



# Towards the interaction between calcium carbide and water during gas-chromatographic determination of trace moisture in ultra-high purity ammonia

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## ABSTRACT

The current study focuses on the processes involved during the flow conversion of water into acetylene in a calcium carbide reaction cell for the trace moisture analysis of ammonia by reaction gas chromatography. The factors negatively affecting the reproducibility and the accuracy of the measurements are suggested and discussed. The intramolecular reaction of the HO—Ca—C≡CH intermediate was found to be a side reaction producing background acetylene during the contact of wet ammonia gas with calcium carbide. The presence of the HO—Ca—C≡CH intermediate among the reaction products is confirmed by an FTIR spectral study of calcium carbide powder exposed to wet gas. The side reaction kinetics is evaluated experimentally and its influence on the results of the gas chromatographic measurements is discussed in relation to the determination of the optimal operating parameters for ammonia analysis. The reaction gas chromatography method for the trace moisture measurements in an ammonia matrix was experimentally compared to an FTIR long-path length gas cell technique to evaluate the accuracy limitations and the resource intensity.

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## 1. Introduction

Moisture determination at trace levels in electronic grade ammonia is one of the most important and at the same time most difficult problems of trace analysis [1–6]. High purity ammonia (>99.9995%) is used as the nitrogen source for the AlGaIn/GaN epilayers in the production of light-emitting diodes (LEDs), semiconductor lasers, and high electron mobility transistors (HEMTs) [7–9]. Trace moisture strongly affects the performance of grown layers during the chemical vapour deposition process (CVD) and causes reduction of the process yield.

While standard methods of water content evaluation (dew point, Karl-Fisher titration, conductivity measurement, electro-

static capacitance, direct gas chromatography) are not compatible with ammonia due to its physical and chemical properties, the methods based on Fourier transform infrared spectroscopy (FTIR), tunable laser spectroscopy (TDLAS), and reactive gas chromatography (GC) are considered for the quantitative determination of trace moisture in ammonia [1–6].

FTIR spectroscopy has been reported to provide rapid, reliable and sensitive determination of water traces in high-purity ammonia with detection limits as low as 10 parts per billion (ppb) [5]. However, a number of specific requirements to the hardware design and operating parameters should be taken into account for the success of the analysis. A long-path length cell is employed to provide high sensitivity, which require increased equilibration times due to the relatively large volume and surface area of the cell. This along with the requirement for a high sample flow rate (several liters per minute) and increased sampling time (a large number of IR scans is essential to achieve a decrease in spectral noise) results in the wastage of considerable amounts of valuable analyte. Typically for the low ppbv detection of water vapour, each infrared data point is obtained from the addition of anywhere between 200 and 400

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spectral scans. Large sample flow rates may also cause significant problems with repeatability and stability of the gas-phase sampling from the cylinder due to the disturbance of the vapour-liquid equilibrium in the ammonia [5]. The hardware design also requires constant purging of the spectrometer with a relatively large flow of purified dry inert gas (20 slpm) to ensure the stability of the background. As a consequence, the resource intensity of this analytical technique and some specific aspects of the procedure make it less suitable for ammonia quality control and real-time monitoring of the purification process.

Gas chromatography has been proven to be the most versatile technique for the purity control of hydride and corrosive gases and gained extensive application for measuring trace moisture, permanent gases, carbon dioxide, and light hydrocarbons in ultra-pure gases for the semiconductor industry [10–22]. From this point of view, gas chromatography with the pre-column conversion of water to acetylene in a chemical reaction cell with calcium carbide may serve as a viable alternative to FTIR- and laser-based techniques as it offers low-cost and efficient quantification of formed acetylene consuming very small amounts of sample [23–26]. The applicability of this approach for the determination of trace moisture in ammonia has been considered by Monroe [3]. The potential sensitivity of the method for water has been reported to be in the range of 30–50 ppb for acetylene detection by gas chromatography with a discharge ionization detector (GC/DID) [3]. However, it has been found that the reaction kinetics of water with  $\text{CaC}_2$  in an ammonia matrix appears to be different than that in helium giving significant variation in the results. The conclusion was drawn that increased residence time of the sample favours a more complete conversion of the water to acetylene in the presence of ammonia. Purging of the reactor with dry helium under 200 °C between the measurements was recommended to eliminate the influence of side reactions. Nevertheless, the approach of incubating the sample in the reaction cell together with regular conditioning of the reactor is not appropriate since it may adversely affect the representativeness of the samples by disturbing the dynamic equilibrium between the water adsorbed on the surface of the reactor and the water contained in the sample which could only be reached under constant isothermal flow conditions.

