facilities. The unit utilizes sampling and purging cycles to overcome the shortcoming of sensor

saturation inherent with electrochemical NH_3 sensors (Li *et al.*, 2005). Twenty-eight portable monitoring units were fabricated and successfully used in a multistate and multidisciplinary poultry house research project (Gates *et al.*, 2005). This device was also used in monitoring NH_3 emission from turkey houses (Gay *et al.*, 2006).

5.7.2. Other EC sensors

Three other EC sensors were found in the literature. Hoy *et al.* (1992) and Hoy and Willig (1994) described a Series 6004 QuadScan Gas monitoring system, connected with a printer, for continuous measurement of NH_3 . This system consisted of two main components, the Series 6004 gas receiver and three Series 4485 NH_3 gas transmitters. The Series 4485 was a two-wire transmitter designed for monitoring ambient NH_3 gas concentration. The transmitter itself consisted of two components, an EC sensor, and an electronic transmitter. The standard 4485 had a measurement range of 0–100 ppm.

Jiang and Sands (2000) measured NH_3 concentrations in broiler buildings with an EC sensor (ETI series 4700 Twistik Transmitter), but did not give details about the sensor and its performance.

An iTX Multi-gas monitor with a biased sensor (iTX Multi-gas Monitor ISC, PA) was used by Hayes *et al.* (2006) to determine NH_3 concentrations at four integrated pig units over a 2-year period.

5.8. Chemcassette[®] detection system

The colorimetric principle is employed by the Chemcassette[®] detection system (Zellweger Analytics Inc., Lincolnshire, IL). A carefully prepared reel of porous paper tape is impregnated with a chemical. The paper acts as both a trapping and analysis medium, detecting and measuring nanogram amounts of target gas. Upon exposure to the target gas, the paper tape changes color in direct proportion to the sample gas concentration. A photo-optical system measures its color intensity change and determines the sampled gas concentration (Fig. 15).

The system can measure different gases with different Chemcassettes, which are individually formulated for specific gases or a family of gases. The low-level NH_3 detection Chemcassette has a range of 0.5–30 ppm. The system measures gas concentrations continuously and the response time is several seconds. A single-point Chemcassette system cost US\$5200 and an NH_3 cassette tape cost US\$46 in 2000. According to the manufacturer, this system is the only gas detection method providing physical evidence of gas presence and the technique virtually eliminates in-field calibration.

Bicudo *et al.* (2000) described a Zellweger MDA single-point continuous air monitor at animal facilities in Minnesota. The accuracy of the instrument was $\pm 20\%$ of the actual reading.

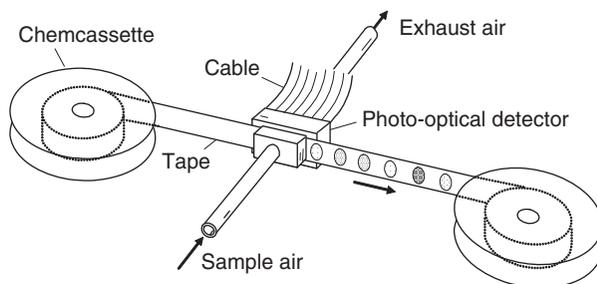


Figure 15 Schematic of ammonia measurement with Chemcassette Monitor. Source: Product description, Zellweger Analytics Inc.

5.9. Solid-state sensor

The solid-state or electronic NH_3 sensor is a relatively new measurement method. It benefits from the boom of the electronic sensor technology in the latter part of the twentieth century. There are several types of these sensors that are sensitive to NH_3 (Göpel and Schierbaum, 1991; Timmer *et al.*, 2005).

There exist some advantages of solid-state NH_3 sensors, including simplicity, low price, quick response, and automatic measurement, compared with other available NH_3 measurement technologies. Their limitations include low accuracy, drifting, and interference by humidity and other gases. Several types of NH_3 sensors have been tested in animal houses. However, they were still in the development stage.

Krause and Janssen (1990, 1991) used a chemical NH_3 sensor to measure NH_3 distribution in animal houses. The sensor had a detection range of 1–1000 ppm, a response time of <1 s and an accuracy of $\pm 10\%$ between 4 and 500 ppm. Krause (1993) described a test of a semiconductor NH_3 sensor, but did not indicate whether it was the same sensor reported in 1990 and 1991.

Berckmans *et al.* (1994) conducted a test of a solid-state NH_3 sensor, developed by the Inter-university Micro Electronic Center (IMEC), Belgium, in livestock buildings. The sensor had a detection range of 0–100 ppm NH_3 and a response time of 10–15 s. It was a thick film semiconducting metal oxide sensor consisting of a heater element, a dielectric layer, a contact layer, and a gas-sensitive semiconductive metal oxide layer (Fig. 16). The conductivity of semiconducting metal oxide films at a certain temperature was influenced by the presence of NH_3 gas in the surrounding atmosphere. The sensor's optimum operating temperature was around 350–400 °C.

