



Application of copper sulfate pentahydrate as an ammonia removal reagent for the determination of trace impurities in ammonia by gas chromatography

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ABSTRACT

Rapid analysis of trace permanent gas impurities in high purity ammonia gas for the microelectronics industry is described, using a gas chromatograph equipped with a photoionization detector. Our system incorporates a reactive precolumn in combination with the analytical column to remove the ammonia matrix peak that otherwise would complicate the measurements due to baseline fluctuations and loss of analytes. The performance of 21 precolumn candidate materials was evaluated. Copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was shown to selectively react with ammonia at room temperature and atmospheric column pressures, without affecting the hydrogen, oxygen, nitrogen, methane or carbon monoxide peak areas. To prevent loss of trace carbon dioxide, an additional boron trioxide reactant layer was inserted above the copper sulfate pentahydrate bed in the reactive precolumn. Using the combined materials, calibration curves for carbon dioxide proved to be equivalent in both ammonia and helium matrix gases. These curves were equivalent in both matrix gases. The quantitative performance of the system was also evaluated. Peak repeatabilities, based on eight injections, were in the range of 4.1–8.2% relative standard deviation; and detection limits were 6.9 ppb for H_2 , 1.8 ppb for O_2 , 1.6 ppb for N_2 , 6.4 ppb for CH_4 , 13 ppb for CO , and 5.4 ppb for CO_2 .

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1. Introduction

Compound semiconductor technology attracting attention worldwide is applied to various products such as a semiconductor laser, light emitting diodes (LEDs), and high-speed electronic device. For high efficiency LEDs and device performance enhancement, it is necessary to reduce the mixture of impurities that act as non-radiative recombination centers. Purity control of ammonia used as a raw material in these processes is thus very important. High purity ammonia (NH_3) is used in the production of electronic devices, especially gallium nitride (GaN) LEDs [1]. Of particular interest is the effect of impurities present in the ammonia process gas on the brightness of LEDs. Research on the influence that impurities in ammonia have on the epitaxial growth of GaN compound semiconductor has revealed moisture in ammonia to be one factor causing a loss of brightness fall of LEDs [2,3]. The moisture in ammonia is readily captured by the InGaN quantum wells emission layer, so increased moisture levels of concentration in ammonia cause a

loss of electroluminescence intensity. Oxygen and carbon dioxide have a similar influence on LEDs electroluminescence intensity.

The demand for high purity ammonia by the electronics industry is thus steadily increasing, placing manufacturers under growing pressure.

Cavity ringdown laser analyzers (CRDSs) are used for measuring trace moisture in ammonia, and gas chromatography (GC) is the commonest tool for detecting and analyzing impurities in ammonia other than moisture [4]. Other techniques such as Fourier transform infrared spectroscopy (FT-IR) and oxygen analyzers require large volumes of sample gases to be analyzed, and are able to measure only a few components [5,6]. They are also easily influenced by the presence of high concentrations of contaminants such as the moisture contained in ammonia. This makes gas chromatography probably the most powerful and versatile technique available to the modern analyst. The authors studied the GC system, in which a precolumn is used to pre-treat the sample. As a result, we have demonstrated the analysis of various impurities in pure gases such as oxygen, hydrogen and nitrogen using catalyst or hydrogen storage alloys [7–9].

In gas chromatography, 'pre-cut' or 'heart-cut' methods are commonly used. These techniques can separate the impurities from the main matrix (in this case, ammonia) by using multiple separation columns and different carrier gases before final analysis in the analytical column and detector [10]. However, these conventional

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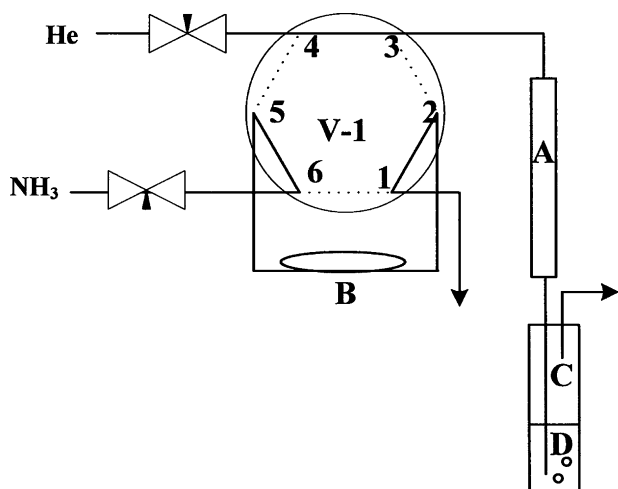