The current study contributes to the understanding of the processes involved during the flow conversion of water into acetylene in a calcium carbide reaction cell for trace moisture analysis in ammonia. This publication is focused on interactions between the components involved in the reaction process ( $\text{CaC}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{CaO}$ ,  $\text{C}_2\text{H}_2$ ) employing an FTIR spectral study of calcium carbide exposed to wet gas. The experimental evaluation of the side reaction kinetics and its influence on the results of the gas chromatographic measurements will be discussed with respect to the determination of the optimal operating parameters for ammonia analysis. The experimental comparison of the reaction GC method with the FTIR long-path length gas cell technique will be made and considerations for the feasibility of the method for qualification of high purity ammonia will be given.

## 2. Material and methods

### 2.1. Gas chromatography setup

The reaction gas chromatography system has been developed based on a Chromos GC-1000 gas chromatograph (Chromos Ltd, Russia) equipped with a flame ionization detector (FID). A schematic diagram of the system is presented in Fig. 1. A detailed description of the system components and optimized operating conditions are given in Table 1.

**Table 1**

Operating conditions of the reaction GC-FID system for determination of trace moisture in ammonia.

Component of the GC system	Characteristics
Detector	FID, 150 °C
Separation column (SC)	15% PEG-600 on PTFE, 40 °C 60/80 mesh 3 m × 3 mm i.d. stainless steel tube
Reaction cell (RC)	Calcium carbide, 40 °C 40/60 mesh 0.32 m × 10 mm i.d. stainless steel tube
Sample loop (SL)	1.5 ml, 40 °C
Carrier gas (CG)	$\text{N}_2$ 99.9999%, 30 ml min <sup>-1</sup>

The GC system incorporates the reaction cell (RC), where the sample is treated with calcium carbide to form acetylene, followed by an electrically actuated 6-port sampling valve (SV) and the analytical column filled with 15% PEG-600/PTFE to separate the acetylene from the ammonia matrix. Nitrogen of 99.9999% purity (NII KM Ltd, Russia) is used as a carrier gas (CG). The separation is isothermal with both the reaction cell and the analytical column mounted in the same oven. The temperature-controlled sampling valve (SV) and bypass valve (BV) are maintained at 40 °C. The flame ionization detector (FID) allows for the detection of the formed acetylene down to a 10<sup>-7</sup> vol. level. Chromatographic data collection and processing is performed with the Chromos<sup>®</sup> software (ver. 2.22.27) supplied with the gas chromatograph.

Calcium carbide (10 mm pieces, ~80% technical grade, Sigma-Aldrich Chemie GmbH, Germany) was grounded under a dry argon atmosphere in a planetary ball mill PM-100 (Retsch Technology, Germany) using a pressure-tight jar with tungsten carbide balls, sieved with a 40/60 mesh sieve and then filled into a piece of stainless steel tubing packed with glass wool at both ends. The void volume of the reactor was 16 ml out of 24.6 ml total cell volume giving a void fraction equal to 0.65.

### 2.2. FTIR-spectrometry setup

#### 2.2.1. Gas-cell moisture measurements

A Shimadzu IRAffinity-1 FTIR spectrophotometer (Shimadzu Corp., Japan) equipped with high-sensitivity thermally-stabilized DLATGS detector and Ge-coated KBr optics was used for moisture measurements. The housings of the interferometer and source/laser compartment, as well as the sample and detector compartments were supplied with additional internal purging lines for dry nitrogen flushing (<0.01 ppm moisture, 2 slpm) to ensure low and stable background levels of moisture in the beam path.

A temperature-controlled 20 m path length gas cell with gold-coated mirrors and ZnSe windows (PIKE Technologies, USA) was used for gas sampling under ambient pressure. The glass cell body was equipped with 2 stainless steel valves for inlet and outlet as well as a safety valve, and a pressure sensor. The gas distribution system of the cell was connected to a vacuum station HI-CUBE-80 Eco (Pfeifer Vacuum Technology AG, Germany) for evacuation and flushing of the cell and gas lines under heating.

The gas inlet temperature was maintained at the same level as the cell wall temperature (50 °C). Spectra were recorded at a resolution of 4 cm<sup>-1</sup> using Happ-Genzel apodization. For each run a minimum of 200 scans were averaged within the 4000–3600 cm<sup>-1</sup> range. Instrument control and data processing were done utilizing Shimadzu IRsolution<sup>®</sup> software, version 1.5, supplied by Shimadzu (Shimadzu Corp., Japan).

#### 2.2.2. Calcium carbide IR study

Solid calcium carbide samples were characterised by infrared spectroscopy using the FTIR spectrophotometer IRAffinity-1 (Shi-

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