Hess and Hügle (1994) tested an NH_3 measuring system called SOLIDOX- NH_3 , manufactured in Germany, in animal houses a few times but with difficulties.

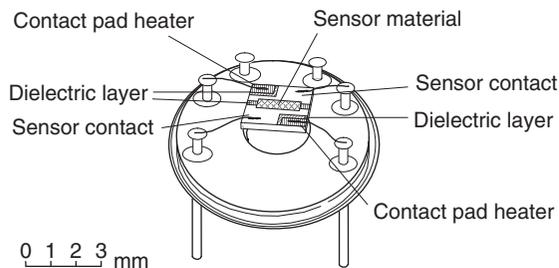


Figure 16 Ammonia sensor developed by IMEC, Belgium. *Source:* Ni (1998).

5.10. Comparison of measurement devices

When different devices are employed for NH_3 concentration measurement at animal facilities, their comparability is an interesting question. So far, there have been several studies conducted to answer this question (Table 5).

Skewes and Harmon (1995) evaluated the AQT and Gastec passive tubes against Gastec active tubes in eight broiler houses. The authors concluded that the AQT estimated NH_3 levels accurately at 20–25 ppm and the passive tubes estimated average NH_3 levels accurately at low levels of NH_3 . Their study indicated that the passive and the active tubes could not agree well, though both were products from the same manufacturer.

Mennen *et al.* (1996) compared six devices, including a DOAS system (OPIS, Sweden), a photoacoustic monitor (KEMA, the Netherlands), and a CL NO_x monitor with NH_3 converter, in a test chamber and in the field conditions for the Netherlands National Air Quality Monitoring Network. The converter method was found to have interference by NH_4^+ . The noise level of the DOAS system appeared high. The photoacoustic monitor suffered from many problems, leaving only 1% useful data. All three were rejected as network monitors.

Wheeler *et al.* (2000b) compared two Dräger EC sensors, the Kwik-Draw gas detector tube, and the Sensidyne passive gas tube in a lab, three environmental chambers, and three high-rise poultry houses. Although all devices agreed well in the lab test, there was a significant difference between the Dräger sensor and the active tube in environmental chambers. There were poor correlations among the three types of sensors in poultry houses.

Ni (unpublished data) analyzed NH_3 concentration data measured in the exhaust chimney in a pig house with a Dräger EC sensor and with a CL analyzer. The correlation coefficient of NH_3 concentrations was 0.55 from 3900 paired data recorded by the two devices over a month.

Other studies showed satisfactory comparison results. Dewey *et al.* (2000) compared pHydrionTM NH_3 test strips against Dräger tubes, and concluded that the test strips provided a precise and cost-effective means of detecting NH_3 concentrations in swine confinement buildings.

Table 5 Summary of comparison studies of ammonia measurement devices

Compared device	Test condition and conclusion	Reference
1. AQT 2. Gastec passive tubes 3. Gastec active tubes	Eight broiler houses: AQT and passive tubes agreed well with active tubes at 20–25 ppm and lower levels, respectively	Skewes and Harmon (1995)
1. DOAS 2. NH ₃ converter +CL NO _x monitor 3. Photoacoustic monitor	Test chamber and field: All rejected as network monitors	Mennen <i>et al.</i> (1996)
1. Dräger EC sensors 2. Kwik-Draw active tubes 3. Sensidyne passive tubes	Laboratory: All three devices agreed well Environmental chambers: EC sensors and active tubes differed significantly Layer houses: Poor correlations existed among three devices	Wheeler <i>et al.</i> (2000b)
1. Dräger EC sensor 2. CL analyzer	Pig house: Correlation coefficient $r = 0.55$ for 3900 paired data points	Ni (unpublished data)
1. pHydriion™ NH ₃ test strips 2. Dräger tubes	Pig house: Test strips were precise and cost-effective as compared with Dräger tubes	Dewey <i>et al.</i> (2000)
1. Gas tubes 2. CL analyzer	Pig house: Gas tubes could accurately measure NH ₃ using three sample averages	Parbst <i>et al.</i> (2000)
1. Open-path FTIR 2. Open-path UV-DOAS	Pig farm: Agreement was reasonably good	Secret (2001a)

AQT, Ammonia Quick Test; CL, chemiluminescence; FTIR, Fourier transform infrared; NH₃, ammonia; UV-DOAS, ultraviolet differential optical absorption spectrometer.

Parbst *et al.* (2000) evaluated 0.25–3 ppm gas detection tubes (Dräger Model 6733231) in finishing swine buildings in summer and winter against a CL analyzer (TEI Model 17C) being used in a long-term study (Heber *et al.*, 2001). The authors concluded that NH₃ concentrations could be accurately evaluated using the mean of three gas detection tube samples.

Secret (2001a) collocated the optical paths of an open-path FTIR system and an open-path UV-DOAS system. The FTIR path was 159 m and the UV-DOAS path was 150 m. The author concluded that the agreement was reasonably good ($R^2 = 0.94$), although there was a 15-ppb difference between their responses at lower concentrations.