Fig. 1. Experimental flow for ammonia removal. A: ammonia removal reagent in 10 cm × 5 mm i.d. glass tubing, B: 1.5 mL sample loop for ammonia gas, C: microimpinger, D: 20 mL water added in phenolphthalein ethanol solution.

methods have several drawbacks. One is the complexity of the gas flow system setup. The analysis is influenced by the pressure balance of the carrier gas and redirection of its flow when using a highly sensitive detector such as a photoionization detector (PID) or pulsed discharge helium ionization detector (PDHID) [11–14]. Another problem is desorption and adsorption of the impurities by the columns when they interact with the ammonia. This desorption can be seen in the analysis of carbon dioxide in ammonia using the conventional method. It has been confirmed that hundreds of ppb of carbon dioxide originate in the column filler (Paula polymer system). This impedes confirmation of the blank value for carbon dioxide, which is always necessary for measurement, causing a large measurement error. In the case of adsorption, ammonia readily binds to a column but desorbs much less readily, causing deterioration of the filler in the column. In addition, the oxygen in ammonia is readily adsorbed by the deteriorated column, which prevents the detection of very low amounts of oxygen. In addition, although heating of the ammonia pre-cut column is effective in releasing ammonia from column filler, it is necessary in each analysis to wait several minutes for the column temperature to stabilize.

These problems prompted us to undertake the present study. We describe a new and simple GC analytical method for determining trace impurities in ammonia, using a precolumn that removes the ammonia matrix without affecting trace impurities such as oxygen, hydrogen or nitrogen.

2. Experimental

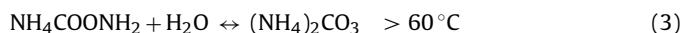
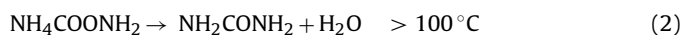
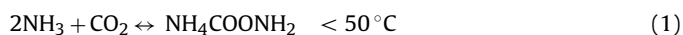
2.1. Apparatus and materials

First, reagents which chemically react with ammonia were chosen, and the ammonia removal test was performed. The ammonia removal test unit is illustrated in Fig. 1. To monitor its ammonia removal efficacy, a microimpinger was installed downstream of the ammonia removal column. The microimpinger was filled with water to which a few drops of phenolphthalein ethanol solution were added as an indicator. The transition interval of the phenolphthalein ethanol solution is pH 8.3 (colorless) to pH 10.0 (red). If ammonia is being removed, the solution should stay colorless. If it is not removed, the solution will turn red. For a removal test of NH₃, reagents that react chemically with NH₃ or that appear to adsorb NH₃ physically were selected for the NH₃ removal. Only those reagents with the ability

to remove ammonia sufficiently were used for the GC experiments.

A schematic diagram of the experimental apparatus is shown in Fig. 2. A gas chromatograph with a PID (Hitachi, GC-263-50, Tokyo, Japan) was used in this experiment. This system, including the gas sampler, can be programmed with an integrator (Shimadzu, C-R7A, Kyoto, Japan) through an interface, and is able to analyze and automatically report its results. The columns, operating conditions of the GC and the detectors used in this experiment are listed in Table 1. Helium with a purity exceeding 99.9999% was obtained as the carrier and discharge gas by purification (Helium gas super purifier, Taiyo Nippon Sanso) and the use of a liquid nitrogen-cooled stainless steel column filled with molecular sieve.

To remove ammonia as the major component from the sample gas, a precolumn was installed between the gas sampling valve and the analytical column. Reagents that react chemically with NH₃ or that appeared to physically adsorb NH₃ were selected for the NH₃ adsorption. The reagent for the precolumn was selected from several reagents that were evaluated as to whether they could absorb all the ammonia in the sample gas but not the trace impurities in the ammonia using the examination in Fig. 1. The precolumn was a 10 cm × 5 mm i.d. glass tube filled with an ammonia removal reagent. In a comparative experiment, a GC-PDHID (GC: GL Science, GC-4000 DSF D41, Tokyo, Japan; PDHID: Valco Instruments, D-4-1, Houston, TX, USA) was employed using a conventional method based on valve changes. A schematic diagram of the comparative apparatus is shown in Fig. 3. To separate the impurities from the ammonia, pre-cut and back-flush processes were used. A series of experiments designed to establish the optimum operating conditions for the precolumn and GC were conducted using reference gas mixtures comprising 1 ppm each of H₂, O₂ and N₂ in helium and 1 ppm each of CH₄, CO and CO₂ in helium. Mass flow controllers (MFC; HORIBA STEC, SEC-4400MO, Japan) were used to prepare the low-concentration samples in ammonia gas from their reference gases and high purity ammonia. All ammonia lines were heated at 70 °C. In the analysis of impurities in ammonia, the supply condition of ammonia was studied [4]. Because ammonia reacts with carbon dioxide and moisture as follows if these gases exist in ammonia, a precise temperature is needed to stabilize the supply of ammonia.



