Sampling and Measurement of Ammonia Concentration at Animal Facilities – A Review

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Written for presentation at the
2001 ASAE Annual International Meeting
Sponsored by ASAE
Sacramento Convention Center
Sacramento, California, USA
July 30 – August 1, 2001

Abstract. Scientific understanding and technical control of ammonia (NH₃) at animal facilities largely depend on sampling and measurement techniques. Good sampling/measurement techniques provide high quality data that are essential in the study and abatement of NH₃ emission. For many years until now, there have been only a few publications that address the application of these techniques at animal facilities under field conditions. This review emphasizes the sampling and measurement of NH₃ applied under field conditions and draws an updated picture of the state-of-the-art of NH₃ concentration measurement at animal facilities. Four types of sampling techniques and nine groups of measuring devices for NH₃ concentration are described and summarized. Variables of measurement, and principles, procedures, advantages and disadvantages of various sampling/measurement techniques are reviewed. Recommendations are made for future research including development of methodologies and standards.

Keywords. Air quality, Environment, Agriculture, Instrument, Sensor
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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 problems and has attracted more and more attention from the public and government regulators.

It is believed 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 (van Breemen et al., 1982; Roelofs and Houdijk, 1991; Slanina, 1994). Van der Hoek (1998) estimated that 80–95% of the total NH$_3$ emission in Europe originates from agricultural practices. Their estimates also indicated that ammonia emission from animal excreta contributed over 80% and emissions from use of fertilizers contributed less than 20% of the total NH$_3$ emission. Kurvits and Marta (1998) reported that most NH$_3$ emissions in Canada are from farm animals. The authors also estimated a 21% increase of NH$_3$ emission from animal husbandry in Canada from 1990 to 1995.

High concentrations of NH$_3$ inside the animal houses also represent potential health hazards to humans and animals (Reece et al., 1980; Carr et al., 1990; Crook et al., 1991; Wheeler et al., 2000a). Chronic respiratory diseases of swine production facility workers have been attributed to dust and NH$_3$ (Donham et al., 1995). Animal respiratory diseases, such as sneezing, coughing, or pneumonia, increased when NH$_3$ concentrations were 20–40 ppm as compared with 5–15 ppm (Busse, 1993).

Although studies of agricultural NH$_3$ have increased in recent years, reliable field measurements of NH$_3$ at animal facilities (animal houses, and manure storage and treatment) are a major need. This is especially true for North America. Kurvits and Marta (1998) explained that the NH$_3$ emission factors used for the Canadian Inventory were taken from the United States Environmental Protection Agency (USEPA), which in turn were based largely on a 1992 Dutch report of emission in the Netherlands.

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 as well as abatement of NH$_3$ emissions.

For many years until now, there have been only a few publications focusing on the measurement of NH$_3$ at animal facilities. Some of the publications reported specific measurement setups. Van ’t Klooster and Heitlager (1992) presented a special report describing in detail a system at the Research Institute for Pig Husbandry (RIPH) in Rosmalen, the Netherlands. Berckmans and Ni (1993) described a field installation on a commercial pig farm in Belgium. Heber et al. (2001) provided a detailed description of a field test system including NH$_3$ measurements in eight commercial swine buildings.

Ammonia measurement techniques have been reviewed in other publications. Kamin et al. (1979) included, in their comprehensive study of NH$_3$, one chapter on NH$_3$ measurement and monitoring techniques. However, there have been new techniques developed and introduced in agriculture since their book was published. Van Ouwerkerk (1993) reviewed various techniques of NH$_3$ emission measurement at animal houses. McGinn and Janzen (1998) presented measurement techniques to determine the loss of NH$_3$ from manure-amended soils, including micrometeorological techniques and a chamber method, but no measurement of NH$_3$ at animal facilities was discussed. Monteny and Erisman (1998) discussed NH$_3$ measurement in dairy cow buildings including the measurement of ventilation rate in naturally ventilated barns. Ni (1998) reviewed NH$_3$ measurement techniques especially related to animal houses. Phillips et al.
(2001) recently published a comprehensive review of techniques for NH$_3$ emission measurement.

However, most of the useful information is still scattered in the literature. Furthermore, technical difficulties in field sampling and measurement need more careful study. 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 objective of this paper was to draw an accurate picture of the state-of-the-art of NH$_3$ sampling/measurement methods/devices based on reported applications at animal facilities, to address technical and practical difficulties in their implementation, and to delineate the future research needs in the area of measurement methodology.

A General View of Ammonia Measurement

To obtain accurate information about NH$_3$ at animal facilities, suitable measurement techniques have to be adopted and one or more measurement variables have to be chosen depending on measurement objectives. These variables include NH$_3$ concentration, air exchange rate (or ventilation rate), air temperature, and air pressure. An example of measurement at animal house is illustrated in fig. 1.

![Measurement variables and objectives](image.png)

Figure 1: Measurement variables for ammonia concentration and emission at animal building.

To obtain atmospheric NH$_3$ concentrations inside and outside animal buildings, measurement of concentrations at required locations is indispensable while all the other variables are optional, because they are relatively less important. To obtain NH$_3$ emission from animal building or manure storage, the measurement of NH$_3$ concentration difference between the outgoing and incoming air is essential along with the air exchange rate (or ventilation rate). Phillips et al. (2001) provided a comprehensive review of available techniques for measuring building air exchange rates.

Most NH$_3$ concentration measuring devices provide direct reading in volumetric concentrations. However, mass concentrations are required to calculate NH$_3$ emissions. The volume of gas depends on temperature and pressure and is therefore not constant. When converting from volumetric concentration 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 need to be known. However, although measurement of air temperature was often included in published works, air pressure measurements are seldom found. Atmosphere pressure varies between about 980 and 1040 mbar, a 6% variation, or a ±3% from standard atmosphere, which is 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.

Figure 2: An overview of techniques applied to measure ammonia concentrations at animal facilities.
Ammonia Sampling

Location and Time of Sampling

Because of the large volume of air flowing through animal houses or flowing over manure storage and treatment 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 gas measurement at animal facilities, “sampling” is defined in this work as:

“The technique and procedure that specifies the location where air sample is taken, controls the time of measurement (interval, frequency, and duration), and regulates the mass (usually volume) of sample air to be measured.”

The necessity of selecting location and time of sampling is obvious, because there are temporal and spatial variations of NH$_3$ concentration in animal buildings and open-air manure storage and treatment. An animal building is a ventilated and imperfectly mixed air space, where temperature and concentration gradients exist. Changes in room temperature and building ventilation usually follow diurnal and seasonal patterns. 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 other locations. Field studies have confirmed non-homogeneity of NH$_3$ concentrations in livestock houses (Krause and Janssen, 1990; 1991; Berckmans et al., 1994; Ni et al., 2000b). An example of NH$_3$ concentration variations at three different locations during a 24-h period, and the effect of ventilation airflow on the concentrations is provided in fig. 3, which also shows the temporal variation of the NH$_3$ concentrations.

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

Accurate control of air sample volume is necessary for some analytical techniques (e.g. wet chemistry using acid traps) that only determine total mass of NH$_3$. In order to get volume specific NH$_3$ data (concentration) of the air, the volume of the air sample must be known. Sometime a sampling/control device is needed to perform sampling. However, the
manipulations of space, time, and mass are not always necessary depending on different measurement objectives.

**Methods and Devices of Sampling**

**Closed Sampling: Sampling Chambers**

Closed sampling methods involve a physical enclosure or a sampling chamber to create a limited headspace over the NH$_3$ release surface that is physically separated from surroundings. A sampling chamber has an open-bottom face and is usually equipped with air inlet(s) and outlet(s). The chamber is placed on the floors of animal buildings or on the surfaces of liquid or solid manure storages that release NH$_3$. Sample air is drawn from the outlet and/or inlet of the chamber.