To date, however, it is still unknown which technique provides results that are the closest to the “true” NH_3 concentrations under agricultural field conditions. The tests summarized in this section only compared selected techniques with unknown characteristics against each other, not against a standard technique, which does not yet exist. Therefore, standard techniques and relevant methodologies need to be developed, and the existing NH_3 concentration measuring devices need to be tested, compared, and evaluated.

6. AMMONIA CONCENTRATION DATA

6.1. Advances in data collection

Research into NH_3 at animal facilities has undergone dramatic changes since the 1960s. This is clearly demonstrated in change observed in reported NH_3 concentration data.

First, the level of research into NH_3 at animal facilities has expanded from small tests to multi-institutional and international projects. The data quantity has increased exponentially. The study conducted in broiler pens by Valentine (1964) contained ~300 wet-chemistry samples of NH_3 concentrations. The six-university project from 2004 to 2005 with continuous measurement systems (Heber *et al.*, 2006) produced 2 million NH_3 concentration data points, each with a 1-min average. The ongoing NAEMS project is expected to generate 13 million NH_3 concentration data points from field measurement at animal barns and lagoons (PAAQL, 2007).

Second, sampling and measurement covers longer periods of time and more animal facilities, especially when the study objective is to determine baseline emissions. A research project in Northern Europe included 14 housing types for cattle, pigs, and poultry in England, the Netherlands, Denmark, and Germany (Groot Koerkamp *et al.*, 1998). The NAEMS is monitoring two to four mechanically or naturally ventilated buildings continuously for two years at each of five dairies, five pork production sites, three egg layer operations, and one broiler ranch. It is also monitoring 10 lagoons and a dairy corral for 20 days in each season at 11 farms.

Third, high-frequency concentration data is providing richer information. While TWA data are still useful, more and more research is employing advanced sampling and measurement techniques to acquire data that contain dynamics of NH_3 concentration and allows obtaining insight into

the complicated NH_3 generation and emission mechanism at animal facilities (Mosquera *et al.*, 2005).

Lastly, most of the research on NH_3 is coupled with measurements of other pollutants, including other gases (e.g., greenhouse gases and H_2S), particulate matter, and odor, at the animal facilities. Multi-pollutant studies reduce the overall costs and increase understanding of the interaction of pollutant generation and emission. An example of this is the effect of pH changes on NH_3 and H_2S in liquid manure. Higher pH promotes NH_3 release while reducing H_2S release and vice versa. Another example is the effect of CO_2 release that accelerates NH_3 release at certain dynamic conditions (Ni *et al.*, 2000c,d). Furthermore, multi-pollutant studies are favorable for developing and testing abatement technologies that could produce multiple benefits.

The increase in the quantity and complexity of NH_3 data has created new challenges to ensure the quality of data collection and processing.

6.2. Data precision and bias

Collection of high quality data is critical to any research program. Erroneous data are worse than no data because bad data misleads scientific conclusions, regulatory decisions, abatement technique evaluations, and health risk assessments.

Much of the information accompanying NH_3 data reported in the literature was insufficient to provide a reasonable assessment of data quality. This was due to two problems. First, data quality did not receive enough attention in many studies. In most published articles, there was little information about quality assurance and quality control (QAQC), for example, calibration of measurement systems, assessment of precision and bias. Second, proper and consistent data quality terminology is lacking, adding to the difficulty in comparing inter-project results. Different data quality indicators (DQIs) were used to describe the measurement quality in various reports. These DQIs include “accuracy,” “inaccuracy,” “precision,” “error,” “sensitivity,” and “standard deviation.” This increases the difficulty of comparing results.

The U.S. EPA recommends using the terms “precision” and “bias,” rather than “accuracy,” to convey information usually associated with accuracy. According to U.S. EPA (1998), accuracy is a measure of the closeness of an individual measurement or the average of a number of measurements to the true value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that result from sampling and analytical operations (Fig. 17). Precision is a measure of agreement among replicate measurements of the same property, under prescribed similar conditions. Bias is the systematic or persistent distortion of a measurement process that causes errors in one direction.

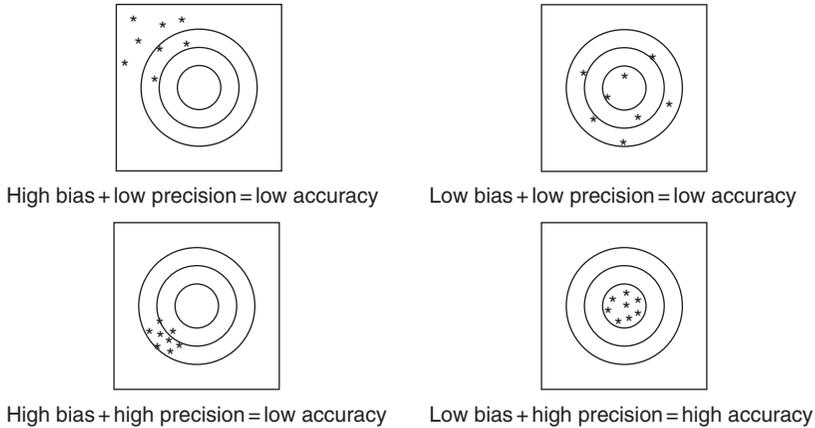


Figure 17 Random measurement uncertainties and measurement bias: Shots at a target. *Source: USEPA (1998).*

There are several potential error sources that can lower precision and increase bias when conducting NH_3 studies at animal facilities. Understanding these errors and the related preventive or corrective measures will help improve data quality.