2.2. The precolumn

The ammonia removal reagents used in the experiments were mainly made by Kanto Chemical Co., Inc. (Tokyo, Japan) and Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and were of analytical or correspondingly high grade. Only reagents from which the removal of ammonia had been confirmed were used for the GC experiments, since some reagents contained moisture or hydrates. First, valve V-1 was manually switched to the preparation position, as shown in Fig. 2. High purity helium gas was passed through the precolumn at approximately 30 mL/min to purge any moisture remaining in the reagent. The precolumn was at normal room temperature. After the precolumn were purged of moisture for one day, valve V-1 was switched back to the analytical position. The appearance of the precolumn packed with CuSO₄·5H₂O is shown in Fig. 4. The preparation precolumn was connected in series with the GC.

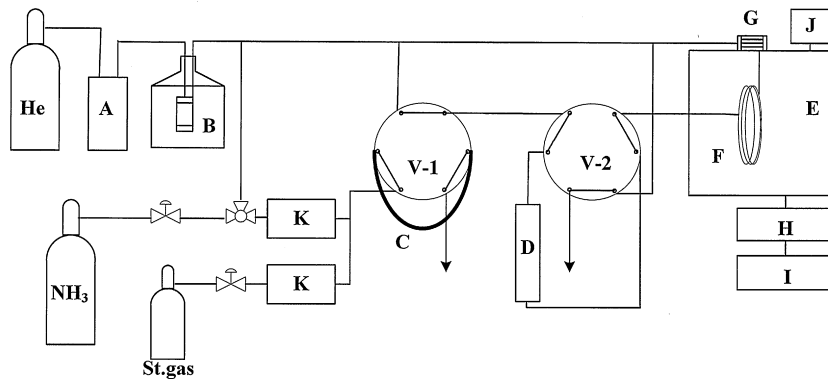


Fig. 2. Schematic diagram of apparatus for determining impurities in ammonia. A: He purification, B: liquid nitrogen-cooled stainless steel column with molecular sieve, C: sample loop, D: precolumn, E: GC oven, F: analytical column, G: PID, H: interface, I: integrator, J: pre-amplifier, K: mass flow controller, V-1: air-actuated six-port rotary valve, V-2: manually operated six-port rotary valve.

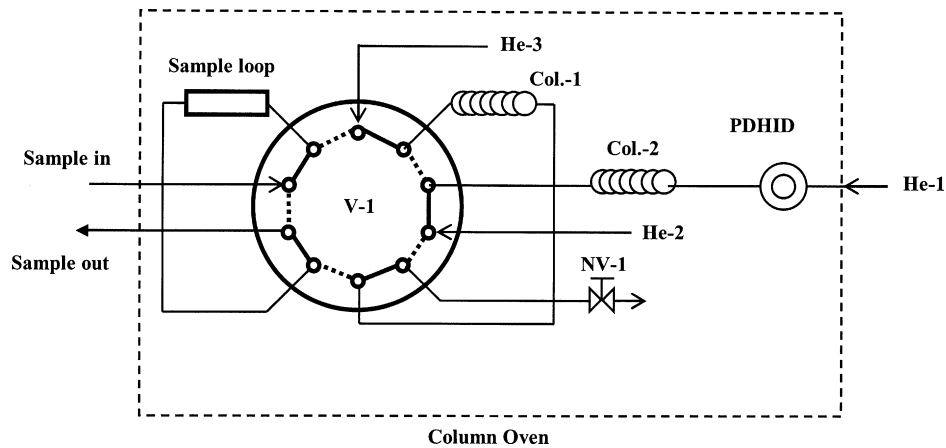


Fig. 3. Schematic diagram of apparatus for determination of impurities in ammonia using the conventional method. He-1: PDHID discharge He, He-2: carrier gas, He-3: carrier gas (main), Col-1: column for ammonia pre-cut, Col-2: analytical column, NV-1: needle valve, V-1: air-actuated ten-port rotary valve.

Table 1
Operating conditions of GC-PID and GC-PDHID.