Closed sampling methods provide a small-scale cut-off space under field conditions and therefore enable easily controllable studies. For example, airflow through the chamber can be easily measured and adjusted to investigate its effect on gas release (fig. 4). However, the enclosure may also alter airflow patterns and gas concentration gradients of the sampling headspace that would naturally occur. Thus, there is a significant difference between artificial and natural airflow patterns and gas concentration gradients above the NH$_3$ release surface.

**Flow controller**

**Air stirring fan**

**In-situ analysis**

**Zero-air**

**Inlet**

**Outlet**

**Lagoon**

**Floating platform**

Figure 4. Schematic of a closed method used for lagoon ammonia sampling.

Source: Aneja et al. (2000).

Sampling chambers have been given various names, e.g. Lindvall box, dynamic chamber, wind tunnel, hood, convective flux chamber, etc. Their volumes were between 0.02 to 108 m$^3$ and most of them had box-like shapes. Airflow through the chamber was supplied by a fan (installed in the inlet or outlet) or a compressed air cylinder. Most tested involved blowing ambient air, filtered or not, through the chamber, while others blew zero-air (fig. 4). Some chambers utilized a stirring fan inside the chamber to mix air. A summary of the sampling chambers is given in table 1.

The earliest sampling chamber used in animal building was a Lindvall Box (1.5 × 1.0 × 0.4 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 at animal facilities by Scholtens (1990), Kant et al. (1992), Elzing and Swiercra (1993), and Kroodsma et al. (1993).

Elwinger and Svensson (1996) described a battery-powered dynamic chamber, developed by Svensson and Ferm (1993), to sample and measure NH$_3$ emissions in an experimental broiler house. Andersson (1995) converted manure culverts in a 160-m$^2$ pig house into a measuring system by covering the slatted floor with boards and placing inlets and outlets of the system. Ferguson et al. (1997) developed an isolated 19-L container laid over a portion of the litter in a
broiler room to sample equilibrium NH$_3$ concentrations every 20 min. A small fan in the container mixed the sample air at a constant velocity (1.0 m/s).

Table 1. Summary of the reviewed sampling chambers.

<table>
<thead>
<tr>
<th>Chamber name</th>
<th>Shape</th>
<th>Dimension</th>
<th>Incoming air</th>
<th>Emission source</th>
<th>Stir fan</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lindvall box</td>
<td>Box</td>
<td>1.5×1.0×0.4 m$^3$</td>
<td>Cleaned</td>
<td>Animal houses</td>
<td>No</td>
<td>1</td>
</tr>
<tr>
<td>Dynamic chamber</td>
<td>Box</td>
<td>0.40×0.30×0.18 m$^3$</td>
<td>Ambient</td>
<td>Broiler house</td>
<td>No</td>
<td>2</td>
</tr>
<tr>
<td>Chamber</td>
<td>Box</td>
<td>L: 5.4 m</td>
<td>Ambient</td>
<td>Pig house</td>
<td>No</td>
<td>3</td>
</tr>
<tr>
<td>Container</td>
<td>---</td>
<td>Vol.: 19 L</td>
<td>None</td>
<td>Broiler litter</td>
<td>Yes</td>
<td>4</td>
</tr>
<tr>
<td>Chamber</td>
<td>Box</td>
<td>1.22×0.76×0.41 m$^3$</td>
<td>Ambient (0.2m/s)</td>
<td>Broiler litter</td>
<td>No</td>
<td>5</td>
</tr>
<tr>
<td>Dynamic chamber</td>
<td>Box</td>
<td>Bottom: 0.25 m$^2$</td>
<td>Ambient</td>
<td>Pig house</td>
<td>Yes</td>
<td>6</td>
</tr>
<tr>
<td>Open dynamic chamber</td>
<td>Box</td>
<td>6×3×2 m$^3$ and 9×6×2 m$^3$</td>
<td>Ambient (1–11 m$^3$/h)</td>
<td>Treated manure</td>
<td>No</td>
<td>7</td>
</tr>
<tr>
<td>Wind tunnel</td>
<td>---</td>
<td>2×0.5 m$^2$</td>
<td>Ambient (1.0m/s)</td>
<td>Concrete floor</td>
<td>No</td>
<td>8</td>
</tr>
<tr>
<td>Hood</td>
<td>Box</td>
<td>Open face: 0.9 m$^2$</td>
<td>Filtered (1.0 m/s)</td>
<td>Dairy farm</td>
<td>No</td>
<td>9</td>
</tr>
<tr>
<td>Buoyant Convective Flux Chamber</td>
<td>Box</td>
<td>1.22×0.61×0.25 m$^3$</td>
<td>Filtered (1.1 m/s)</td>
<td>Lagoon</td>
<td>No</td>
<td>10</td>
</tr>
<tr>
<td>Dynamic chamber</td>
<td>Cylinder</td>
<td>0.27m(Φ)×0.42m(h)</td>
<td>Zero-air (2.4–4.7 L/min)</td>
<td>Lagoon</td>
<td>Yes</td>
<td>11</td>
</tr>
</tbody>
</table>


Brewer and Thomas (1997) used a Plexiglas chamber to cover the litter in a commercial broiler house. Svensson et al. (1997) employed a dynamic chamber combined with diffusion samplers and gas detection tubes in a naturally ventilated pig house. Air from 2.0 m above the bedding surface was sucked into the chamber by a fan. An air-mixing fan was installed inside the chamber. Amon et al. (1997) described two large-scale open dynamic chambers developed in Austria to collect emission data. The incoming air to the chamber was fresh ambient air. The chamber was used to study gas emissions from aerobically composted and anaerobically stored solid manure. Misselbrook et al. (1998) conducted sampling on concrete floors and a commercial dairy yard using a “wind tunnel” and a “hood”, respectively.
Heber et al. (2000a) developed a buoyant convective flux chamber for odor and gas sampling using 1.0 m/s air speed in the chamber. It floated about 0.17 m above the water and covered 0.74 m$^2$ of swine lagoon surface. The air to the chamber was provided by an air supply unit that contained activated charcoal, zeolite and permanganate. Aneja et al. (2000) used a 27 cm diameter, 42 cm height open bottom cylinder with a Teflon-coated wall and a stirring fan. The cylinder was inserted into a buoyant platform and was ventilated with compressed zero-grade air. It was used to sample NH$_3$ from lagoons (fig. 4).

**Point Sampling and Time Control: Air Stream Controller**

Single- or multi-point sampling selects one or more point locations where sample air is diffused to NH$_3$ samplers or sensors, or is pumped to NH$_3$ measuring devices. This sampling method does not disturb the NH$_3$ source and its surroundings. It is the most widely used sampling method, especially when using measuring devices such as detection tubes, because of its simplicity.

When multi-point sampling is needed with a single measuring device, an air stream controller can be used to regulate the time and location of sampling by controlling selected air stream(s) from multiple locations, usually transported in tubing, to the measuring device. Computer aided stream controllers enable automation and efficient use of limited numbers of expensive analytical instruments.

An air stream controller placed between several NH$_3$ → NO converters and a NO$_x$ analyzer was described by van Ouwerkerk (1993). Berckmans and Ni (1993) employed a similar device that regulated air sample streams two minutes for each of six converters. Neser et al. (1997) used an air stream controller to scan through four sampling points including three laying hen compartments and one incoming air location, 15 min at each sampling point. Heber et al. (2000b; 2001) and Ni et al. (2000a; 2000b) described an air stream controller to regulate air streams from up to six sampling locations, each lasting 10 to 15 min, to a single NH$_3$ → NO converter that was followed by an NH$_3$ analyzer (fig. 2).

