Comparison of Analysis Methods for Ammonia from Swine Production Facilities

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ABSTRACT: This study was performed to evaluate the accuracy, validation and applicability of UV spectrophotometer (UV), Ion Chromatography (IC), and Detector tube (DT) methods for measuring ammonia (NH₃) concentration in a swine confinement house and swine slurry storage tank. The mean values of NH₃ emitted from the house and slurry were 5.333 ppm and 42.192 ppm for the IC method; 4.13 ppm and 36.29 ppm for the Detector tube; and 5.417 ppm and 34.193 ppm for the UV method. The accuracy and the correlation of an ammonia level analyzed by the IC method compared to the UV method were 98% and 0.998(R²) in the swine confinement house and 94% and 0.997(R²) in the swine slurry storage tank. On the other hand, those of ammonia level measured by the Detector tube compared to the UV method were 77% and 0.957(R²) in the swine confinement house and 82% and 0.941(R²) in the swine slurry storage tank. This indicated that the accuracy and the correlation of the IC method compared to the UV method were higher than those of the Detector tube method compared to the UV method. Therefore, it was concluded that the IC method was more accurate in measuring ammonia concentration in a swine house and a swine slurry storage tank. The Detector tube method should not be applied to the swine slurry storage tank in which ammonia concentration is generally higher than 30 ppm because low accuracy is caused by a gross space between scales inscribed in the Detector tube. (Asian-Aust. J. Anim. Sci. 2004. Vol 17, No. 11 : 1608-1614)

Key Words: UV, IC, Detector Tube, NH₃, Swine Confinement House

INTRODUCTION

Currently the intensive animal industries create large volumes of odorous and hazardous gases and wastewater and cause many environmental problems (Goopy et al., 2004). Of them, ammonia has been recognized to be an irritant to the human and animal respiratory system. Its emission from livestock production facilities causes global warming and acid rain which, in turn, increases acidity in soil. Agriculture contributes to 50% of the global NH₃ emissions (Schlesinger and Hartley, 1992). Over 70% is emitted from intensive livestock farming in Europe (Buijsman et al., 1987; Jarvis and Pain, 1990; Asman, 1992). Ammonia emission from agriculture and livestock farming has not been estimated in Korea, but could be as high as Europe. The sources of ammonia emission from livestock farming originates mainly from livestock houses, manure storages, waste management facilities, and agricultural fields sprayed with manure. High levels of ammonia result in neighbors close to the farming area complaining about the odor and often leads to lawsuits against livestock producers. Therefore, ammonia emission from livestock farming has to be abated.

Accurate and precise techniques for measurement of ammonia concentration need to be evaluated in addition to establishing a strategy for reduction of ammonia emission from livestock production sources. Table 1 shows the current methods of quantifying the concentration of ammonia emitted from livestock farming: the detector tubes, wet chemistry based on absorption in acid, fluorescence, gas chromatography, non-dispersive infrared analysers, passive diffusion device, denuder, electrochemical cell, chemiluminescence, long path optical method, and electronic nose. However, their limits of accuracy and validity for assessing emission rates of ammonia have not yet been studied.

Although the UV spectrophotometer is an official method to measure ammonia concentration in aerial environments (Atmospheric Environmental Protection Law in Korea, 2000), it is known to have problems with validity and accuracy of measurement. Therefore, the purpose of this study was to compare the accuracy and validity of three analysis methods for ammonia. Samples of ammonia in the swine confinement house and a swine slurry storage tank were analyzed by UV spectrophotometry, by Detector tube, and by Ion Chromatography.

MATERIALS AND METHODS

Housing and management

Experiments were performed at the swine confinement house, located at the Collegiate Livestock Experimental Station at Seoul National University. About 200 growing-fattening pigs were housed in the swine confinement house (L×W×H=20 m×12 m×3 m) with a concrete slatted floor. It has two rows, each of which contains ten pens on both sides. Ten crossbred (Landrace×Yorkshire×Duroc) growing-finishing pigs, which weighed about 45kg, were housed randomly in each pen. All pigs were fed a 16% crude
protein corn-soybean meal-based diet that satisfied the NRC nutrient requirements. Pigs were fed by automatic feeder and provided with drinking water with nipples attached at the fence of the pen. Indoor air was removed by the four exhaust fans equipped at the opposite wall. Each exhaust fan has a capacity of 8,360 m$^3$/h at maximum and was operated continuously at the minimum flow rate, recommended by MWPS (1988), to mainly control temperature and relative humidity in the enclosed pig building.