(A) GC-PID		(B) GC-PDHID	
<i>GC for H₂, O₂, N₂, CH₄, CO</i>		<i>GC for H₂, O₂, N₂, CH₄, CO</i>	
Analytical column	MS-5A, 60/80 mesh, 3 m × 3 mm i.d. stainless steel tube	Column 1	Chemipak NOT, 1 m × 1/8 in. i.d. stainless steel tube
Column temperature	50 °C	Column 2	MS-13X, 60/80 mesh, 2 m × 1/8 in. i.d. stainless steel tube
Carrier gas	He, 40 mL/min	Column temperature	70 °C
Sample loop	1.5 mL	Carrier gas	He, 20 mL/min
Precolumn	10 cm × 5 mm i.d.	Sample loop	3.0 mL
Precolumn temp.	25 °C (room temperature)	Back-flush column temp.	120 °C
<i>GC for CO₂, CH₄</i>		<i>GC for CO₂, CH₄</i>	
Analytical column	Active carbon, 30/80 mesh, 2 m × 3 mm i.d. stainless steel tube	Analytical column	Hayesep T, 80/100 mesh, 2 m × 1/8 in. i.d. stainless steel tube
Column temperature	70 °C	Column 2	2 m × 1/16 in. i.d. stainless steel tube
Carrier gas	He, 33 mL/min	Column temperature	70 °C
Sample loop	1.5 mL	Carrier gas	He, 20 mL/min
Precolumn	10 cm × 5 mm i.d.	Sample loop	3.0 mL
Precolumn temp.	25 °C (room temperature)	Back-flush column temp.	120 °C
<i>PID</i>		<i>PDHID</i>	
Discharge gas	He, 33 mL/min	Discharge gas	He, 25 mL/min
PID temperature	120 °C	PDHID temperature	140 °C
Applied potential	950 V	PDHID range	10
Discharge current	200 μA	Discharge current	<2 nA

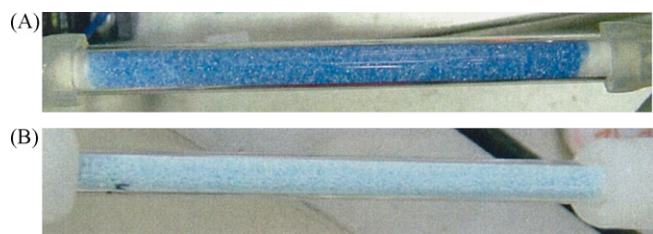


Fig. 4. Appearance of precolumn packed with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. 10 cm \times 5 mm i.d. glass tubing, (A) unused and (B) He-purged.

Table 2
Ammonia removal reagents for H_2 , O_2 and N_2 in ammonia.

Reagent	NH_3 remover	H_2	O_2 determination	N_2
NaBr	–	N/D	N/D	N/D
CaCl_2	+	–	–	–
$\text{Cu}(\text{OH})_2$	+	+	–	–
$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	–	N/D	N/D	N/D
CuSO_4	+	–	–	–
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	+	+	+	+
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	+	–	–	–
ZnO	–	N/D	N/D	N/D

–: Impossible, +: possible, N/D: there is no data of GC.

3. Results and discussion

3.1. Selection of the ammonia removal reagent for oxygen

Some of the reagents were examined for ammonia removal and effect on chromatography of impurity components. The measurement of hydrogen, oxygen, and nitrogen in ammonia was attempted using GC. The results are shown in Table 2.

Copper sulfate pentahydrate was the only reagent in which none of the components, including oxygen, were adsorbed, although adsorption or desorption of oxygen occurred in most of the other reagents. In some reagents, the oxygen and nitrogen peak area appeared to decrease, whereas in others, it appeared to increase. The measurement of methane and carbon monoxide in ammonia was also possible using copper sulfate pentahydrate.

Fig. 5 shows a typical chromatogram obtained by our method and obtained using the conventional GC-PDHID (pre-cut) method.

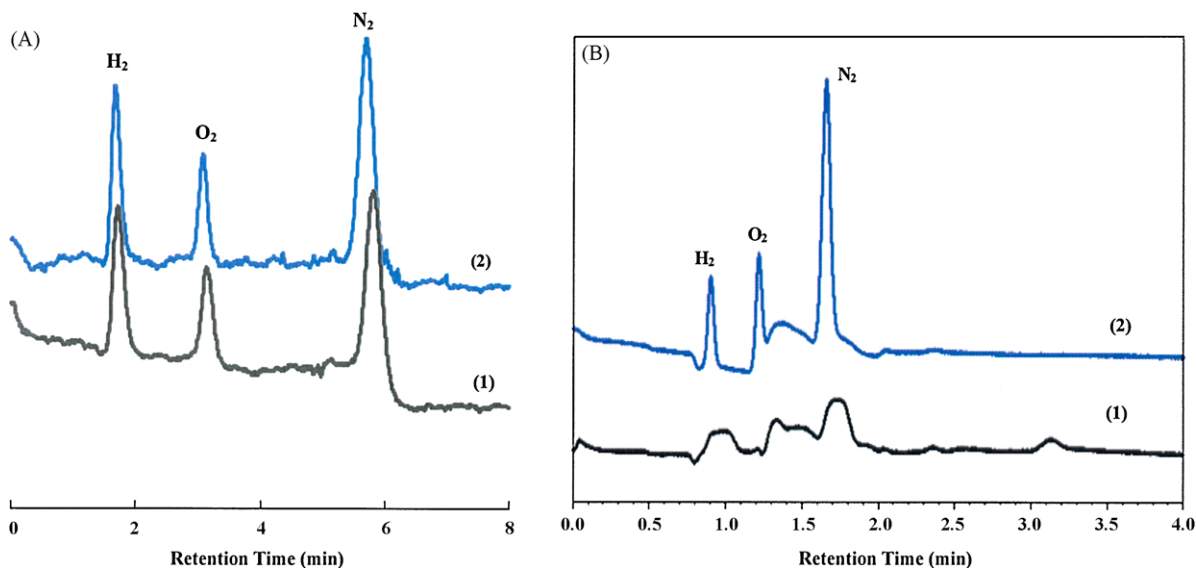
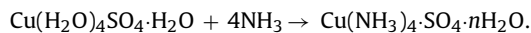