6.3. Error reduction

Errors are common in physical measurements and methods of error analysis are well established (Taylor, 1997). Errors in NH_3 concentration data can be introduced from instrument calibration, air sampling, sample measurement, and data processing. While most of these error sources are universal in scientific research, a few of them deserve particular attention. Table 6 summarizes these sources that most frequently occur, and provides suggestions to reduce them.

6.3.1. Errors from calibration

Calibration is the setting or correcting of a measuring device or base level, usually by adjusting it to match or conform to a dependably known and unvarying measure. Calibration of measurement systems assures data quality and provides information about characteristics of these systems, such as response, drift, linearity, stability, and precision. Errors can be easily introduced into NH_3 data by improper calibration.

Calibration of an NH_3 measuring system is usually realized by challenging the system with known concentrations of NH_3 mixed in dry nitrogen or in dry air. The difference between the known NH_3 concentrations and the

Table 6 Potential error sources and reduction methods in ammonia concentration measurement

Potential error sources	Comments and reduction methods
Calibration	
Inaccurate gas	It is a potentially serious source-level error. Select high quality gas from specialty gas vendor and use unexpired gas.
Inadequate procedure	It may be design error. Select adequate gas introduction location, calibration frequency, duration, and flow rate.
Incorrect operation	It is human error. Practice QAQC and use automated calibration setup and software.
Sampling	
Spatial variation	It is inevitable and might be at great extent. Carefully select sufficient number of representative sampling locations.
Temporal variation	It always exists. Use TWA sampling device or high frequency sampling to cover day and night to reduce diurnal errors. Use long-term sampling to cover winter and summer to reduce seasonal errors.
Gas adsorption/desorption at contacting surfaces of sampling system	It affects system response time, especially at low NH_3 concentrations. Reduce sampling tubing and increase sampling system temperature.
Condensation in sampling system	It absorbs NH_3 and affects sensor operation. It could be harmful for some instruments. Insulate or heat sampling system to keep the temperature above that at the sampling locations.
Dust in sampling system	It causes leaks in the sampling system. Use dust filters at the sampling inlets.
Insufficient sample air flow	It will introduce errors to the analyzer. Increase and monitor sample air flow.
Inadequate sampling duration	It causes insufficient sample volume for acid trap samplers and introduces temporal errors. It will also be too short for analyzers to reach equilibrium. Select proper sampling duration.
Incorrect sample volume	It introduces errors to acid traps. Calibrate and monitor the device for volume measurement.
Disturbance at gas release	Too much disturbance at gas release surface causes unrealistic data when using sampling chambers. Simulate natural

Table 6 (continued)

Potential error sources	Comments and reduction methods
Leaks in sampling system	conditions if the objective is to determine baseline NH ₃ emission. It mixes air from nonsampling locations with the air from sampling locations in negative pressure sampling system. Improve the design of the sampling system and check it periodically or monitor it continuously.
Incorrect sampling operation	It is human error. Practice QAQC and use automatic sampling monitoring equipment and software.
Measurement	
Low instrument precision and sensitivity	It is expected random error. Select instrument of high precision and suitable sensitivity may reduce error. Avoid using expired disposable sensors.
Slow instrument dynamic response	It may introduce serious errors in MPSS. Use instrument with small time constant.
Poor instrument stability	It may be random or systematic errors. Avoid using unstable instrument and perform periodic calibration.
Interferences of water vapor and other gases	It is random or systematic error. Develop and use new calibration methodology and select better devices.
Incorrect operation	It is human error. Practice QAQC and use automated measurement monitoring software.
Data processing	
Incorrect temperature data	Change from 20 °C to 10 °C increases 3.5% in converted mass concentrations. Use correct temperature for concentration conversion.
Incorrect atmospheric pressure data	A variation of ±0.06 atm may introduce ±6% of error when converting volumetric to mass concentrations. Use correct pressure for concentration conversion.
Improper validation and treatment of data	It leads to erroneous data selection and calculation. Have a good understanding about the field test and the data that it generates. Only use valid data in result calculation.

(continued)

Table 6 (continued)

Potential error sources	Comments and reduction methods
Improper interpolation and extrapolation of data	It creates data that are unreliable. Understand the limitation of data and use interpolation and extrapolation carefully.
Incomplete data	They have limitations to represent real conditions. Avoid using the data that do not satisfy data quality objectives.
Incorrect selection of gas equilibrium time	It occurs in centralized multi-point sampling data. Select the equilibrium time based on test results.
Insufficient or missing test notes	It brings difficulty for data validation, correction, and interpretation. Make good test notes about the system status and human activity that has effected or will affect data.
Misinterpretation of test notes	It will introduce various errors. Direct experience and good understanding about the test setup and operation is needed.