**Experimental design**

Ten air samples were taken for 30 days, performed once every 3 days, in May 2003. Measurements of ammonia in the house were made at the front, middle, and rear of the central alley, 0.3 m high above floor level (Figure 1). Measurements were made at the air outlet (Ø 2 cm) from the side wall of circular PVC column, which was filled with swine slurry at the base of the column. This was aimed to simulate the swine slurry storage, of diameter 300 mm and height 1 m. The circular column containing anaerobic swine slurry was stored in a laboratory controlled with the range of 12 to 18°C.

**Air sampling method**

An impinger which contained an absorption solution (0.1 N, H$_2$SO$_4$) of 10 ml was used to sample air. The impinger was connected with a moisture trap holding silica gel (200 g) to the air sampler (Gillian, No. 800519) by a polyethylene tube (Figure 2). The duration and flow rate of

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Merit</th>
<th>Demerit</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>Detector tubes</td>
<td>- convenient, cheap and quick</td>
<td>- limit of range</td>
<td>Drager (1997)</td>
</tr>
<tr>
<td>Wet chemistry (based on absorption in acid)</td>
<td>- simple, cheap, reliable and suitable for low concentrate of ammonia in air</td>
<td>- high labor input</td>
<td>Parkinson and Day (1979)</td>
</tr>
<tr>
<td></td>
<td>- very high accuracy and precision</td>
<td>- basically non-continuous</td>
<td>Fehsenfeld (1995)</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>- simple and cheap</td>
<td>- low accuracy</td>
<td>Nakano et al. (1995)</td>
</tr>
<tr>
<td></td>
<td>- short sampling time</td>
<td>- requires skillful analytical technique</td>
<td>Vaughan et al. (1996)</td>
</tr>
<tr>
<td>Gas chromatography</td>
<td>- very precise</td>
<td>- expensive</td>
<td>Griffiths (1993)</td>
</tr>
<tr>
<td></td>
<td>- able to detect a low concentration</td>
<td>- basically non-continuous</td>
<td>Yamamoto et al. (1994)</td>
</tr>
<tr>
<td>Non-dispersive infrared analysers</td>
<td>- relatively accurate</td>
<td>- complete selectivity for ammonia is not possible</td>
<td>Janac et al. (1971)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- correction temperature and pressure required</td>
<td>Hollander (1993)</td>
</tr>
<tr>
<td>Passive diffusion device</td>
<td>- high precision</td>
<td>- necessary to trap a detectable amount of gas</td>
<td>Adema et al. (1991)</td>
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<tr>
<td></td>
<td></td>
<td>- calibration for each scenario</td>
<td>Blatter et al. (1992)</td>
</tr>
<tr>
<td>Denuder</td>
<td>- very high accuracy and precision</td>
<td>- complex procedure</td>
<td>Ferm (1979)</td>
</tr>
<tr>
<td>Electrochemical cell</td>
<td>- simple and quick</td>
<td>- low accuracy and precision</td>
<td>Boehm (1983)</td>
</tr>
<tr>
<td>Chemiluminescence</td>
<td>- high accuracy</td>
<td>- careful and frequent calibration required</td>
<td>Scholtens (1993)</td>
</tr>
<tr>
<td>Long path optical method</td>
<td>- advantages in averaging across a plume required in a number of flux measurement technique</td>
<td>- low accuracy and precision</td>
<td>Mennen et al. (1996)</td>
</tr>
<tr>
<td>Electronic nose</td>
<td>- useful even in the direct measurement of ammonia flux</td>
<td>- not yet well characterized in accuracy and precision</td>
<td>Persaud and Travers (1991)</td>
</tr>
</tbody>
</table>
air sampling were set at 90 min and 2 L/min in the swine confinement house and 15 min and 2 L/min in the swine slurry column. For the detector tube method, a representative value of a NH3 concentration was taken as the average of three measurements at 30 min intervals in the swine confinement house and at 5 min intervals in the swine slurry column. This was intended to maximize the precision of values measured with the detector tube method.