**Open-path Sampling: Optical Detection Device**

Open-path sampling uses optical detection device, which consists of an emitter telescope and a receiver/detector. The source light from the emitter, ultra violet (UV) or infrared (IR), is beamed in one direction through a space (hence an open path), which contains gaseous NH$_3$, to the receiver/detector (fig. 5).

Depending on the technology, the length of the open-path between the light source and receiver can be several meters, 100–150 m (Secrest, 2000), up to 500 m (Amon et al., 1997) or 750 m (Mount et al., 2001). The source and the receiver can be at the 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. The open-path technique provides path-averaged gas concentrations.

Open-path sampling has a shorter history than point sampling for agricultural NH$_3$. One advantage of the open-path technique is that it does not disturb the system being measured. Also no adsorption of NH$_3$ or other gases on parts of the measuring device is possible. 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 inverted dispersion models. Climatic 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).
Open-path sampling for NH$_3$ concentration was conducted outside an animal building for emission rate assessment. Secrest (2000) 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 Ultra Violet Differential Optical Absorption 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 downwind paths to measure all the exhaust plumes from nine finishing swine barns in North Carolina. The OP-FTIR beam passed through the fan plume one meter from the fan outlet. Mount et al. (2001) measured NH$_3$ emission on a dairy farm with a path length up to 750 m.

**Sampling Air Volume Control**

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, but the authors did not give detailed information about this device.

Phillips et al. (2000) utilized a revised “Ferm tube,” a passive sampling device, in a large dairy cow house. The essential feature of this sampler 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. Any NH$_3$ passing through the sampler was captured by a coating of oxalic acid deposited on the inside wall of the tube by the evaporation of a solution in acetone. Like other acid trap samplers, captured NH$_3$ after exposure of the sampler was tested using colorimetry or other analytical methods.

Jacobson et al. (1998) collected air samples in 10-L Tedlar bags each week from the ventilation exhaust air and inside the barns for measurement of NH$_3$ concentration using colorimetric tubes. Heber et al. (2000a) used 50-L Tedlar bags for lagoon air sampling. However, while these bags defined the sample air volume, the main purpose of their use was for sample storage and/or transportation.

**Ammonia Concentration Measuring Devices**

*Classification*

Some characteristics of the techniques summarized in fig. 2 can be used to classify features to be considered during the selection process. However, the characteristics of different techniques are all relative to each other. Classifications are made in this paper according to analytical methods (wet or dry), sensitivity, delivery of measurement results (direct or indirect readout),
type of sensor use (single or multiple use), method of sampling air delivery (active or passive sampling), response time, and cost of the device (table 2).

Table 2. Characteristics of some reviewed ammonia measuring devices.

<table>
<thead>
<tr>
<th>Device Type</th>
<th>Wet or Dry</th>
<th>Sens. 1</th>
<th>Point or path</th>
<th>Readout</th>
<th>Sensor use 2</th>
<th>Active or passive 3</th>
<th>Resp. 4</th>
<th>Cost 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standardized wet chemistry</td>
<td>Wet</td>
<td>0.01–1 mg/L</td>
<td>Point</td>
<td>Indirect</td>
<td>S</td>
<td>A</td>
<td>h</td>
<td>L 6</td>
</tr>
<tr>
<td>pH paper/test strip</td>
<td>Wet</td>
<td>ppm</td>
<td>Point</td>
<td>Direct</td>
<td>S</td>
<td>P</td>
<td>s</td>
<td>VL</td>
</tr>
<tr>
<td>Gas tubes</td>
<td>Dry</td>
<td>ppm</td>
<td>Point</td>
<td>Direct</td>
<td>S</td>
<td>A</td>
<td>min</td>
<td>L</td>
</tr>
<tr>
<td>Passive gas tubes</td>
<td>Dry</td>
<td>ppm</td>
<td>Point</td>
<td>Direct</td>
<td>S</td>
<td>P</td>
<td>h</td>
<td>L</td>
</tr>
<tr>
<td>Passive sampler</td>
<td>Dry</td>
<td>ppb</td>
<td>Point</td>
<td>Indirect</td>
<td>S</td>
<td>P</td>
<td>h</td>
<td>L</td>
</tr>
<tr>
<td>EC sensors</td>
<td>Dry</td>
<td>ppm</td>
<td>Point</td>
<td>Direct</td>
<td>M</td>
<td>A/P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NOx analyzers</td>
<td>Dry</td>
<td>ppb</td>
<td>Point</td>
<td>Direct</td>
<td>M</td>
<td>A</td>
<td>2 min</td>
<td>VH</td>
</tr>
<tr>
<td>FTIR spectroscopy</td>
<td>Dry</td>
<td>ppb</td>
<td>Path</td>
<td>Direct</td>
<td>M</td>
<td>P</td>
<td></td>
<td>VH</td>
</tr>
<tr>
<td>Rosemount NDIR 7</td>
<td>Dry</td>
<td>ppm</td>
<td>Point</td>
<td>Direct</td>
<td>M</td>
<td>A</td>
<td>s</td>
<td>H-VH</td>
</tr>
<tr>
<td>PAS 1302 8</td>
<td>Dry</td>
<td>0.01–1 ppm</td>
<td>Point</td>
<td>Direct</td>
<td>M</td>
<td>A</td>
<td>35 s 9</td>
<td>VH</td>
</tr>
<tr>
<td>UV-ODAS</td>
<td>Dry</td>
<td>ppb</td>
<td>Path</td>
<td>Direct</td>
<td>M</td>
<td>P</td>
<td></td>
<td>H</td>
</tr>
<tr>
<td>Chemcassette</td>
<td>Dry</td>
<td>ppm</td>
<td>Point</td>
<td>Direct</td>
<td>S</td>
<td>A</td>
<td>s</td>
<td>H</td>
</tr>
<tr>
<td>Solid state sensor</td>
<td>Dry</td>
<td>ppm</td>
<td>Point</td>
<td>Direct</td>
<td>M</td>
<td>P</td>
<td>s</td>
<td>M</td>
</tr>
</tbody>
</table>

Notes: 1 Sensitivity, expressed in concentration level; 2 S, single use. M, multiple use; 3 A, active. P, passive; 4 Response time: h, hours. min, minutes. s, seconds; 5 Costs are approximate and may vary depending on time and location of purchase, providers and accessories. Cost is investment only; maintenance and operation are not included. VL, very low (<$1/sample). L, low ($1–10/sample). M, medium (<$5000/device). H, high (>5000 –10000/device). VH, very high (>10000/device); 6 Analytical instrument used to analyze the collection medium is not counted; 7 Rosemount® Non-dispersive Infrared Analyzer; 8 Photoacoustic Spectroscopy Type 1302; 9 For one gas or vapor if the tube is shorter than one meter.

Wet and Dry

According to Kamin et al. (1979), analytical methods of NH₃ can be classified as “wet method”, which uses an aqueous medium, and “dry method”, which is the method of direct analysis of NH₃ in the gas phase.

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 of the techniques were reported to be highly sensitive, for example, the method of converting NH$_3$ to NO followed by NO$_x$ analysis is sensitive at the ppb level. Other techniques provide sensitivity at ppm level, e.g. 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.

**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 reported techniques provide direct readout. Some of them are followed by automatic data retrieving and processing.

Techniques with indirect readout 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 not suitable for large numbers of measurements.