MPSS, multi-point sampling system; QAQC, Quality Assurance and Quality Control; TWA, time weighted average.

system outputs guides the correction of the measurement by adjusting system hardware or software, or by correcting concentration data during data processing.

Calibration of NH_3 sampling and measurement devices at animal facilities has not been emphasized enough. Only a small portion of the publications described the procedure. They include calibrating NH_3 analyzers (Heber *et al.*, 2001; Mosquera *et al.*, 2005; Ogink and Kroodsma, 1996; van't Klooster and Heitlager, 1992), PAS gas analyzers (Rom, 1993), EC sensors (Wheeler *et al.*, 1999), and UV-DOAS and FTIR systems (Secrest, 2001a).

Commercial measuring devices are typically calibrated by the manufacturer or supplier before shipping to the consumer following purchase, repair, or maintenance. Although there are devices with claimed self-calibration capacity (Mount *et al.*, 2001), calibration is required for most analytical instruments before initial use. Re-calibration after using the device for a certain time is necessary because instrument drift occurs. Manufacturers usually recommend calibration intervals, specify calibration procedure, and provide calibration accessories. An initial check of a new instrument with reference NH_3 is advisable.

Disposable measuring devices, such as active and passive gas detection tubes, cannot be calibrated by users. However, they can be verified for their

precision and bias by randomly selecting some tubes, for example, 5% from a batch of tubes and using them to measure calibration gas with known NH_3 concentrations.

There are three potential error sources that can lead to inadequate calibration. The first one is from the source level, the calibration gas, or the “standard.” We evaluated three gas cylinders of 53.1, 33.2, and 9.33 ppm certified NH_3 in air and found significant errors in them. The gases had been ordered from the same gas supplier at the same time requesting that they be analyzed twice with at least one week apart between analyses and both analyses should agree to within 1%. The gas company used FTIR as the analytical method. Upon receiving the gases, we compared the gas cylinders with each other. An NH_3 analyzer (TEI Model 17C) was first confirmed for its linearity by using the NH_3 directly from the cylinders and after 50% dilution with certified zero air. The analyzer was then calibrated against the 53.1 ppm cylinder. However, when the 53.1 ppm NH_3 cylinder was used as a “standard,” the 40.5 and 5.77 ppm cylinders surprisingly resulted in 33.2 and 9.33 ppm readings, respectively, with the same analyzer. The 53.1 ppm gas was confirmed to be the most reliable based on measurements with two other devices: Dräger NH_3 detection tubes and a Chillgard Refrigerant Leak Detection System. The cylinders with 40.5 and 5.77 ppm certified concentrations were therefore returned to the gas provider, who admitted their inaccurate concentrations, for recertification. However, the recertified gases still showed significant differences compared with the 53.1 ppm NH_3 cylinder (Table 7).

Unfortunately, this type of source-level error was not an isolated incident. According to the U.S. EPA audit results for EPA Protocol Gas from April 2003 to February 2004, 57% of specialty gas vendors failed the audit and the overall failure rate was 11% or 14 out of 126 cylinders containing blends of sulfur dioxide (SO_2), nitric oxide (NO), and CO_2 (Scott Specialty Gases, 2004).

Moreover, unlike some other gases with agricultural origin, for example, H_2S and methane (CH_4), NH_3 is not yet available as a compressed gas with Standard Reference Materials from the National Institute of Standards and

Table 7 Verification of three certified ammonia gas cylinders

Cylinder	Certified concentration (ppm)	Concentrations measured at NH_3 analyzer (ppm)	
		No dilution	50% dilution
A	53.1	53.1	26.6
B	33.2	40.5	20.0
C	9.33	5.77	2.80
B (recertified)	29.6	16.9	
C (recertified)	9.6	6.0	

Technology (NIST) (USEPA, 1997). The NIST provides U.S. industry, government, and the public with measurements, standards, and information services. The U.S. EPA traceability protocol for assay and certification of gaseous calibration standards (USEPA, 1997) allows for Gas Manufacturers Intermediate Standards (GMIS) and NIST Traceable Reference Materials (NTRM) Gas Calibration Standards to be prepared by gas manufacturers and certified by NIST.

If a measuring system is calibrated against an incorrect NH_3 concentration, the systematic error passes on to the collected and processed data. The cause of this error goes back to NH_3 gas standards and is related to the gas suppliers.

The accuracy of calibration gas is out of control by the users conducting NH_3 measurements at animal facilities. However, selecting products from the most reputable gas companies and using unexpired gas will reduce the risk of introducing this error to the NH_3 measurement data. Additionally, checking the new calibration gases with a high quality stable instrument such as the FTIR helps to assure that there were no gross errors by the supplier.