Methods of NH3 measurement

**UV Spectrophotometer (UV) method** : The basic principle of the UV spectrophotometry method for measuring NH3 is that the absorption solution, a strong acid solution such as sulfuric acid (H2SO4) or hydrochloric acid (HCl), reacts with ammonia (NH3) in the air and NH3 is ionized to an ammonium ion (NH4+). It is adsorbed by the anion of the strong acid solution, such as sulfate (SO42-) or chloride (Cl-), and then transformed into (NH4)2SO4 or NH4Cl. The substance deposited in the absorption solution, such as (NH4)2SO4 or NH4Cl, is detected quantitatively by the UV spectrophotometry method. The concentration of NH3 in air is calculated after modifying the ammonia concentration measured by the UV spectrophotometry method. A sulfuric acid (H2SO4) solution was used as the absorption solution in this study. It reacted with NH3 gas drawn from the swine confinement house and the swine slurry column. After sampling, the absorption solution in the impinger was carried to the laboratory and then was filtered by nuclope filter (0.4 µm pore size, 37 mm diameter), diluted moderately and pipetted to 3 ml. After adding Nessler's reagent (0.2ml) suggested from NIOSH (2nd Manual, 1998), it was detected by the UV spectrophotometer (UV-1601, SHIMADZU, Japan), which was set at 440 nm wavelength of UV. Before measurement, the calibration process with the six working standards (0, 2, 4, 8, 12, 16 µg/ml) was performed using (NH4)2SO4 (Sigma, U.S.) as a standard solution. Application of six working standards is intended to improve an accuracy of baseline. The ammonia concentration was calculated by following Equation (1).

\[ \text{NH}_3 (\mu g/l) = \frac{\text{Total quantity of flow(fL)} \times \text{Molecular weight of NH}_3}{1000 \times \text{Concentration of the blank(µg/ml)}} \]

In order to convert the concentration of NH3 calculated by Equation (1) into the concentration on the bases of volume ratio (V/V) unit, Equation (2) was applied.

\[ \text{NH}_3 (\mu g/l) = \frac{\text{Total quantity of flow(fL)} \times \text{Molecular weight of NH}_3}{1000 \times \text{Concentration of the blank(µg/ml)}} \]

**Detector tube (DT) method** : The detector tube method for analyzing NH3 is composed of a scaled glass vial containing a chemical absorbed onto inert support granules. The basic mechanism of the method is that chemical reacts with the ammonia in the air drawn by the hand-pump, the chemical’s color changes, and the degree of change in color indicates the ammonia concentration. The detector tubes applied in this study were No. 3L (1-30 ppm; GASTECH, Japan) or No. 3La (5-100 ppm; GASTECH, Japan), depending upon the strength of ammonia at the sampling sites. The air sampling with the detector tube method continued for one minute with a syringe-type vacuum pump (Pump kit No. 101, GASTECH, Japan).

**Ion Chromatography (IC) method** : The principle of this method is to detect and quantify ammonium ions (NH4+), into which NH3 in its gas state is converted through an absorption solution, by IC. Recently, NIOSH (2000) has suggested it as a new method for quantifying NH3, but until now, it has never been applied in livestock production. The IC utilized in the study was the 761 Compact IC (Metrohm, Switzerland), which was set in a laboratory. Besides no addition of Nessler’s reagent, The sampling and analysis procedure for measuring ammonia by the IC method was consistent with that of the UV spectrophotometry method. Table 2 gives the required conditions of the IC for analyzing ammonia.

**Statistical analyses**

SAS procedure (PROC CORR) in SAS package
program (1989) was used to calculate simple correlation coefficient and the degree of correlation and to determine the significance among the values of NH$_3$ analyzed with the three methods.