**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 re-used. 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 needed with the Chemcassette Gas Monitor is a single use sensor, although one cassette can provide multiple readings.

**Active and Passive Sampling**

An active sampling technique needs a pump, whether hand or electric powered, to force the sample air flowing to the sensor. Techniques with active sampling also enable transportation of sample air through sampling tubing to realize multi-point measurements with a single set of measuring device.

A passive sampling technique lets air diffuse into the sensor, or lets air stay “as is” in the open measurement point, thus a pump is not required. Sensors for passive sampling need to be placed right at the sampling location during measurement. Passive sampling depending on diffusion takes longer to finish a measurement. Because of this, it can provide time-weighted-average (TWA) concentration in a single point measurement. Some active methods (e.g. wet chemistry using acid traps) also provide TWA concentrations.

**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 (TEI, 1995), time needed for an instrument to reach from 0 to 90% at zero to span difference in gas
concentrations, to describe specifications of the instrument. The response of passive diffusion sampling can be as long as 8 or 24 h.

Cost

Costs of the reported techniques vary widely. The lowest of single-measurement is $< 0.10 (e.g. pH paper test strips) if only sensor material is counted. A gas detection tube may cost about $5.00.

The most expensive measuring device with a multi-use sensor can be $>20,000 (e.g. the Photo-Acoustic Spectroscopy (PAS)). Cost may also be much different if accessories (e.g., calibration kit, stream controller, etc.) are added to the instrument.

**Wet Methods**

**Standardized Wet Methods**

Most wet methods are standardized methods (table 3). With wet methods, once valid samples of ammonium ions are obtained in solution, it is relatively simple to arrive at final analytical results in the laboratory.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Sensitivity</th>
<th>Comments</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colorimetry-Nessler</td>
<td>0.02 mg/L</td>
<td>Traditional method, widely used in past; Numerous interferences by other compounds, including aldehydes, sulfur dioxide, amines, and metals; Pre-purification by distillation often recommended.</td>
<td>1</td>
</tr>
<tr>
<td>Colorimetry-indophenol</td>
<td>0.01 mg/L</td>
<td>Widely used; Adapted for automated analysis; Less sensitive to interference than Nessler method; pH-dependent.</td>
<td>2</td>
</tr>
<tr>
<td>Photometry</td>
<td>NA</td>
<td>Relatively simple but cannot handle large amount of samples.</td>
<td>3</td>
</tr>
<tr>
<td>Photometry-Nessler</td>
<td>NA</td>
<td>NA</td>
<td>4</td>
</tr>
<tr>
<td>Conductimetry</td>
<td>0.1 mg/L</td>
<td>Potential interference from other redox species.</td>
<td>5</td>
</tr>
<tr>
<td>Titrimetry</td>
<td>1 mg/L</td>
<td>All acids and bases interfere.</td>
<td>6</td>
</tr>
</tbody>
</table>


These methods rely on collecting gaseous NH₃ into a suitable acid solution (acid trap, or scrubber) and then performing concentration determination (fig. 6). The volume of air passed through the scrubber is recorded and the NH₃ concentration in the air is calculated (Hashimoto, 1972).
The most commonly used acid traps for measuring NH₃ at animal facilities include boric acid (H₃BO₃) (Curtis et al., 1975), sulfuric acid (H₂SO₄) (Valli et al., 1991; Krieger et al., 1993, Guingand, 1997 #1681; Pfeiffer et al., 1993; Jiang and Sands, 2000), and orthophosphoric acid (Asteraki et al., 1997; Kay and Lee, 1997; Misselbrook et al., 1998).

Three general methods of colorimetric techniques have accounted for the majority of practical use to determine the NH₃ concentration in the acid traps. 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 NH₃ 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 available and the time required to perform a comparatively accurate measurement is short. Jiang and Sands (2000) analyzed NH₃ concentration in broiler buildings using Nessler method and a spectrophotometer.

Non-colorimetric wet-chemical techniques include acid conductimetry and titrimetry. Conductimetry was used for measuring NH₃ emission from an animal house (Mannebeck and Oldenburg, 1991). Generally these techniques tend to be less sensitive than the colorimetric method and are subject to a host of interferences (Kamin et al., 1979). Titrimetry was also used for measuring NH₃ in animal houses (Curtis et al., 1975; Verstegen et al., 1976). It is relatively simple and inexpensive, but is less sensitive and is subject to interference.

pH Test Paper Methods

Moum et al. (1969) developed a very simple method by employing pH test paper and neutral distilled water as an NH₃ trap. The measuring range was 0–100 ppm and the accuracy was ±5 ppm. One follow-up use was tested by Seltzer et al. (1969). The method is inexpensive and provides direct in-situ readout. However, it has low sensitivity and precision.

Using a commercialized version of this method, Dewey et al. (2000) tested pHYdrion™ NH₃ test strips (Micro Essential Laboratory, Brooklyn, NY) in a swine unit in 1994. The pHYdrion cost only $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 NH₃ 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 NH₃. Skewes and Harmon (1995) tested the AQT
in eight commercial broiler houses and concluded that it estimated NH$_3$ levels accurately at 20–25 ppm levels.

**Gas Detection Tubes**

Gas detection tubes are based on adsorption of tested air pollutant on solid surfaces accompanied by a color reaction. There are two types of disposable tubes: active sampling tube and passive sampling tubes. 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$_3$ measurement. Meyer and Bundy (1991) measured NH$_3$ concentrations in 200 pig farrowing houses with gas detection tubes.

Gas tubes are relatively low cost, usually $5 to 8 per tube and $300 to 500 for a hand pump. Dewey *et al.* (2000) reported $306.00 for the hand pump (Dräger Accuro Pump, Dräger Safety Inc., Pittsburgh, Pennsylvania) and $4.12 for each tube.

Leithe (1971) and Leichnitz (1985) stated that the standard deviation of the results of Dräger gas detection tubes is about 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 Ammonia Low Range Detector Tube No. 3La. Liu *et al.* (1993) concluded that the accuracy of NH$_3$ detector tubes from 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 approximately 10% and the inaccuracy was about 15%. Both precision and inaccuracy of Kitagawa tube (Type 105SC) were approximately 2%. The precision and inaccuracy of the gas tubes became worse at lower NH$_3$ concentration levels.

**Active sampling tubes**

Active sampling involves a hand-pump that sucks a pre-defined volume of air per stroke (fig. 7). 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.

The Dräger Tube is probably the most widely used gas tube product. Patni and Clarke (1991) used Dräger tubes to measure short-term NH$_3$ concentrations in a dairy cattle barn, a heifer barn, swine barns and caged-layer barns. Scholtens (1993) tested and compared the Dräger tubes with the Kitagawa tubes. Stowell and Foster (2000) and Stowell *et al.* (2000) reported using Dräger tubes to sample NH$_3$ in exhaust air from three selected fans of a 960-head High-Rise™ swine building. The use of Kitagawa ® gas detector was reported by Reece *et al.* (1979), Johnston *et al.* (1981), Scholtens (1993) and Svensson *et al.* (1997). De Praetere and van Der Biest (1990), and Jacobson *et al.* (1992) reported the measurement of NH$_3$ using Gastec Tubes. Xin *et al.* (1996) used Sensidyne detector tubes (Sensidyne, Clearwater, FL) to check NH$_3$ concentration at bird level in poultry buildings.
Wheeler et al. (1999) tested the Kwik-Draw® Pump (Mine Safety Appliances Company, Part number#487500) with MSA detector tubes (MSA #804405), which was designed for one-hand operation and consistent delivery of a 100-mL sample volume. An integral counter helps track number of sample pump strokes.