The second main error comes from improper procedure and operation of calibration. Ammonia measuring devices used at animal facilities are usually field-calibrated under steady-state conditions by applying a zero input using zero air and a step input using span gas. Multi-point calibration, which consists of a zero and several different levels of spans, can be used to determine the linearity of the device. Calibration gases can be introduced at the inlets of NH_3 sensors/analyzers or at the sampling location, from which the entire sampling and measurement system can be checked. Calibration procedure defines the calibration frequency, duration, gas flow rate, and so on. Calibration frequency should be based on characteristics of different instruments. Excessively frequent calibration is not only expensive, but also causes loss of normal measurement time. However, belated calibration will increase uncertainty in the measured data. Carefully determining the procedure according to the characteristics of the sampling and measurement devices will ensure better calibration data quality. Errors resulting from various improper operations, for example, incorrect concentration recording, are human errors. They can be reduced by practicing QAQC and using automated calibration devices and software.

The third error is related to interferences from other components in air. Calibration gas is usually a mixture of pure and dry gases, different from the actual air at animal facilities that is a mixture of water vapor, other gases, and particulate matter. This difference can introduce errors in measurement data when the instrument is adjusted to the calibration gas but measures the actual air. Theoretically, these errors can be corrected if the instrument manufacturer provides reliable data about the interferences and the concentrations of interfering components are known. However, in practice, it is not always easy to realize.

6.3.2. Errors from sampling

Inadequate sampling design, setup, and operation can introduce spatial and temporal errors. Lefcourt (2002) suggested that the most accurate method for estimating NH_3 emission rates would be to collect and mix all of the exhaust streams prior to continuously measuring NH_3 concentration and airflow. However, this method is unfeasible at animal facilities. Because of the nature of dynamic situations and the limited air samples at animal facilities, errors are inevitable in practical situations. Spatial and temporal NH_3 concentration variations could occur to a great extent in animal barns as shown in Fig. 3. More sample locations will reduce these errors but the number of samples is usually limited by the availability of equipment. In a centralized MPSS using a single set of analytical instruments, there is a trade-off between temporal and spatial information. More sampling points mean less frequent sampling. Therefore, sampling locations should be carefully selected to optimize representativeness.

To reduce errors due to diurnal concentration variations, sampling should cover day and night using TWA sampling/measurement devices or high frequency sampling. Similarly, long-term measurement to cover winter and summer should be used to reduce seasonal errors.

Condensation and dust in the sampling system not only introduces errors in NH_3 concentration data, but is also harmful to the instrument and sampling system. The centralized point-sampling system, which includes air transportation tubing, and the measurement instrument should be kept at a temperature at least the same as the air temperature at sampling locations. Dust filters can be used to prevent dust from coming into the sampling system and causing leakage.

Inadequate sample airflow and sampling duration can introduce errors and should be avoided. For acid trap sampling, low sample airflow and short sampling duration result in low sample air volume, which may produce undetectable NH_3 concentrations in the trap. On the contrary, too much sample air will cause saturation of the acid solution.

Sampling airflow rate should satisfy the requirement of the analytical instrument. Most of these instruments need 0.3–1.0 l/min of sample air. Required sampling duration depends on the response time of the measurement instrument and should allow the analyzer to reach equilibrium in multi-point sampling. In the reported studies, the sampling duration varied from 1 min (Ogink and Kroodsmas, 1996), 2 min (Berckmans *et al.*, 1998), 15 min (Neser *et al.*, 1997), to 30 min (Heber *et al.*, 2005).

Errors from sampling can also be introduced by improper interference of the air flow in sampling chambers, leakage of the negative pressure sampling system, and incorrect operation of the sampling system. These errors can usually be reduced by careful design, maintenance, and execution of QAQC.

6.3.3. Errors from measurement

Measurement errors are related to the measurement devices and their operations. Some of the error sources are inherent to instruments themselves.

Ammonia concentrations at animal facilities are almost always under transient conditions with high frequency and large magnitude of variations (Ni *et al.*, 2000b). These variations do not introduce serious temporal concentration errors to sensors that provide TWA concentrations (e.g., passive gas tubes). However, they do introduce errors to instruments that provide “real-time” NH_3 concentrations (e.g., FTIR, PAS, and NO_x analyzer) during measurement but have inadequate frequency responses compared with the dynamic changes in concentrations. Accurate dynamic measurement requires a small time constant of the instrument (Doebelin, 1983).

The magnitude and correction of this type of error and its relationship with specific measuring devices, sampling method, animal facility size, and so on need more investigation. Furthermore, the true frequencies of NH_3 concentration changes under various conditions (e.g., in open air, inside buildings, with different sizes of buildings, at different seasons, under different weather) have not yet been fully characterized and deserve further study. Nevertheless, measurement instruments with poor response time should be avoided, if possible.

