DETERMINATION OF ATMOSPHERIC AMMONIA BY ALKALIZED POROUS SILICA BEADS COLLECTION AND CHEMILUMINESCENT NITROGEN DETECTOR — GAS CHROMATOGRAPHY

Nobuyuki KASHIHIRA, Kazuo MAKINO, Kuwako KIRITA, and Yoshichika WATANABE
Training Institute for Environmental Pollution Control
(3-3 Namiki, Tokorozawa, Saitama 359)

A simple and rapid method for determination of atmospheric ammonia has been investigated. The method is based on preconcentration with alkalized Porasil A and on analysis with a chemiluminescent nitrogen detector-gas chromatography (CLD-GC). Collection on and thermal release from the adsorbent are almost quantitative. From temperature dependence of retention volumes, it is possible to make a sampling of 5 liters at 20 °C, which allows to determine 10 ppb of ammonia in air. Results with the present method are in good agreement with those by the acid collection and the Indophenol method.

1. Introduction

Atmospheric ammonia is normally determined by preconcentration on an acid-imregnated filter paper or in an acidic solution, followed by colorimetric measurement such as the Indophenol or the Bispyrazolone method. However, low sensitivity of the methods and a relatively high blank value of the filter paper require quite a large volume of a sample gas. The more sensitive detection systems have been developed for monitoring ambient ammonia directly or incorporated with proper preconcentration.1) Some of these methods, however, suffer interference from other atmospheric pollutants depending upon the detecting device, e.g. nitrogen oxides and amines with chemiluminescent method.2) This may be avoided by gas chromatographic separation.

Gas chromatography of ammonia was first done with a thermal conductivity detector (TCD), but is not familiar yet due to its rather poor sensitivity. Recently, nitrogen sensitive detector, i.e. a flame thermionic detector (FTD), has made possible to determine pg levels of nitrogen compounds, which allows us determination of ammonia at a few ppm in gas phase by a direct syringe injection.3) However, little work has been reported on a way of field sampling for atmospheric ammonia in a range of ppm to ppb levels. Ambient temperature adsorption-thermal desorption technique on solid adsorbent is advantageous with respect to easy handling and no reagent blank. W.A. McClenny et al4) used Chromosorb T for ambient gaseous collection, followed by detection with chemiluminescence or optoacoustic detection systems. Porous polymer beads have been applied for collection of amines5,6) which are homologue to ammonia.

*Gas chromatographic measurement of N-containing compounds (III). The previous paper is; N. Kashihira, K. Kirita, Y. Watanabe, and K. Tanaka, Bunseki Kagaku 29 853 (1980).
The present paper reports on determination of ammonia at ppb levels with chemiluminescent nitrogen detector-gas chromatography (CLD-GC),7) in combination with collection on alkalized Porasil A tube. CLD is very specific and quite sensitive to ammonia. Therefore, a direct injection of ammonia to a gas chromatograph after preconcentration on a proper adsorbent is possible since there is no interference from other atmospheric pollutants which are normally a serious problem in the case of FID-GC.

2. Experimental
2-1. Apparatus: As gas chromatograph, Shimadzu 4BM-GC equipped with the chemiluminescent nitrogen detector (CLD) was used. Gas chromatographic separation was performed with Chromosorb 103 (80-100 mesh) (Jones-Manville) packed in a glass column (3 mm i.d., 3 m long) isothermally at 130 °C. Flow rates of nitrogen carrier gas and oxygen supporting gas for CLD were 40 ml/min and 160 ml/min, respectively. A temperature of injection port was kept at 160 °C.