![Diagram of Dräger gas test tube and hand pump]

**Figure 7: Dräger gas test tube and hand pump**

**Passive Sampling Tubes**

Like the active tubes, the passive sampling tubes are also sealed before using. However, only one sealed end of passive 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 NH$_3$ sampling tubes from different manufacturers have also been used at animal facilities. Patni and Clarke (1991) used Dräger tubes for TWA NH$_3$ 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-hour 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.

**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; 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. 8). Interferometers used in FTIR instruments manufactured in recent years are similar in design to the one built at the end of 19th 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 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.
Figure 8: Schematic diagram of interferometer. Drawn according to White (1990) and Johnston (1991).

A few of the many models of FTIR spectroscopy have been used for NH₃ 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 spectroscopy (Harris, personal communications) was used in an outdoor open-path measurement of NH₃ emission from swine buildings in North Carolina (Harris et al., 2001). An FTIR ETG w/ Bomen-100 interferometer and sterling cycle cooled detector was used in Missouri (Secrest, 2000; 2001).

Other uses of FTIR spectroscopy included an NH₃ gas analyzer in the IR/VIS and UV spectral regions (Keck et al., 1994), an IR spectrometer and a data logging system measuring NH₃ emission from pig and dairy barns in Germany (Jungbluth and Büscher, 1996; Hartung et al., 1997; Jungbluth et al., 1997), and two other reports by Hauser and Fölsch (1993) and Gallmann and Hartung (2000) without technical details.

**Non-Dispersive Infrared Gas Analyzer**

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).

**Photo Acoustic Multi-gas Monitor**

In Photo Acoustic Spectroscopy (PAS), the gas to be measured is irradiated by intermittent light of pre-selected wavelengths. The gas molecules absorb some of the light energy and convert it into an acoustic signal, which is detected by a microphone. The general principle of the PAS system (Innova AirTech Instruments A/S, Ballerup, Denmark) is illustrated in fig. 9.

The PAS monitor can automatically measure multiple gases with a single instrument. When gas samples are drawn from ambient air around the analyzer, the measurement time is approximately 30 s for one gas or water vapor, and about 120 s if five gases plus water vapor are measured. Increasing the length of the sampling tube increases the time required to pump in a new air sample and therefore increases the measurement time. The PAS requires less frequent calibration as compared with NOₓ analyzers. However, its investment is relatively high and it is subject to interference of water at high relative humidities.
A NDIR PAS (Type 1302, Brüel & Kjær, Nærum, Denmark) was used intensively in the Netherlands by the RIPH in different studies (van 't Klooster and Heitlager, 1992; den Brok and Verdoes, 1997; Hendriks and Vrielink, 1997; Verdoes and Ogink, 1997; Osada et al., 1998). Use of PAS in Germany included Hoy (1995), who measured five gases quasi-continuously, Snell and Van den Weghe (1999), who used it in a pig building, and Brunsch (1997), who measured gas concentrations in a poultry farm by combining a Type 1302 monitor with a multipoint sampler Type 1309. The PAS has been used in the USA by Ferguson et al. (1997) in a broiler house and by Pratt et al. (2000) in horse stalls in Kentucky.

**Rosemount and Beckman Industrial Models**

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. 10).

Brewer et al. (1997) used a Rosemount Analytical Model 880A gas analyzer with a dynamic chamber to measure NH$_3$ 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.

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.
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.

Opsis AR-500 UV Open-path Monitor

The Opsis AR-500 open-path monitoring system (Opsis Inc., San Marcos, CA) is designated by the USEPA as an Equivalent Method for measuring the criteria pollutants SO₂, NO₂, and O₃ in ambient air. It 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. 11).

According to an environmental technology verification test (Myers et al., 2000), the AR-500 had an NH₃ detection limit between 2.8 and 5.8 ppb with good linearity. Its relative accuracy was 3.3 to 11% over the range of 24 to 200 ppb.

Secrest (2000; 2001) used a UV DOAS Model AR500 (Opsis AB, Furulund, Sweden) with a Czerny-Turner spectrometer and "ER-110" series (110 mm optics) telescopes to measure ambient NH₃ concentration on swine farms in Missouri and Maryland.

WSU 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 NH₃ was measured in the UV bands near a wavelength of 210 nm at an integration time of several seconds to an accuracy of approximately ±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 towards the light source, 4) a receiver telescope to focus the light spectrally absorbed by the atmosphere onto a dispersing spectrograph, 5) a multi-element 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).
Chemiluminescence Analyzer

Chemiluminescence (CL) NH₃ analyzers involve an indirect measurement of NH₃ based on converting NH₃ to nitric oxide (NO) and then performing NO analysis by CL method. The NH₃ content is obtained by either chemical or mathematical subtraction of the background NO signal (Pranitis and Meyerhoff, 1987). This technique requires two instrument modules, an NH₃ converter and an NOx analyzer.

The converter is kept at a temperature of 795°C and stainless-steel is used as the catalytic active metal. At this temperature, NH₃ is converted into NO by the following reaction (Aneja et al., 1978):

\[
\Delta \quad 4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O} \\
\text{Fe}_2\text{O}_3 \\
\text{CrO}_3
\]

The gas phase reaction of NO and ozone (O₃) produces NO₂ and a characteristic luminescence in the analyzer (fig. 12). When electronically excited NO₂ molecules decay to lower energy states, light emission occurs:

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 + h\nu
\]

Pressure in the NO₂ 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 NOx analyzer, some NO may oxidize to NO₂. A molybdenum converter at 325 °C converts any NO₂ into NO prior to entering the reaction chamber of the NOx analyzer (van ’t Klooster and Heitlager, 1992).

The advantages of this technique include high sensitivity (1 ppb), high precision (±0.5 ppb), linearity (±1% full scale), and automation (TEI, 1995). The disadvantages include highly priced parts (e.g., internal gas scrubbers) by some manufacturers, and relatively large initial investment and complicated maintenance. The CL method has been used for NH₃ measurement at animal facilities in the Netherlands, UK, Belgium, and the USA.
Figure 12: Schematic diagram of the general principle of chemiluminescent detector for nitrogen dioxide and nitric oxide. PMT, photo-multiplier tube. Source: Stern et al. (1984).

Matthëus-IMAG Converter and Monitor-Labs Analyzer

Van ’t Klooster et al. (1992) Verdoes and Ogink (1997), and den Brok and Verdoes (1997) used NH₃ → NO converters type Matthëus-IMAG and a dual-channel NOₓ analyzer (Monitor-Labs Model 8840) in the RIPH at the Netherlands. Scholtens (1990), Aarnink et al. (1993), and Groenestein et al. (1997) used an instrument of the same model in the Institute of Agricultural Engineering, the Netherlands. Once a week the monitor was calibrated with a gas of 40 ppm NO in N₂ and the flow of the different channels was checked. Dust filters were changed when necessary. A similar system was reported by Demmers et al. (1999) in the U.K.

Matthëus-IMAG Converter and THIS NOₓ Analyzer

Berckmans and Ni (1993) described another system in Belgium that had five NH₃ → 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 NOₓ analyzer (Model 42-I, Thermal Instrument System, Franklin, MA (currently Thermo Electron Corporation)). The converters had conversion efficiencies between 95 and 99% at NH₃ concentrations below 30 ppm according to the manufacturer. However, one of the five converters was found unstable (Ni, unpublished).