Figure 18 presents an example of a problematic gas analyzer during our study at a multiroom animal building. The NH_3 concentrations obtained by analyzer B could have caused serious misinterpretation if it had not been compared with analyzer A, which reflected good dynamics following the concentration change when the system switched sampling locations every 10 min. Location #3, measured from 0:40 to 0:50 and from 2:10 to 2:20,

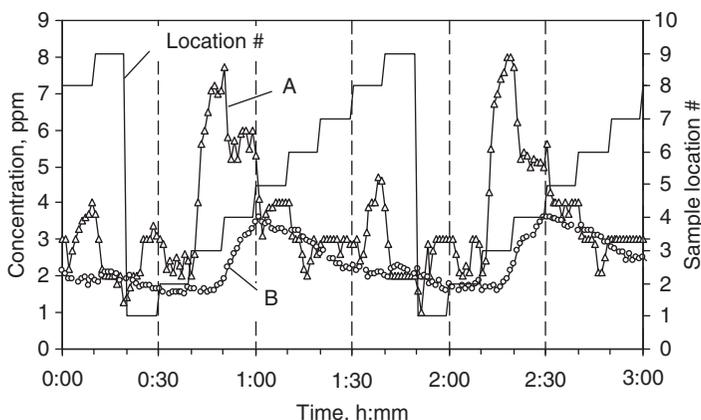


Figure 18 Comparison of a fast response analyzer (A) with a slow response analyzer (B) when sampling ammonia at nine different locations.

had the highest NH_3 concentration according to analyzer A. Instead, analyzer B, which had slow response, showed that this location had the lowest concentration.

Except for the pH paper method, almost all of the NH_3 measurement techniques were initially developed for nonagriculture use. They were introduced to the animal industry after successful use in other fields. For instance, the Chemcassette monitor that had existed for over 30 years was first reported in agriculture use in 2000 (Bicudo *et al.*, 2000). The conditions under which the instruments were developed and factory calibrated might be very different from the conditions at animal facilities.

Air produced from animal facilities is a mixture of a large number of gases plus relatively high moisture content compared with the commercial calibration gases. Some of the NH_3 measuring devices are sensitive to water vapor and gases other than NH_3 . Interferences are therefore possible during field measurements.

Four of the seven comparison studies summarized in Table 5 demonstrated at least some degree of disagreement between the tested measuring devices. The increasing inconsistency of the three devices tested in the lab, environmental chamber, and commercial layer house reported by Wheeler *et al.* (2000b) could probably be explained by increasing interferences among the three test locations. The gases that interfere with detection tubes may be more prevalent in commercial poultry houses than one might expect.

Discussion about development or improvement of NH_3 measuring devices specifically targeting the agricultural environment has not been found in the literature. The potential errors caused by agricultural air interference are not fully understood and are not compensated in field data.

Therefore, there is a need to develop test methodology and conduct studies to determine field performance of available measuring devices. Recommendations on the use of these devices and the field data they produced will help to improve agricultural NH_3 measurement significantly.

6.3.4. Errors from data processing

Data processing is mainly a statistical procedure that involves data validation and calculation with predefined criteria and algorithms. It is different from data management and data analysis. Data management is an administrative procedure that engages data organization, distribution, retrieval, storage, and backup. Data analysis is a scientific procedure that requires insightful knowledge for interpreting, exploiting, and synthesizing the information carried by or hidden behind the data.

Data processing can be complex in some comprehensive research projects, of which the data sets can consist of large amount of information that the NH_3 concentrations are dependant on. To satisfy these conditions, customized computer program has been developed to process the data (Eisentraut *et al.*, 2004).

When calculating NH_3 release or emission, sample air temperature and atmospheric pressure are used to convert the volumetric NH_3 concentration to mass concentration. The air temperature and pressure should be those at the location where the samples are taken, not where the samples are analyzed, which may be different from the sampling locations. Sampling location temperatures at animal facilities vary diurnally and seasonally, especially outdoors. Changing the temperature from 20°C to 10°C increases the converted NH_3 mass concentration by 3.5%. A variation of ± 0.03 atmospheric pressure introduces $\pm 3\%$ of difference in NH_3 concentration conversion. Therefore, using accurate temperature and pressure data can reduce errors in NH_3 concentration processing.

Not all the collected NH_3 concentration data are usable due to various reasons. Raw data are invalid until they are validated. Only valid data should be used for compilation of final results because data quality is more important than data quantity. Validation is a process that may introduce errors. Suspicious data should be linked to possible reasons before validating or invalidating them.

Missing data can sometimes be filled by interpolation or extrapolation. However, these methods have their limitations. Their improper use can create data that are unreliable.

Data completeness is a measure of the amount of valid data obtained from a measurement system, expressed as a percentage of the number of valid measurements that should have been collected, that is, measurements that were planned to be collected (USEPA, 1998). Data completeness is often set at 75% or more (PAAQL, 2007). Incomplete data have limitations for representing real situations at animal facilities. Errors will be introduced if using NH_3 concentrations covering only a few hours in the morning to represent the mean concentration of the day. Similarly, spatially deficient data, relative to the original sampling design, are inadequate to represent the entire sampling space.

Selection of gas equilibration time affects the results of the NH_3 processed data for the MPSS using single measurement instrument. The equilibration time should be determined based on the response time of the sampling and measurement system.

