DETERMINATION OF AMMONIA IN THE ATMOSPHERE BY GAS CHROMATOGRAPHY WITH A FLAME THERMIONIC DETECTOR

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Abstract - A gas chromatographic system equipped with a flame thermionic detector (FTD) has been developed for the determination of trace levels of ammonia in the atmosphere. This system is based on preconcentration with alkalized Porasil B and analysis with GC-FTD. Collection and thermal release from the adsorbent are almost quantitative. This method is applicable to determine ppb levels of atmospheric ammonia with a sampling volume of 2 l.

Key words ammonia, flame thermionic detector, gas chromatography

The determination of atmospheric ammonia by the commonly used indophenol procedure is highly reliable, but has limiting sensitivity. We reported the more sensitive procedure by solvent-extraction of indophenol with quaternary ammonium salts [1]. Recently, gas chromatography (GC) with a flame thermionic detector (FTD) has been made to have high sensitivity for organic nitrogen compounds. In spite of inorganic gas, ammonia was also detected by the way of mixing the other organic gas [2]. Here, a gas chromatographic system equipped with FTD has been developed for the determination of trace levels of ammonia in the atmosphere. The system is based on preconcentration with an adsorbent trap and analysis with GC-FTD.

EXPERIMENTAL

The system for GC analysis with the preconcentration is shown in Fig.1.

Apparatus As the basic equipment, gas chromatographic analysis was performed with a Shimadzu GC-14-A gas chromatograph equipped with a flame thermionic detector (FTD). Gas chromatographic separation was performed with a glass column packed with 15 % PEG 6000+5% KOH coated on Chromosorb 103 (0.3 cm i.d., 2.1 m in length) isothermally at 105 °C. Flow rate of helium carrier gas mixed with 1 % methane was 40 ml/min. The optimum flow rates of hydrogen and air for FTD were 3.5 ml/min and 150ml/min, respectively. The temperatures of injection port and detector were 260 °C and 260 °C, respectively.

The collection tube was a Pyrex glass (0.6 cm.i.d., 6.5 cm in length) packed with 0.7 g of 5 % KOH coated Porasil B (80/100 mesh by Waters Assoc., Inc). The tube was conditioned as the mentioned in the reference [3]. The thermal

desorption of the sample gas from the collection tube was performed by heating rapidly at 315 °C with a curie-point pyrolyzer (Japan Analytical Industry Co., JHP-3S) [4]. Two 4-ports Teflon valves were used for collecting air samples onto the collection tube and to transfer the collected components from the tube to GC column. The collection tube and the two valves were connected with Teflon seals and Teflon tubes (0.2 cm o.d.,) The drying tube of a Pyrex glass tube (0.6 cm i.d., 7 cm in length) was filled with KOH and the filling was secured with alkalized quartz wool. The connection of the valve and GC was heated to about 90 °C in order to prevent the adsorption of components in the inlet line. All valves and tubes were cleaned before use by heating them to about 90 °C and flushing with high purity nitrogen. Standard gas of ammonia with the concentration of ppb level was prepared by dynamic dilution of 92 ppm ammonia gas (Takachihokagaku Co.,Ltd.) with high purity nitrogen.

Fig. 1 Schematic diagram of the system of preconcentration/gas chromatography

1: Filter, 2: Drying tube, 3: Curie point pyrolyzer, 4: Collection tube, 5: Pump, 6: Flow meter, 7: Packed glass column, 8: FTD detector, 9: Carrier gas

TABLE 1 Analytical conditions of the system

Gas chromatography	
Gas chromatograph	Shimadzu GC 14-A
Column	Glass, 3 mm i.d. × 2.1 m long
Packing	15% PEG6000 + 1% KOH
Support	Cromosorb 103
Oven temp.	105°C
Carrier gas	He mixed with 1% CH ₄
Flow rate	40 ml/min
Detector	FTD
Hydrogen flow rate	3.5 ml/min
Air flow rate	150 ml/min
Injection temp.	260°C
Detector temp.	260°C
Range	10 × 2 ⁴
Preconcentration	
Collection tube	6 mm i.d. × 65 mm long
Adsorbent	Porasil B coated with 5% KOH
Temperature	ambient temperature
Sampling rate	200 ml/min
Sampling volume	2 l
Thermal desorption	
Pyrolyzer	Japan Analytical Industry Curie point pyrolyser JHP-2
Temperature	315 °C
Desorption time	4 min