### RESULTS AND DISCUSSION

#### Comparison of ammonia concentrations by the sampling sites and the measurement methods

The mean ammonia concentrations in the middle of the swine confinement house were 6.252 (±0.55) ppm with the UV method, 6.202 (±0.56) ppm for the IC method, and 4.693 (±0.39) ppm for the Detector tube method. At the front and rear side of the swine confinement house, the mean NH$_3$ concentrations were analyzed to be 5.133 (±0.56) ppm and 4.917 (±0.53) ppm for the UV method, 5.017 (±0.59) ppm and 4.781 (±0.57) ppm for the IC method, and 3.943 (±0.52) ppm and 3.750 (±0.43) ppm for the Detector tube method, respectively. The NH$_3$ concentration in the swine confinement house can vary with stocking density, type of shed, and ventilation rate (Groot, 1994). In addition, there are other important factors; including environmental temperature and relative humidity, wash down frequency, and feed quality, which affect NH$_3$ concentration in the swine house. An NH$_3$ concentration of 3.3 to 6.8 ppm detected in the study was very low compared with the report of Metz et al. (1998) stating that 8 to 25 ppm of ammonia was generally released in a swine house. The values are below the recommended maximum NH$_3$ concentrations, 25 ppm, suggested by OSHA (Occupational Safety & Health Administration). This may be attributed to increased ventilation rate and superior manure management system in the swine confinement house. The mean ammonia concentrations at the front and rear of the shed were measured about 1 ppm higher than that of the middle of the shed, which probably is due to a poor air mixing. Ammonia concentration was measured 0.2 ppm lower at the front of the shed compared to the rear of the shed. This difference may be attributed to a measurement error. In swine slurry column, an initial NH$_3$ concentration ranged with 58 to 70 ppm was reduced at 12 to 20 ppm at the last sampling over the span of 30 days. The reduction may be caused by pH decrease in swine slurry with increasing slurry age (Rom, 1993).

Table 3 and Figure 4 show the accuracy rate and deviation for the values of ammonia concentration measured with the IC and the Detector tube methods compared to the UV method (the standard technique for quantifying NH$_3$ in the atmosphere in Korea). The difference in NH$_3$ concentration analyzed with the UV and the IC method was found to be 0.01-0.22 ppm in the swine confinement house and 1.32-2.93 ppm in the swine slurry storage tank. This indicated that an IC method has an accuracy of 98% in the swine confinement house and 94% in the swine slurry column, which was compared with the UV method. On the other hand, in comparison to the values of NH$_3$ concentrations analyzed with the UV and the

![Figure 3. Comparison of NH$_3$ concentration with the sampling sites and the analysis methods (UV, IC and Detector tube).](image-url)
Swine manure storage analyzing ammonia. Would probably be considered as a reliable technique for particles or alien matters suspended in the absorption has an instrumental disadvantage to be hindered by the dust is the standard method for measuring ammonia in Korea, it

Detector tube method in both the swine confinement house and 12% higher in the swine slurry storage tank. It is concluded that the IC method is more accurate than the Detector tube method in both the swine confinement house and 2.93-10.31 ppm in the swine slurry storage tank. Observed was 1.06-1.53 ppm in the swine confinement house, and 0.943-10.31 ppm in the swine slurry storage tank. This shows an accuracy of 77% for the Detector tube method compared with the UV method in swine confinement house and 82% in the swine slurry storage tank. It is assumed that the ammonia concentration measured with the Detector tube was about 21% higher in the swine confinement house and 12% higher in the swine slurry storage tank. It is concluded that the IC method is more accurate than the Detector tube method in both the swine confinement house and the swine slurry storage tank. Although the UV method is the standard method for measuring ammonia in Korea, it has an instrumental disadvantage to be hindered by the dust particles or alien matters suspended in the absorption solution (Skoog et al., 1999). Therefore, the IC method would probably be considered as a reliable technique for analyzing ammonia.

**Correlation of the ammonia concentrations among the three analysis methods**

Table 4 presents the correlation coefficients and levels of significance for the correlations between the UV, IC and Detector tube methods (also see Figures 4 and 5). The correlation coefficients for the NH3 concentrations between UV-IC, UV-Detector tube, and IC-Detector tube were above 0.94 in the swine confinement house (middle, front, and rear) and the swine slurry storage tank and also their probability values were significant (p<0.05). In the front, middle, and rear of the swine confinement house, the correlation coefficient between the IC method and the UV method was about 0.34 higher than between the UV method and Detector tube and between the IC method and Detector tube. This could be explained by the fact that NH3 concentration analyzed with the Detector tube was about 1.04-1.32 ppm lower than with the IC and UV method. This is assumed to be the influence of the dust generated in the swine confinement house or interfering substances, such as amines (R-NH2), for detecting ammonia with the detector tube. Gas sampling by the IC and the UV method takes about an hour while the Detector tube method takes only one minute. Dust flowed into the absorption solution in impinger is expected to interfere with accuracy of measurement by the IC and UV method. It is suggested that the ammonia adsorbed on the dust surface will be desorbed and add to ammonia concentration in the adsorption water. This interpretation is supported by the statement that dust adsorbing the odorous compounds in swine houses suspeness in the air or deposits on the floor (Day et al., 1965; Bart et al., 1984; Yeh et al., 2001). Also, in swine slurry, the level of correlation between the IC method and the UV method was slightly higher (R2=0.997) than between the UV method and Detector tube (R2=0.941) and between the IC method and Detector tube (R2=0.966). This indicated that the ammonia concentration measured with the