Fig. 5. Chromatographic profiles obtained by the present (A) and the conventional (B) method. The GC-PID and precolumn operating conditions are given in the text. (1): He-based, (2): NH_3 -based, (A): H_2 (152 ppb), O_2 (28 ppb), N_2 (51 ppb), (B): H_2 (36 ppb), O_2 (38 ppb), N_2 (42 ppb).

Since the conventional method required a valve change operation during the analysis, a change in the baseline was seen near the oxygen and the nitrogen peaks of the chromatogram. The peak shapes of hydrogen, oxygen and nitrogen were different between ammonia and in helium, and this influenced quantifiability. The chromatogram demonstrates the difficulty of analyzing trace impurities in ammonia using the conventional method. On the other hand, our method provided a suitable baseline and separation without any obstructions, since the ammonia was completely removed from the sample gas. The peak shape in ammonia corresponded to that in helium.

The presumed reaction of ammonia and copper sulfate pentahydrate is shown below.



Unused copper sulfate pentahydrate, which is dark blue, turned light blue on removal of moisture by helium purge, and copper sulfate pentahydrate that reacted with ammonia changed from light blue to purple-blue. These phenomena indicate the lifetime of the precolumn and show when it needs to be replaced.

There is another benefit of our method. The adsorption of oxygen was observed in some of the reagents shown in Table 2. A reagent such as $\text{Cu}(\text{OH})_2$ which is known to absorb oxygen, allows selective determination of argon in sample gases containing a mixture of both oxygen and argon. In a separation column such as an MS-5A, because neither oxygen nor argon is easily separated, any argon in the ammonia can be selectively measured using this method.

Measurement of argon in ammonia is also possible by combining an oxygen removal catalyst with an ammonia removal column.

3.2. Selection of an ammonia removal reagent for carbon dioxide analysis

As carbon dioxide was adsorbed with an increasing number of sample injections in the precolumn filled with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, several of the reagents listed in Table 3 were examined for ammonia removal in tandemly arranged columns, as shown in Fig. 6. An attempt was made to measure carbon dioxide and methane levels in ammonia using the precolumn and GC. The results of the removal in the reagents are also listed in Table 3. The use of boron trioxide (B_2O_3) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ enabled determination of carbon dioxide in ammonia without any adsorption of carbon dioxide. The

Table 3
Ammonia removal reagents for CO₂ in ammonia.

First reagent	Second reagent	CO ₂ detection
CuSO ₄ ·5H ₂ O		+
CuSO ₄	A*	–
ZnSO ₄ ·7H ₂ O	A*	+
CaCl ₂	A*	–
Cu(OH) ₂		–
NaBr	A*	–
FeSO ₄ ·7H ₂ O	A*	+
FeSO ₄ ·2H ₂ O	A*	–
NaCl	A*	–
AlPO ₄	A*	–
MnO ₂	A*	–
Ni(NO ₃) ₂ ·6H ₂ O	A*	–
C ₆ H ₈ O ₆	A*	–
Aluminium powder	A*	–
(COOH) ₂ ·2H ₂ O	A*	–
B ₂ O ₃	A*	++
KBr	A*	+
H ₃ BO ₃	A*	+
Al ₂ (SO ₄) ₃	A*	+

A*: CuSO₄·5H₂O, –: increased or not detected; +: gradual adsorption, ++: detected.