Procedure The system is designed that is capable of preconcentrating the sample gas on an adsorbent tube, desorbing it to an analytical column, and detecting ammonia with FTD. Air sample was preconcentrated by passing it through the collection tube at a flow rate of 200 ml/min with a sampling volume of 2 l. When the sample gas transfer was completed, the collection tube was rapidly heated up to 315°C for 4 min by a curie-point pyrolyzer and the components were released by the carrier gas onto the analytical column. Prior to the next analysis, the collection tube was baked for 4 min at 315 °C with high purity nitrogen at a flow rate of 200 ml /min. Stability of the system was checked by standard gas at the beginning and the end of continuous measurements.

RESULTS AND DISCUSSION

Collection capacity The good adsorbent is required to have a large capacity at ambient temperature and to allow complete desorption by heating. The collection capacity of this system was measured by flowing standard gas through the collection tube. Standard gas containing 31 ng of ammonia and a known volume of high purity nitrogen to purge were sampled onto the collection tube at a flow rate of 200 ml/min at 34°C (ambient temperature); then the GC analysis was performed. From Fig. 2, the collection capacity was about 4 l at 34 °C (ambient temperature), and the collection efficiency was almost 100 % at a flow rate of 200 ml/min for 10 min-sampling time at ambient temperature, so a 10-min sampling time was chosen for use.

Recovery efficiency Recovery efficiencies for ammonia from the collection tube were measured by changing the thermal desorption time for 1 - 4 min. Standard gas containing 31 ng of ammonia was injected onto the collection tube with high purity nitrogen; then GC analysis was performed. The results were compared for different desorption time. The recovery efficiencies for ammonia were almost 100 % under the conditions of 1 - 4 min desorption time at 315°C, so a 4 min-desorption time was chosen for use.

Fig. 2 Collection efficiency for ammonia vs. sampling volume at a flow rate of 200 ml/min at 34°C.

Fig. 3 Gas chromatogram obtained for the atmosphere at Hiyoshi

Calibration curve, reproducibility and detection limit A calibration curve was made by injecting standard gas onto the collection tube with high purity nitrogen. The calibration curve was linear over the range of 0.5 - 100 ng. The reproducibility was less than 5 % in the range of 5 - 20 ppb levels. Detection limit with signal-to-noise of 3 was 3 pg, which allowed to determine 2 ppt of ammonia with a sampling volume of 2 l.

Measurement of atmospheric ammonia The proposed system was applied to the determination of ammonia at Hiyoshi in the urban atmosphere of Yokohama. Ammonia concentrations in air samples collected for 10 min-sampling time were measured as described (Table 2). The result obtained by indophenol method was 18 ppb for 3-hr period and found to be satisfactory. This system

is useful to determine atmospheric ammonia at a short time resolution.

TABLE 2 Measurements of atmospheric ammonia at Hiyoshi by the system

Sampling date	Concn. of NH ₃ (ppb)
24 July, 1991	
14:25 - 14:35	20.6
14:52 - 15:02	20.5
16:09 - 16:19	19.8
16:44 - 16:54	19.7
17:28 - 17:38	19.7

REFERENCES

1. N.Yamamoto, N. Kasahara and T.Shirai, *Talanta*, 11, 1063 (1990).
2. S. Yasui and K.Tanimoto, *Proceedings of 27 th Annual Meeting of The Japan Society for Analytical Chemistry*, p.395 (1978).
3. K.Kuwata, Y.Yamazaki and M.Uehori, *Bunseki kagaku*, 29, 170 (1980).
4. M.Nomiya, M.Kim and H.Inoue, *Proceedings of 39 th Annual Meeting of The Japan Society for Analytical Chemistry*, p.435 (1990).