2-2. Materials: Ammonia standard solution was prepared by diluting ammonia solution (30 %) (Wako Pure Chemicals, 'S' grade) with water and standardized by the titrimetric method with hydrochloric acid. Ammonia standard gas was made by vaporizing about 1 µl of ammonia solution (30 %) in a nitrogen filled sampling bottle (1 liter). This was further diluted with nitrogen gas in another bottle, if necessary. Its concentration was calibrated by comparing peak heights of the gas chromatogram with those of the ammonia standard solution. The ammonia gas stream with a constant concentration at ppb levels was prepared by diluting ammonia vapor permeating through a permeation tube wall with air compressed from a laboratory room with an air pump. The diluent air was not made any special purification but desiccation with silica gel. Therefore, it was not clean. The permeation tube, first developed by O'Keefe to obtain known concentration of gases,8) was prepared by filling concentrated ammonia solution, instead of liquefied ammonia, in Teflone tube whose both ends were plugged off with a glass ball.9) Since the permeation rate can not be calibrated by gravimetric weight loss for the present tube, concentrations of the diluted sample gas were determined either by colorimetry after collection in an acidic solution or by the present method. The collection tube was a glass tube (6 mm i.d., 10 cm long), packed with about 1 gram of 5 % KOH coated Porasil A (80-100 mesh) (Waters Assoc. Inc.), one end of which was plugged with a silicone rubber and the other was attached with a syringe needle. The tube was conditioned as mentioned in the reference.6)

2-3. Analytical Procedures: (1) Gas chromatographic analysis: A few liters of an air sample were drawn through the collection tube without the syringe needle and the silicone rubber plug at 0.5-0.7 l/min with the air pump. After installing the sampled tube in a carrier gas flow system and equilibrating it at the inlet pressure of the gas chromatograph, a temperature of the tube was raised upto 280 °C in 1-2 minutes and then the nitrogen carrier gas was switched to flow through the tube for injection of a content liberated by thermal heating into the gas chromatographic column by a six-way cock. A measurement was done with peak heights of the ammonia peak on the chromatogram. (2) Retention volume measurement: A sampling capacity of the collection tube was measured by a passage of a sample gas (120 ppb) from the permeation tube through alkalized Porasil A tube in a thermostat at a certain temperature and sampling
rate of 0.5 l/min. A fraction (about 100 ml/min) of the exit air stream from the tube was monitored for ammonia by CLD.

3. Results and Discussion
3-1. Detection of ammonia with chemiluminescent nitrogen detector

A sensitivity of CLD for ammonia is governed by effectiveness of ammonia conversion to nitrogen monoxide in combustion of ammonia. A simple combustion of ammonia in oxygen leads to a formation of only nitrogen and water.10 However, with the catalyst as the present case, the process (1) becomes the main path,

\[ 4\text{NH}_3 + 5\text{O}_2 \xrightarrow{\text{Pt}} 4\text{NO} + 6\text{H}_2\text{O} \]  

(1)

and almost all ammonia are converted to nitrogen monoxide at 800 °C.2,10 A response of ammonia to CLD was measured by injecting about 40 ng of ammonia solution to CLD directly without column separation. A result is shown in Fig. 1 in which the ordinate is the intensity of nitrogen monoxide on CLD, while the abscissa represents the number of moles corresponding to 10 ng for ammonia. In Fig. 1 it is also shown responses of some other nitrogen compounds to CLD for comparison. Concentration of nitrogen monoxide in gas phase converted from ammonia on CLD coincided roughly to the calculated values from amounts of ammonia injected. These results show a satisfactory conversion of ammonia to nitrogen monoxide. The amounts of ammonia and the intensities of nitrogen monoxide's signal had a good correlation to give a straight line up to 150 ng, above which CLD was scaled out at the present system. A sensitivity of CLD for ammonia is quite resemble to that of FTD, but the former is less affected by solvent or hydrocarbons than the latter.