Fig. 6. Ammonia removal column (precolumn) for CO₂ in NH₃. A: glass wool, B: first reagent, C: second reagent.

unused B₂O₃ retained a small amount of carbon dioxide. To prepare this precolumn, carbon dioxide, originally adhered to B₂O₃, is completely liberated by several injections of ammonia gas. Typical chromatograms obtained using this method are shown in Fig. 7. During the analysis of carbon dioxide in ammonia, the ammonia

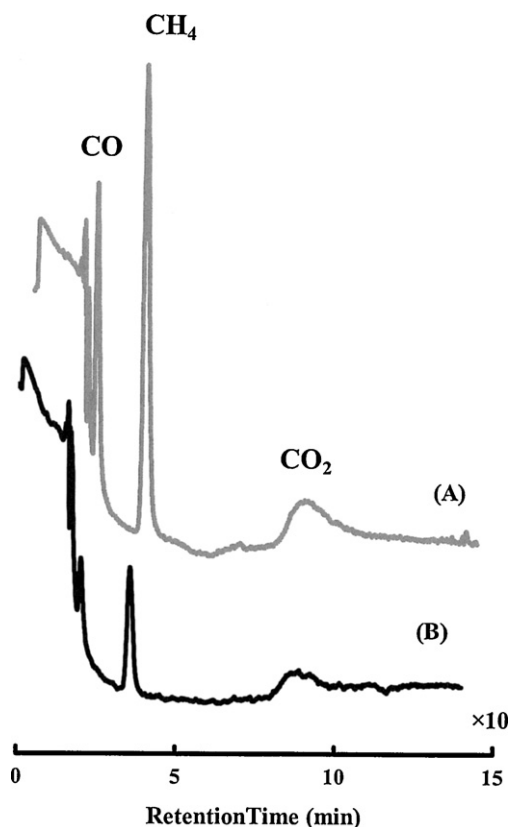


Fig. 7. Typical chromatograms of mixed gases obtained using our method. (A) 100 ppb CO, CH₄, CO₂ in NH₃ and (B) 30 ppb CO, CH₄, CO₂ in NH₃.

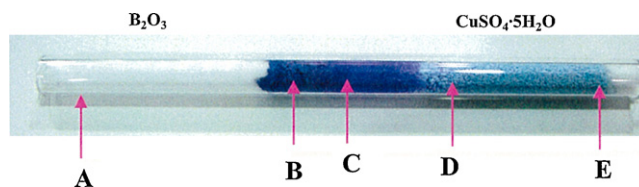


Fig. 8. Appearance of used ammonia removal column for CO₂ in NH₃. (A–E) Sample position for X-rays fluorescence testing.

was completely removed and only the residual ingredients were detected by GC-PID.

3.3. Reaction mechanism

Ammonia reacts with not only CuSO₄·5H₂O but also with B₂O₃. Ammonia adsorption with B₂O₃ is based on following reactions.



To confirm the mechanism of ammonia removal, a wavelength dispersive X-ray fluorescence spectrometer (WD-XRF) (Rigaku, ZSX 100e, Tokyo, Japan) was used to investigate the reagents CuSO₄·5H₂O and B₂O₃. The measurement results of X-ray fluorescence spectra are shown in Fig. 8 and Table 4. Nitrogen (N) in the reagents used increased in both B₂O₃ and CuSO₄·5H₂O by comparison with N in unused reagents. The amount of N adhering to CuSO₄·5H₂O is greater than in B₂O₃. It can be presumed that the cause of exclusion of ammonia is chiefly CuSO₄·5H₂O rather than B₂O₃. Ammonia was in fact detected by several sample injections with only B₂O₃.

However, B₂O₃ is essential for the precolumn. When the pre-column consisted of CuSO₄·5H₂O only, CuSO₄·5H₂O removed both carbon dioxide and ammonia from ammonia gas containing carbon dioxide. On the other hand, CuSO₄·5H₂O did not remove carbon dioxide from helium gas containing carbon dioxide, demonstrating that B₂O₃ or its reaction products (BN or (NH₄)₂O·2B₂O₃·4H₂O) separated carbon dioxide and ammonia.

As for sensitivity to carbon dioxide, a constant value was obtained in both ammonia and helium. B₂O₃ and CuSO₄·5H₂O were used to determine carbon dioxide in the following separate experiments on ammonia removal reagents.

Since the concentration of carbon dioxide measured in this experiment was low, no heating of the stainless steel tubing for ammonia sample gas lines was performed. However, heating of stainless steel tubing is required if the measurement of high concentrations of carbon dioxide in ammonia is expected.

Table 4
Fluorescence X-rays measurement results (WD-XRF).

Sample (Fig. 8)	Analysis value (mass %)					
	B	N	O	S	Cu	Others ^a
A	17.6	1.87	79.1			1.43
B		5.31	30	15.8	48.7	0.19
C		4.15	25.4	18.3	52	0.15
D		1.34	29.3	17.8	51.5	0.06
E		0	33	16.8	49.5	0.7
B ₂ O ₃ ^b	16.4	1.34	78.8			3.46
CuSO ₄ ^b		0	31.1	17.9	50.3	0.7

^a Minor component of 0.1% or less (Si, P, S, Fe, etc.).