TEI Converter and Analyzer

Heber et al. (2001) reported four NH₃ analyzers (Model 17C, Thermal Environmental Instruments, Inc., Franklin, MA (currently Thermo Electron Corporation)) used in a comprehensive field study of gas emission measurement in Indiana and Illinois. Each NH₃ 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. 2). Several papers on NH₃ emissions using these analyzers have been published (Heber et al., 1997a; 1997b; 2000b; 2001; Ni et al., 2000a; 2000b).
Harris et al. (2001) and Walker (personal communication) 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 NH$_3$ concentrations. McCulloch et al. (unpublished) 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.

**MT Converter and API Analyzer**

When measuring lagoon NH$_3$ emission in North Carolina, Aneja et al. (2000) transferred sampling air to a Measurement Technologies 1000N stainless steel NH$_3$ converter. The sample flow from the converter was routed to a CL NO$_x$ analyzer (Model 200, Advanced Pollution Instrumentation, San Diego, CA).

**Chemcassette Detection System**

The colorimetric principle (fig. 13) 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.

![Figure 13. Schematic of ammonia measurement with Chemcassette Monitor.](image)

The system can measure different gases with different Chemcassettes, which are individually formulated for a specific gas or family of gases. The low-level NH$_3$ detection Chemcassette has a range of 0.5–30.0 ppm. The system measures gas concentrations continuously and the response speed is several seconds. A Single Point Chemcassette system costs $5,200 and an NH$_3$ cassette tape costs $46. 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 ±20 % of the actual reading.
**Electrochemical Sensor**

Electrochemical (EC) NH$_3$ sensors consist of two electrodes and detects NH$_3$ with the following EC reactions:

on the measuring electrode,

$$2 \text{NH}_3 \rightarrow \text{N}_2 + 6 \text{H}^+ + 6 \text{e}^- \quad (3)$$

and on the counter electrode,

$$3/2 \text{O}_2 + 6 \text{H}^+ + 6 \text{e}^- \rightarrow 3 \text{H}_2\text{O}. \quad (4)$$

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

**Quadscan Gas Monitoring System**

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 consists 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. The authors did not provide details of the gas receiver or the EC sensor.

**Dräger Sensor**

Heinrichs and Oldenburg (1993) used a Dräger apparatus for measuring NH$_3$ in a fattening pig house, but did not provide details of the system. Another Dräger apparatus, with a measurement range of 1–100 ppm of NH$_3$, was tested in a field installation in Belgium (Ni, unpublished).

A Dräger NH$_3$ sensor (Polytron 2, Dräger Safety, Inc. Pittsburgh, PA) connected to a data logger was used in broiler houses (Wheeler *et al.*., 1998; 1999; 2000a). The sensor was battery powered. Its scale was 0–300 ppm and its precision was ±3% or ±9 ppm. The sensor was successful at a reasonable cost for research or demonstration projects. The unit consisted of a multi-gas body (Polytron 2, $985) with a sensing unit ($395). The multi-gas body can combine with specific sensor units to measure over 60 toxic gases including NH$_3$. The expected life of an NH$_3$ sensor is equal to or longer than 18 months.

**Twistik Transmitter**

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.

**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. There are several types of these sensors that are sensitive to NH$_3$ (Göpel and Schierbaum, 1991).

There exist several advantages of solid state NH$_3$ sensors, including simplicity, low price, quick response, and automatic measurement. Their limitations include low accuracy, drift, 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) first 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 <1 s and an accuracy of ± 10% between 4–500 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) described 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 semi-conducting metal oxide sensor consisting of a heater element, a dielectric layer, a contact layer, and a gas sensitive semi-conductive metal oxide layer (fig. 14). The conductivity of semi-conducting 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 for a few times but with difficulties.

Figure 14. Ammonia sensor developed by IMEC, Belgium.

**Comparison Studies of Measuring Devices**

When different devices are employed for NH$_3$ concentration measurement at animal facilities, one question may naturally be raised: How comparable are they? So far, there have been several studies conducted to answer this question (table 4).

Skewes and Harmon (1995) evaluated the AQT and the Gastec passive tubes against the 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 company.

Ni (unpublished) 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 3,900 paired data recorded by the two devices over more than one month.
### Table 4. Summary of comparison studies of ammonia measuring devices.

<table>
<thead>
<tr>
<th>Compared devices</th>
<th>Test conditions and conclusions</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. AQT</td>
<td>- Eight broiler houses: AQT and passive tubes agreed well with active tubes at 20–25 ppm and lower levels, respectively.</td>
<td>1</td>
</tr>
<tr>
<td>2. Gastec passive tubes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Gastec active tubes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Dräger EC sensors</td>
<td>- Laboratory: all three devices agreed well.</td>
<td>2</td>
</tr>
<tr>
<td>2. Kwik-Draw active tubes</td>
<td>- Environmental chambers: EC sensors and active tubes differed significantly.</td>
<td></td>
</tr>
<tr>
<td>1. Dräger EC sensor</td>
<td>- Pig house: correlation coefficient $r = 0.55$ for 3,900 paired data points.</td>
<td>3</td>
</tr>
<tr>
<td>2. CL analyzer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. pHydrion™ NH₃ test strips</td>
<td>- Pig house: test strips were precise and cost-effective as compared with Dräger tubes.</td>
<td>4</td>
</tr>
<tr>
<td>2. Dräger tubes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Gas tubes</td>
<td>- Pig house: gas tubes could accurately measure NH₃ using three sample averages.</td>
<td>5</td>
</tr>
<tr>
<td>2. CL analyzer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Open-path FTIR</td>
<td>- Pig farm: agreement was reasonably good.</td>
<td>6</td>
</tr>
<tr>
<td>2. Open-path UV-DOAS</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


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.

Other studies showed satisfactory comparison results. Dewey *et al.* (2000) compared pHydron™ NH₃ test strips against Dräger tubes, and concluded that the test strips provided a precise and cost-effective means of detecting NH₃ concentrations in swine confinement buildings.

Parbst *et al.* (2000) evaluated 0.25 to 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.

Secrest (2000) co-located 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.

### Calibration of Measuring Devices

Calibration of measuring devices assures data quality and provides information about characteristics of the devices, such as response, drift, linearity, stability, and precision.
Commercial measuring devices are usually calibrated by the supplier or manufacturer before shipping to the consumer following purchase, repair, or maintenance. However, 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 drift of the instrument occurs. Instrument manufacturers usually recommend calibration intervals, specify calibration procedure, and provide calibration accessories.

Individual disposable measuring devices, such as active and passive gas detection tubes, cannot be calibrated by users, thus no quality control check is possible. However, these devices can be compared by randomly selecting tubes, e.g. 10%, from a batch of new tubes and comparing results against an acceptable reference device, e.g. a calibrated CL system.

Calibration of an NH₃ measuring device is usually realized by measuring NH₃ concentration in certified gas mixtures of NH₃ in nitrogen or NH₃ in air. The difference between the known NH₃ concentrations and the device outputs guides the correction of the measurement by adjusting system hardware or software, or by correcting concentration data during data processing.

Only a small number of publications about NH₃ studies in animal facilities indicate calibrations of measuring devices, which include NH₃ analyzers (van ’t Klooster and Heitlager, 1992; Heber et al., 2001), PAS gas analyzers (Rom, 1993), EC sensors (Wheeler et al., 1999), and UV DOAS and FTIR systems (Secrest, 2000).

Ni and Heber (unpublished) evaluated three cylinders of 53.1, 33.2 and 9.33 ppm certified NH₃ in air. The gases were ordered with the request that they be analyzed twice with at least one week apart between analyses with both analyses agreeing to within 1%. The gas company used FTIR as the analytical method. Upon receiving the gases, the NH₃ directly from the cylinders and after 50% dilution using certified zero air was measured with an NH₃ Analyzer (TEI Model 17C). The readings from the analyzer with and without dilution indicated good linearity of the analyzer (table 5).