3-2. Collection capacity of adsorbent tube

The good adsorbent is required to have a large capacity at ambient temperature (large adsorbing constant) and to allow complete desorption by heating. Collection capacity of the adsorbent tube was determined in twofold; (1) collection efficiency and (2) retention volume. The collection efficiency was measured by connecting two adsorbent tubes in series, on which ammonia was sampled at a constant sampling rate for a certain period. Amount of ammonia on each tube was determined by CLD-GC after injecting it by thermal desorption at 280°C. Next, changing the order of the tube connection, ammonia was measured similarly. Let denote the collection efficiency of the tube A α, of the tube B β, respectively, and assume the tube A to be front-side.
for the first measurement, then the collection efficiencies of both tubes are given by the following relations;

\[ \alpha = \frac{1 - (b_1/a_1)(b_2/a_2)}{1 + (b_1/a_1)} \]  
\[ \beta = \frac{1 - (b_1/a_1)(b_2/a_2)}{1 + (b_2/a_2)} \]

where \( a, b \) are the amounts of ammonia collected on the front tube and the back tube, respectively, and suffixes 1 and 2 denote the first and second measurements, respectively. From these two equations it is apparent that \( \alpha \) and \( \beta \) are independent from ammonia concentration and the total volume sampled, as long as the volume of gas is smaller than the retention volume of the collection tube. Thus, collection efficiency of the tubes can be calculated from a ratio of ammonia collected on the two tubes. Ammonia being observed on the backup tube for neither the first nor the second measurements in the present experiment, the collection efficiency of alkalized Porasil A is almost 100% at sampling rate upto 0.8 l/min, above which a pump used could not attain. The second measure for the capacity of the tube is the retention volume (\( V_r \)) which is defined as the maximum volume of gas to retain the particular compound in the column and expressed by the following equation

\[ V_r = (t_r - t_o) F_c \]

where \( t_r \) is the retention time of the objective, \( t_o \) is the retention time of non-retained substances like carrier gas and \( F_c \) is a flow rate of the carrier gas (sampling rate in the present case). A measurement was performed by a procedure mentioned in the experimental section. No signal observed first due to adsorption of ammonia on solid surface, a signal of nitrogen monoxide converted from ammonia on the catalyst started to appear after a passage of a certain amount of the sample gas depending upon tube temperature. The apparent retention volume (\( V_a \)), called as break-through volume, was calculated with appearing time (break-through time) of this signal multiplied by the fixed sampling rate at given temperature. A dead volume (\( V_d = t_o F_c \)) was quite small (at most 20 ml) compared with \( V_a \). The results are shown in Fig. 2, from which the maximum sampling volume for ammonia is about 6 liters with 1 g of alkalized Porasil A at ambient temperature (ca. 20 °C).

3-3. Recovery from collection tube

From the results upto now, it is shown that alkalized Porasil A is a good adsorbent for ammonia with respect to a large loading capacity. However, the effectiveness
of the collection tube is governed by both collection efficiency and release by heating. For example, although amines and ammonia were collected completely on alkali untreated Porasil A, none of these compounds was recovered by heating at 280 °C. A recovery of ammonia from the collection tube was measured by syringing ammonia standard solution or standard gas to the collection tube, followed by gas chromatographic analysis as mentioned in the section 2-3. A calculation was performed by comparing the resulting peak height with that from the direct injection to the gas chromatograph. The experimental results are tabulated in Table 1. Gaseous ammonia is recovered more than 95 %, while the recovery of ammonia in the solution is only 60-70 %. The reason for this low recovery of the latter is attributed to an effect of water. Water is retained by KOH in the collection tube for quite a long time, as the result ammonia fraction in water delays to enter gas chromatographic column, giving a rise to peak tailing. However, a way of tailing was not so sensitive to amount of water and 10 μl of water gave the similar recovery to 1 μl. A calibration curve was made by the whole procedure for 1 μl of the standard solution at various concentrations, because a humidity in air is condensed on KOH in the actual sampling and it amounts to more than 10 μl of water. From this calibration curve ammonia can be determined as low as 20 ng, although CLD-GC can detect it in a few ng or below.

Table 1 Recovery of ammonia from alkalized Porasil A packed collection tube by heating at 280 °C.