^b Unused, purge ended in.

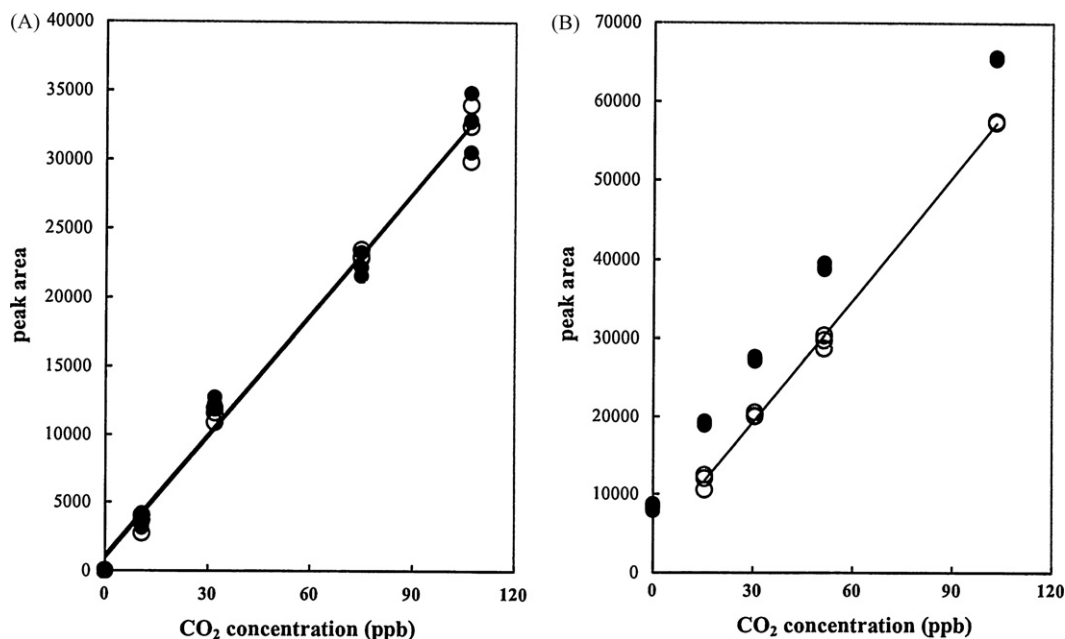


Fig. 9. Calibration curves for CO₂ in He and NH₃ obtained using the present (A) and conventional (B) methods. (●) CO₂/NH₃, (○) CO₂/He, (A) GC-PID and precolumn operating conditions are given in the text.

3.4. Quantitative features

For all components, agreement of the calibration line prepared by helium-based and ammonia-based standard gases was provided using our method. However, a stable baseline was not seen at low concentrations of carbon dioxide with the conventional method. Fig. 9 shows a calibration line using our method and the conventional method for comparison. Ammonia and carbon dioxide were separated in the pre-cut column filled with porous polymers using the conventional method, but carbon dioxide was desorbed from porous polymers on reaction with ammonia. Both carbon dioxide

in the sample gas and carbon dioxide which was desorbed from the separation column were detected together, making the measurement of low-concentration carbon dioxide inaccurate using the conventional method. On the other hand, in our method, the calibration curve of low-concentration carbon dioxide was linear, so no background correction of the analytical value was necessary. This method is anticipated to produce more accurate carbon dioxide measurements than can be obtained by the conventional method.

The purity of high grade ammonia supplied from cylinders is more than 99.999%, however, for the electronics industry, new purity control is necessary for the bulk supply of ammonia. The