Correct data processing requires understanding of the actual circumstances under which the data were obtained, for example, the sampling and measurement system and their operations. The test circumstances and procedures are recorded in test notes or test logs. Insufficient or missing test notes and misinterpretation of these notes can all introduce errors. Test notes should aim at assisting data processing and interpretation. They should record all test operations and measurement system changes that have affected or will affect the data. They should be complete, concise, and easy to understand.

6.4. Standards for ammonia sampling and measurement

Because methodologies that are proven to be scientifically sound were not always available or not always used, many of the field studies did not produce reliable data. Some European researchers believe that ~80% of the publications of agricultural NH_3 emissions are not useable to establish annual emission factors (Gallmann and Hartung, 2000). This has created a lack of confidence in reported data and has made comparison of research results difficult or unreliable. The present situation leads to the conclusion that there is an urgent need to develop standards for agricultural NH_3 measurement and relevant methodologies and technologies in this specific field. Although some attempts to establish standards in air pollution monitoring have been made (Heber *et al.*, 2004), much effort is still needed to make the following standards:

Technical terms: Standardize technical terms for this specific research field including those for describing processes (e.g., NH_3 production, generation, volatilization, release, emission), presenting data (e.g., concentration, emission flux, emission rate, emission per animal unit, emission per animal place, annual emission factor), and indicating data qualities (e.g., precision, bias, accuracy).

Calibration gases: Define approved analytical instruments and procedures used by calibration gas providers for certifying gases. This standard will guide researchers on selecting gas providers and will assure quality of certifications.

Sampling devices and procedures: Standardize closed and open sampling devices (e.g., dimensions and structures of sampling chambers, configuration of micrometeorological sampling, materials used in sampling systems), and sampling procedures (e.g., sampling location, interval, frequency, duration, season).

Measuring devices: Standardize performance requirements (e.g., precision, sensitivity, response time) of measuring devices (including those for NH_3 concentration and airflow rate measurements) for various measurement objectives (e.g., compliance, emission factor determination, abatement evaluation, and health risk assessment).

7. SUMMARY AND CONCLUSIONS

Tremendous advances in sampling and measurement of NH_3 at animal facilities have been achieved during the past four decades. These advances have taken place under the increasing awareness of the environmental problems related to agricultural NH_3 and with the efforts to address these problems at different levels, from the general public, animal producers,

scientists and engineers, to the local and national governments. However, these advances could not have happened without the development of the sampling and measurement methodology, the computer technology, and the analytical instruments.

The state of the art of NH_3 sampling and measurement at animal facilities displays a variety of technical possibilities to satisfy different research and monitoring requirements. Nevertheless, all the sampling and measurement technologies reviewed in this chapter have their advantages and limitations. Selection of the methodology and technology should be based on study objectives, budget limit, and available equipment and expertise.

The three sampling methods (closed, point, and open path) can satisfy most of the research objectives to assess human and animal exposure, determine baseline emissions, compare building structure and mitigation technologies, and model pollutant dispersions. However, spatial variation of NH_3 concentrations at large animal facilities is still a major technical difficulty for NH_3 sampling. The current sampling technology can only cover limited sampling points or sampling paths, leaving significant uncertainties for the NH_3 concentrations at uncovered spaces.

The 31 measurement instruments and sensors tested or applied at animal facilities are featured with different costs, sensitivities, and response times, providing more choices for selection than the sampling devices. Measurement devices exhibit different levels of performance and should be selected according to research objectives. While some low-cost sensors offer TWA NH_3 concentrations, the high-end analytical instruments enable continuous measurement with fast response, thus supplying data containing dynamic information of NH_3 concentrations. Most of these high-end and expensive instruments were found in universities and research institutions where intensive research on agricultural NH_3 was carried out. However, temporal variations of NH_3 concentrations at animal facilities are still not sufficiently characterized and require more investigation. Future study is also needed to assess the performances of measurement instruments under agricultural field conditions.

Particular errors associated with NH_3 concentration data can be introduced by system calibration, air sampling, NH_3 measurement, and data processing. While some of these errors are inevitable, others can be reduced by selecting gas vendors of high reputation, better research design and performance, and execution of QA/QC. Nonetheless, some sources of errors associated with sampling and measurement deserve further investigation.

Because of the incomplete technical standards in research conducted worldwide, confidence in the quality of reported NH_3 data is not yet fully established. Comparison of research results is difficult or impossible in some cases. Development of standards for technical terms, calibration gases, sampling devices and procedures, and measuring devices is needed. Standard

testing methods for assessing sampling and measuring devices and procedures for agricultural NH_3 studies wait to be developed. Cooperation among instrument developers/manufacturers, calibration gas providers, regulators, standard agencies, and agricultural research scientists is necessary to improve agricultural NH_3 sampling and measurement. Similar to what has advanced the NH_3 research at animal facilities in the past decades, the future breakthrough in this field will largely depend on emerging new methodology and technology.

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