Table 5. Measurements of calibration gases with an ammonia analyzer when calibrated to the 53.1-ppm concentration.

<table>
<thead>
<tr>
<th>Certified NH₃ concentrations ppm</th>
<th>Readings at NH₃ analyzer, ppm</th>
<th>No dilution</th>
<th>Percentage difference</th>
<th>50% dilution</th>
</tr>
</thead>
<tbody>
<tr>
<td>53.1</td>
<td>53.1</td>
<td>0.0%</td>
<td>26.6</td>
<td></td>
</tr>
<tr>
<td>33.2</td>
<td>40.5</td>
<td>-18.0%</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>9.33</td>
<td>5.77</td>
<td>+61.7%</td>
<td>2.80</td>
<td></td>
</tr>
<tr>
<td>29.6 (recertified)</td>
<td>16.9</td>
<td>+75.1%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.6 (recertified)</td>
<td>6.0</td>
<td>+60.0%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

However, when the analyzer was adjusted to correctly display the 53.1-ppm concentration, the measured concentrations was 40.5 and 5.77 ppm for the 33.2 and 9.33 ppm certified gases, respectively. The 53.1 ppm gas was confirmed to be the most reliable based on measurements with two other devices: NH₃ detection tubes (Dräger) and a photoacoustic IR NH₃ analyzer (Chillgard ® IR Refrigerant Leak Detection System, MSA, Pittsburgh, PA). The two cylinders containing 33.2 and 9.33 ppm NH₃ were therefore returned to the gas provider, who admitted the inaccuracy of the two gases, for recertification. However, the recertified gases still showed significant differences when using the 53.1-ppm NH₃ as a calibration reference.
Discussion

Development and Application of Measurement Techniques

Measurement of NH$_3$ concentrations at animal facilities began in the 1960s with wet chemistry (Valentine, 1964; Moum et al., 1969). With the development of sensor and analytical technology, more and more techniques became available for agricultural NH$_3$ concentration measurement. So far, nine groups of techniques have been introduced and used at animal facilities. They were chosen to meet various objectives, different technical requirements, and budget constraints.

There appears to be an increasing use of dry methods with direct readout in recent years. Some of these methods can handle larger number of measurements with immediate results, provide high frequency and high precision measurements, and enable computer-aided data logging and processing. Their successful application of these techniques advanced the characterization, quantification and modeling of agricultural NH$_3$ emission significantly, e.g. by establishing NH$_3$ emission factors for different sources and by revealing dynamic behaviors of NH$_3$ release from animal wastes.

Data Quality of Agricultural Ammonia Measurement

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

Information accompanying NH$_3$ data reported in the literature is insufficient to provide an assessment of data quality. This is due to two problems. First, data quality has not received enough attention in past studies. In most published studies, there is little information about quality assurance and quality control (QAQC), e.g. calibration of measurement systems, assessment of precision and bias, etc. Second, proper and consistent data quality terminology is lacking, adding the difficulty in comparing research 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 increased difficulties in easy comparison of research results.

According to USEPA (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. 15).

The USEPA recommends using the terms “precision” and “bias”, rather than “accuracy,” to convey information usually associated with accuracy. 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.

To improve data quality in future studies and investigations, errors in agricultural NH$_3$ measurement and measures to reduce these errors need more attention by researchers who voluntarily following USEPA guidelines for QAQC if they are not required to do so.

Sources of Measurement Errors

When conducting NH$_3$ measurement at animal facilities, there are several potential sources of errors that may result from sampling, measurement, and data processing (table 6). While most
of these error sources are common in any scientific research program, a few of them deserve particular attention.

High bias + low precision = low accuracy
Low bias + low precision = low accuracy
High bias + high precision = low accuracy
Low bias + high precision = high accuracy

Figure 15. Random measurement uncertainties and measurement bias: shots at a target.

Calibration Gas

Ammonia measuring devices used in agricultural are usually field-calibrated under steady-state conditions by applying a step input using NH$_3$ calibration gas and a zero input using zero air.

Calibration gas is a serious potential source of systematic error in the NH$_3$ concentration measurement. This was demonstrated by the study of Ni and Heber (unpublished) and explained in table 5, which showed obvious disagreement among NH$_3$ gases with certified concentrations. This case raised a critical question about the reliability of calibration gases. If a measuring system is calibrated against an incorrect NH$_3$ concentration, the systematic error passes on to collected and processed data. The cause of this error goes back to NH$_3$ gas standards, and is related to calibration gas manufacturers: the analytical method they use and the QAQC they follow.

The National Institute of Standards and Technology (NIST) provides U.S. industry, government, and the public with measurements, standards, and information services. The USEPA 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. Unlike some other gases with agricultural origin (e.g. hydrogen sulfide (H$_2$S), methane (CH$_4$), carbon dioxide (CO$_2$), and sulfur dioxide (SO$_2$)), NH$_3$ is not yet available as a compressed gas with Standard Reference Materials from NIST (USEPA, 1997).

High Frequency Variation of Ammonia Concentrations

Ammonia concentrations at animal facilities are almost always under transient conditions with high frequency and large magnitude of variations (Ni et al., 2000b). These concentration
variations do not introduce serious measurement errors to sensors that provide TWA concentrations (e.g. passive gas tubes).

Table 6. Some potential error sources in ammonia concentration measurement.

<table>
<thead>
<tr>
<th>Processes</th>
<th>Sources of errors</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sampling</strong></td>
<td>Diurnal gas concentration variation</td>
<td>Frequently repeated measurements covering day and night may reduce error</td>
</tr>
<tr>
<td></td>
<td>Seasonal gas concentration variation</td>
<td>Long-period measurements covering warm &amp; cold seasons may reduce error</td>
</tr>
<tr>
<td></td>
<td>Spatial gas concentration variation</td>
<td>Carefully selected multi-location sampling may reduce error</td>
</tr>
<tr>
<td></td>
<td>Gas adsorption/desorption from contacting surfaces of sampling system</td>
<td>Affects response time</td>
</tr>
<tr>
<td></td>
<td>Condensation in sampling system</td>
<td>Absorbs NH₃, affects sensor operation</td>
</tr>
<tr>
<td></td>
<td>Dust in sampling system</td>
<td>Use filters</td>
</tr>
<tr>
<td></td>
<td>Leaks in sampling system</td>
<td>Careful test and system improvement may prevent leaks</td>
</tr>
<tr>
<td></td>
<td>Sample volume measurement</td>
<td>For example when using wet chemistry</td>
</tr>
<tr>
<td></td>
<td>Disturbance of NH₃ source</td>
<td>When using sampling chambers</td>
</tr>
<tr>
<td></td>
<td>Operation of sampling</td>
<td>Human errors</td>
</tr>
<tr>
<td><strong>Measurement</strong></td>
<td>Calibration gas</td>
<td>Potentially serious systematic error</td>
</tr>
<tr>
<td></td>
<td>Calibration procedure</td>
<td>QAQC practices may reduce error</td>
</tr>
<tr>
<td></td>
<td>Instrument sensitivity and precision</td>
<td>Expected random error</td>
</tr>
<tr>
<td></td>
<td>Instrument stability</td>
<td>Random or systematic errors</td>
</tr>
<tr>
<td></td>
<td>Inadequate frequency response</td>
<td>Random error</td>
</tr>
<tr>
<td></td>
<td>Interferences of water vapor and other gases</td>
<td>Develop and use new calibration methodology and select better devices</td>
</tr>
<tr>
<td></td>
<td>Operation of measurement</td>
<td>Human errors</td>
</tr>
<tr>
<td><strong>Data processing</strong></td>
<td>Temperature data</td>
<td>For converting mass concentrations</td>
</tr>
<tr>
<td></td>
<td>Atmospheric pressure data</td>
<td>For converting mass concentrations</td>
</tr>
<tr>
<td></td>
<td>Data round off</td>
<td>Expected random error</td>
</tr>
<tr>
<td></td>
<td>Gas equilibrium time selection</td>
<td>Applies only to multiple-location sampling</td>
</tr>
</tbody>
</table>
However, they do introduce errors to instruments (e.g. FTIR, PAS, and NOx analyzer) that provide “real-time” NH$_3$ concentrations 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 device types, sampling method, animal facility size, etc. need more investigation. Furthermore, the true frequencies of NH$_3$ concentrations under various conditions (e.g. in open air, inside buildings, with different sizes of buildings, at different seasons, with different weather, etc.) have not yet been fully characterized and deserve future study.