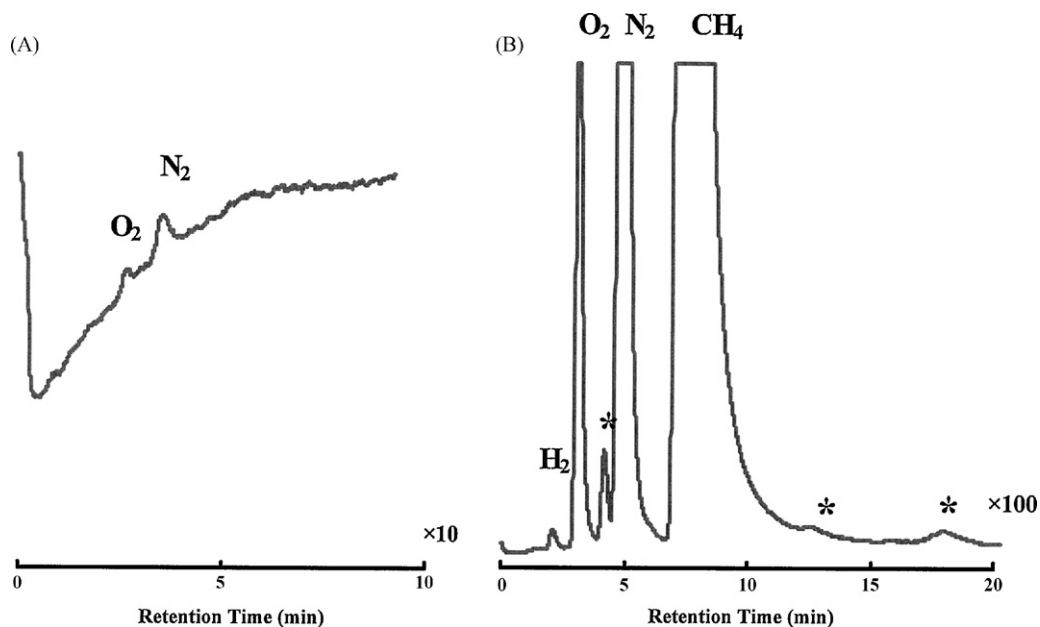
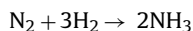


Fig. 10. Typical chromatograms from commercially available gases stored in cylinders. (A) 99.999% ammonia, O₂: 4 ppb, N₂: 6 ppb and (B) 99.9% crude ammonia, H₂: 390 ppb, O₂: 4.4 ppm, N₂: 13.9 ppm, CH₄: 97 ppm; *unknown impurities. (A) Operating conditions are given in Table 1 and (B) PID applied potential 750 V, ammonia is diluted sevenfold with helium.

most commonly used synthesis of ammonia is the Haber–Bosch process that builds ammonia directly from hydrogen and nitrogen.



N_2 is supplied from the atmosphere, and H_2 is supplied by electrolysis of water or the oxidation of coal or naphtha or by steam-reforming natural gas. The impurities detected in ammonia are traceable to these materials. Therefore, atmospheric components from the suppliers of N_2 , and water and hydrocarbons and sulfides from the suppliers of H_2 are likely to be included in ammonia as impurities.

Typical gas chromatograms for two commercially available cylinder ammonia gases with different purity levels are shown in Fig. 10. It is interesting that the levels of various impurities in the samples showed considerable variation. Several unknown impurities, which were not detected using the conventional method, could now be detected in crude ammonia. It is important to be aware not only of H_2 , O_2 , N_2 , CH_4 , CO and CO_2 but also of the presence of other contaminants.

3.5. Repeatability and detection limits

The calibration curves were linear up to 300 ppb under the proposed conditions. The cycle of continuation analysis required about 15 min for the conventional method. In the conventional method, all the ammonia must be purged from the column for pre-cut at each analysis to prevent interference with later injections. A thermal program is needed for the purge and therefore stabilization time is needed before the subsequent analysis. On the other hand, complete purging of ammonia was not needed in our method. Fast continuous analysis was possible without time restrictions, and the analysis cycle for high purity ammonia required only 6 min. The quantitative performance of the system was evaluated using repeated injections of 1.5 mL of ammonia gas containing H_2 (152 ppb), O_2 (28 ppb), N_2 (51 ppb), CH_4 (50 ppb), CO (71 ppb), and CO_2 (75 ppb). Repeatability (relative standard deviation, $n=8$) was 6.0%, 7.0%, 4.3%, 4.1%, 5.1% and 8.2% for H_2 , O_2 , N_2 , CH_4 , CO and CO_2 , respectively. The minimum detectable concentrations ($S/N=3$) were 6.9, 1.8, 1.6, 6.4, 13 and 5.4 ppb for H_2 , O_2 , N_2 , CH_4 , CO and CO_2 , respectively, under the present operating conditions. The precolumn proved usable for measurements more than 70 times without regeneration. The precolumn does not need to be regenerated but needs to be replaced after a breakthrough.

Replacement is easier than regeneration and much shorter times is required for adjustment, making it more effective.

4. Conclusion

The results of the experiments clearly demonstrate the effectiveness and usefulness of our method. Improved gas chromatographic determination of trace impurities in ammonia, using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as the ammonia removal reagent, provides accurate and rapid measurement of impurities without the interference of the ammonia matrix that is seen with the conventional method. Notably, the problem of setting the blank before determining carbon dioxide in ammonia is solved using our method. This method can be used in conjunction with a gas chromatograph attached to an MS (mass spectrometer) as well as a PID.

It should be noted that the present method simply involves pre-processing of the samples and does not affect the GC separation column. The combination of other detectors and analytical columns enables measurement of various components in ammonia.

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