<table>
<thead>
<tr>
<th>a) Standard solution</th>
<th>NH₃ taken(ng)</th>
<th>NH₃ found(ng)</th>
<th>recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3</td>
<td>2.5</td>
<td>47.9</td>
<td></td>
</tr>
<tr>
<td>26.7</td>
<td>15.4</td>
<td>57.5</td>
<td></td>
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<tr>
<td>37.4</td>
<td>23.6</td>
<td>63.1</td>
<td></td>
</tr>
<tr>
<td>53.4</td>
<td>34.1</td>
<td>63.9</td>
<td></td>
</tr>
<tr>
<td>85.4</td>
<td>56.4</td>
<td>66.0</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>b) Standard gas</th>
<th>NH₃ taken(ng)</th>
<th>NH₃ found(ng)</th>
<th>recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>6.2</td>
<td>95.4</td>
<td></td>
</tr>
<tr>
<td>13.0</td>
<td>12.0</td>
<td>99.2</td>
<td></td>
</tr>
<tr>
<td>26.0</td>
<td>24.8</td>
<td>95.4</td>
<td></td>
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<tr>
<td>43.0</td>
<td>50.8</td>
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<td></td>
</tr>
<tr>
<td>71.6</td>
<td>70.1</td>
<td>97.9</td>
<td></td>
</tr>
</tbody>
</table>

3-4. Analysis of ammonia sample gas

Ammonia gas in low concentration prepared with a permeation tube was sampled and analysed as described in the experimental section. Fig. 3 is typical gas chromatogram for ammonia. The average amount of ammonia is 60.15 ng for four measurements by 1 liter of the sample gas at 0.5 l/min and its relative standard deviation is 6.4 % or less. The effect of sampling volume on ammonia collection was examined and the result is shown in Fig. 4, in which the ordinate is the amount of ammonia (ng, left-hand) and the concentration of gas (ppb at 20 °C, right-hand), while the abscissa is the volume of gas sampled. From Fig. 4 amount of ammonia can hold a linear correlation with the sampling volume, consequently nearly constant concentration of the gas, indicating that the present method is suitable for determination of ammonia in atmosphere.

Concentrations of the gas were measured both with the present method and colorimetry. Results with the present method are 132 ppb and 92 ppb by sampling 2 liters of the
sample gas at different temperatures for the permeation tube, while those by the
Indophenol method are 125 ppb and 80 ppb, respectively, by preconcentrating 100 liters
of the gas in 0.1N sulfuric acid solution. They are relatively in a good agreement.
The method was applied to determine ammonia in air of lavatories at our institute and
in a city park. Results were 63.5 ppb and 108 ppb, respectively, by sampling 1 liter.
Atmospheric air around a boundary zone of a cattle farm was also analysed and obtained
as 129 ppb by sampling of 0.4 liters, while a measurement at the cattle shed was failed
due to overscale of the peak with the same amount of sample gas.

A retentivity of ammonia on the collection tube in time has not been studied
systematically, yet. A few measurements showed a recovery of almost all ammonia after
three hours at a room temperature (ca. 20 °C).

Fig. 3 Typical chromatogram of ammonia
by CLD-GC with 2 liters of sample
gas (120 ppb).
GC conditions are given in text. (CLD
range: 2 ppm, f.s., recorder: 20 mV)

Fig. 4 Relation between sample volume
and amounts collected and concen-
tration of ammonia at 20 °C.
(A) amount, (B) concentration

4. Conclusion

With alkali coated Porasil A preconcentration and CLD-GC analysis, atmospheric
ammonia can be analysed without any interferences from other pollutants. By sampling
5 liters of air sample, ammonia can be determined as low as 10 ppb in air which is
sensitive enough to determine ammonia in permissible levels by the offensive odor
control law regulated by Japanese Environmental Agency. Furthermore, a simultaneous
determination of ammonia and amines may also be possible and is now underway at our
institute.

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References


Keyword phrases
- chemiluminescent nitrogen detector-gas chromatography;
- determination of ammonia in air;
- ambient temperature adsorption;
- alkalized Forasil A;
- polymer beads.

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