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Analysis method</th>
<th>correlation coefficient (R^2)</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Swine confinement house</td>
<td>UV-IC</td>
<td>0.998</td>
<td>0.023</td>
</tr>
<tr>
<td></td>
<td>UV-DT^2</td>
<td>0.957</td>
<td>0.041</td>
</tr>
<tr>
<td>Front</td>
<td>IC-DT</td>
<td>0.954</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>UV-IC</td>
<td>0.997</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td>UV-DT</td>
<td>0.973</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td>IC-DT</td>
<td>0.984</td>
<td>0.048</td>
</tr>
<tr>
<td>Rear</td>
<td>UV-IC</td>
<td>0.998</td>
<td>0.024</td>
</tr>
<tr>
<td></td>
<td>UV-DT</td>
<td>0.943</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td>IC-DT</td>
<td>0.945</td>
<td>0.030</td>
</tr>
<tr>
<td>Swine manure storage</td>
<td>UV-IC</td>
<td>0.997</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>UV-DT</td>
<td>0.941</td>
<td>0.036</td>
</tr>
<tr>
<td></td>
<td>IC-DT</td>
<td>0.966</td>
<td>0.028</td>
</tr>
</tbody>
</table>

* UV spectrophotometer method.  
1 Ion Chromatography method.  
2 Detector tube.

Figure 4. Correlation relationship between the analysis methods (UV-IC and UV-Detector tube) as sampling sites in the swine confinement house.

Figure 5. Correlation relationship between the analysis methods (UV-IC & UV-Detector tube) in the swine manure storage.
Detector tube method was 6.0 to 8.0 ppm higher than with the UV method and the IC method. In detecting NH$_3$ emitted from the swine manure stored in the cylindrical column, there was little air flow from outside of the column because the Detector tube method sucked only a small quantity of air. However, because the air sampler applied to the UV method and the IC method consistently absorbed the inner gases released from the swine slurry at the flow rate of 2 L/min for about 20 min, the comparable volume of exterior air must be supplied continuously to maintain the pressure difference between inside and outside of the column. Consequently, it is judged that the ammonia concentration quantified with the IC method and the UV method is 6.0 to 8.0 ppm lower than that of the Detector tube method due to dilution of the sample by flowing outside air into the column.

### Efficiency of the analysis methods (UV, IC and Detector tube) for measuring ammonia

Table 5 gives an outline of the analysis methods (UV, IC, and Detector tube) for measuring NH$_3$ concentration in the air. Because each method has its own instrumental limit in analyzing ammonia concentration, each method has to be applied properly according to the quantity of ammonia in livestock production facilities. The IC method has not been used to quantify NH$_3$ concentration in livestock systems. However, considering that the IC method has high accuracy comparable to the UV method in measuring ammonia and can detect ammonia concentration up to the 10 ppb level, the potential for the use of the IC method in the livestock production field is promising. Main disadvantages of the IC method are the high cost of the equipment and the consumption of long time acquired for obtaining stable readings. Disadvantage of the UV method is that an analyst may have difficulties in determining the titration point time to make the coupler (Nessler’s reagent) and pay much attention to the analysis procedure to obtain high precision.

The Detector tube method has been widely used because it is very simple, easy to treat, and cheaper than the UV and the IC. However, the analytical error by the Detector tube in measuring NH$_3$ concentration over 30 ppm is one reason why an analyst can not read the indicated value accurately due to wide space between each scale marked onto the surface of Detector tube. Therefore, it is concluded that both the UV and the IC methods can be applied accurately and precisely to measure the NH$_3$ concentration in livestock facilities emitting above about 30 ppm of ammonia. This study was done without analysis of variance and calculation of CV (coefficient of variance) due to minimal replicates per sample (n=2) by lack of air sampler. Therefore, a supplementary study is being undertaken to statistically verify findings in this study.

### REFERENCES


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