Interference of Water Vapor, Other Gases and Particular Matter

Except for the pH paper method, almost all of the NH$_3$ measurement techniques were initially developed for non-agricultural use. They were introduced to the animal industry after successful use in other fields. For instance, the Chemcassette Monitor that has existed for over 30 years was first reported in 2000 for agricultural use. The conditions under which the instruments were developed and factory-calibrated are 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.

Three of the six comparison studies summarized in table 4 demonstrated at least some degree of disagreement between the tested measuring devices. The increasing inconsistency of the three devices between 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 (Wheeler et al., 2000b).

No discussion about development or improvement of NH$_3$ measuring devices specifically targeting the agricultural environment was 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 an urgent need to develop test methodology and conduct tests in order 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.

Selection of Sampling Techniques

Sampling location and time is critical to obtain high quality data. Different sampling locations may result in wide variations in measurement data because of spatial NH$_3$ differences. Measurements of varying concentrations that cover excessively short periods produce data with serious temporal limitations.

However, measurement objectives play an important role in selecting sampling location and time. For example, for animal or human exposure studies, sampling locations should be in animal or human respiration zones, whereas the best sampling locations are the building air exhausts for emission measurement.

In the mechanically-ventilated negative-pressure animal house, the sampling position can be chosen at the exhaust fans for emission study. The advantage of this technique is that the gas concentration in the exhaust represents the outgoing gas concentration. Since the ventilation rate can also be measured in the exhaust(s), it is favorable for obtaining relatively accurate gas
emission data. This sampling technique was reported by Berckmans and Ni (1993), Hartung et al. (1997), and Heber et al. (2001).

The temporal variations of NH$_3$ concentrations shown in fig. 3 demonstrated 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 is to be obtained.

It is clear that low frequency sampling results in poor representation of the true NH$_3$ fluctuation pattern and therefore unreliable mean NH$_3$ concentrations. 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). Of course, high frequency sampling is subject to some technical restrictions like the capacity and response time of the measuring device.

**Selection of Measurement Techniques**

Selection of measurement techniques should be based on research objectives, coupled with the existing capabilities of the research institution and the budget constraints of the research. 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. A single-use sensor can only provide one measurement although it is relatively inexpensive. If large number of measurement data is required, the cost per measurement using a high-priced instrument with multi-use sensors may be less expensive than using low-price single-use sensors.

In many cases, small numbers of short-term samples cannot satisfy the accuracy requirements of a careful field investigation. Techniques that produce large quantities of data should therefore be considered. Some expensive instruments, like IR analyzers and NH$_3$ analyzers, are usually only used at institutions conducting intensive research on agricultural NH$_3$.

Standard wet chemistry requires analytical instruments that may already exist at many institutions. When the cost of analytical instruments does not need to be considered, wet chemistry methods are inexpensive and affordable techniques. They are especially useful with small sample numbers. The pH-paper-based test kits are appropriate for obtaining mere indications of in-building NH$_3$ concentrations when accuracy is not a priority.

Applications of high and low sensitivity measuring devices are generally related to indoor and outdoor NH$_3$ measurements, respectively. Indoor NH$_3$ concentrations are usually above 1.0 ppm, and almost all the techniques reviewed in this paper are compatible. Since outdoor NH$_3$ may be at ppb levels, some sensors, e.g. gas detection tubes, are not appropriate due to lack of sensitivity.

Measuring devices with short response times (e.g. less than 2 min) are required to properly study the dynamic behavior and diurnal variations of NH$_3$ concentrations. Sensors with long response times, e.g. passive gas tubes, are very good when only TWA data are needed.

To date, however, it is still unknown which techniques provide results that are the closest to the “true” NH$_3$ concentrations under agricultural field conditions. The tests shown in table 4 only
compared selected techniques with unknown characteristics against each other, not against a standard technique, which does not yet exist. Therefore, a standard technique and relevant methodologies need to be developed, and existing NH₃ concentration measuring devices need to be tested and compared.

**Standards for Agricultural Ammonia Measurement**

Because methodologies that are proven to be scientifically sound are still unavailable, many of the field studies have not produced reliable data. Some European researchers believe that about 80% of the publications of agricultural NH₃ 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 impossible. The present situation leads to the conclusion that there is an urgent need to develop standards for agricultural NH₃ measurement and relevant methodologies in this specific field. The following standards are needed:

- **Technical terms:** Standardize technical terms for this specific research field including those for describing processes (e.g. NH₃ production, generation, volatilization, release, emission, etc.), presenting data (e.g. concentration, emission flux, emission rate, emission per animal unit, emission per animal place, annual emission factor, etc.), and indicating data qualities (e.g. precision, bias, accuracy, etc.).

- **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 micro-meteorological sampling, materials used in sampling systems, etc.), and sampling procedures (e.g. sampling location, interval, frequency, duration, season, etc.).

- **Measuring devices:** Standardize performance requirements (e.g. precision, sensitivity, response time, etc.) of measuring devices (including those for NH₃ concentration and airflow rate measurements) for various measurement objectives (e.g. compliance, emission factor determination, abatement evaluation and health risk assessment, etc.).

**Conclusions**

1. Temporal and spatial variations of NH₃ concentrations at animal facilities are major technical difficulties for NH₃ sampling and measurement.

2. More and more NH₃ measuring devices have been used for studying NH₃ concentrations in agricultural environments, providing more technical possibilities for research with various objectives and advancing the studies of NH₃ emissions and tests of abatement techniques.

3. Some measuring devices exhibit different levels of performance under different measurement conditions. More investigations are needed to assess their performance under field conditions in agriculture.

4. Due to lack of scientifically sound methodologies and insufficient QAQC for NH₃ measurement, there is a lack of confidence in the quality of reported data. Comparison of research results is difficult or impossible in many cases.

5. Some sources of errors associated with sampling and measurement need careful study.
6. There is a potentially serious error in certifications of NH$_3$ calibration gases due to lack of NIST standards for analyzing NH$_3$.

7. Methodologies for assessing sampling and measuring devices and procedures for agricultural NH$_3$ studies need to be developed.

8. Development of standards of technical terms, calibration gases, sampling devices and procedures, and measuring devices is an urgent need.

9. Cooperation of instrument developers/manufacturers, calibration gas providers, regulators, standard agencies, and agricultural research scientists is necessary to improve agricultural NH$_3$ measurement.

Acknowledgements

This study was supported, in part, by the Purdue Center for Animal Waste Management Technologies funded by the USEPA, and the Purdue University Agricultural Research Program. Part of this paper was based on some previous work, which was partially supported by Hangzhou Rural Energy Office, China, and Catholic University of Leuven, Belgium.

References


