Gas Chromatographic Method for in Situ Ammonia Quantification at Parts per Billion Levels

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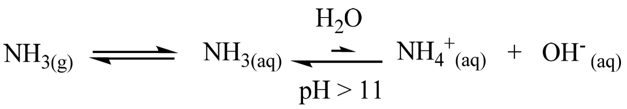
Ammonia Commodity and Energy Carrier. About a century ago, one of the main challenges chemists had to tackle was the conversion of atmospheric nitrogen to ammonia. This process became an urgent necessity to meet the increasingly higher demand of nitrogen-containing fertilizers to ultimately sustain food production for the exponentially growing world population. The Haber−Bosch process, operating ever since, brings nitrogen fixation among the top large-scale catalytic processes operating on the planet, next to photosynthesis and respiration.[1] Other than being a unique chemical intermediate in fertilizer synthesis, ammonia is also a promising candidate as a next-generation sustainable carbon-free energy carrier.[2−5] Although Haber−Bosch has played a crucial role in societal development as we know it today, it also comes with severe environmental consequences. In fact, this process alone accounts for about 1.5% of the global energy demand, currently entirely derived from fossil fuels, and as such, it is responsible for over 300 million metric tons of CO_2 emissions.[6,7] Thus, ramping-up ammonia production with current state-of-the-art Haber−Bosch technology to meet both fertilizer and fuel production would have profound unsustainable impact on the environment.[8] Recently, novel promising and sustainable electrochemical approaches for nitrogen reduction are starting to populate the literature, yet more fundamental research and improvements are essential.[7−14] In the context of novel (electrochemical) NH_3 technology development, the ability to detect ammonia, even at trace levels, is of crucial importance for fast catalyst screening and for their implementation into working devices.

Typically, ammonia is detected by the Berthelot method (or indophenol method), a water-based colorimetric analysis. This method is well-established, widely used, and allows for low ammonia detection limit, but it is heavily dependent on experimental conditions such as pH and the presence of other species in solution. The major drawback of this method is the laborious and time-consuming sample preparation. Among other techniques aimed at sensitive ammonia detection, ion chromatography (IC) has undoubted advantages over the indophenol method because the analysis can be automated. Unfortunately, electrochemically generated ammonia solutions typically contain high concentrations of salts used as supporting electrolyte which may interfere with the analytical IC measurement, e.g., sodium or potassium ions. Other techniques shown to be powerful analytical tools in this field are quantitative ^1H NMR[15,16] and UPLC-MS[17] (ultrahigh performance liquid chromatography−mass spectrometry).[18] They detect ammonium ions derived from acidification of ammonia-containing solutions or derivatize ammonia with suitable chemicals such as dansyl chloride.[17] Nonetheless, ammonia often is produced in a basic aqueous media, and because of its gaseous nature at typical electrochemical experimental conditions, it partitions between the gaseous head space and liquid phase as dissolved gas as shown in Scheme 1. For this reason, ammonia solutions are difficult to store for subsequent quantitative analysis, and the laborious and time-consuming sample preparation must be done immediately after sampling procedures. For IC and quantitative ^1H NMR, trapping the ammonia in an acidic medium as ammonium ions is essential for its quantitative detection. Similarly, for UPLC-MS, ammonia derivatization should be done quickly to obtain a representative sample containing now a more stable compound that can be analyzed at later times. As such, ammonia present in the liquid phase can be trapped or derivatized rather easily, yet quantitative analysis of the ammonia that equilibrates with the head space remains

Scheme 1. Equilibrium Reaction between Gas-Phase Ammonia ($NH_3(g)$), Dissolved Ammonia ($NH_3(aq)$), and Ammonium Ion (NH_4^+)[a]



$$NH_{3(g)} \rightleftharpoons NH_{3(aq)} \underset{pH > 11}{\overset{H_2O}{\rightleftharpoons}} NH_4^{+}{}_{(aq)} + OH^{-}{}_{(aq)}$$

[a]When pH is greater than 11, the equilibrium is fully shifted to the left side of the equation; thus, the only relevant equilibrium to be considered is between ammonia in the gas phase ($NH_3(g)$) and ammonia as dissolved gas ($NH_3(aq)$).

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challenging to address, especially in open systems. Furthermore, the mentioned techniques involve a discrete degree of sampling, sample handling, and sample preparation that require manual dexterity, great attention from the experimentalist, and time dedication in order to be successful. All the above can also potentially introduce errors and contaminations in the measurements.

As a consequence, time-resolved information becomes unfortunately difficult to acquire leading to poor catalyst/system/device characterization and to large errors in the calculation of relevant catalyst parameters, chief among which are rate constants, turnover frequencies, and efficiency parameters. In this Viewpoint we propose a gas chromatographic (GC) method for *in situ* ammonia detection that can be applied to any (electrochemical) device operating under a wide range of conditions. The *in situ* GC method quantifies ammonia present in the gas phase in under 5 min analysis time with a lower detection limit of about 150 ppb v/v (~110 ng/l NH_3 or 6.5 nM NH_3 in the gas phase), a threshold level relevant to studying and screening (electro)catalysts. We further show that the ammonia concentration in the gas phase, directly measured by GC, can be used to calculate the ammonia concentration in the liquid electrolyte solution, thus enabling full quantification of the analyte under consideration as depicted in Figure 1, including ammonia stripped from the system because of GC carrier gas. The method allows for collection of time-resolved data giving access to relevant parameters to measure catalyst performance. Importantly, ammonia quantification is done *in situ*, thus avoiding altogether sample manipulation and time-consuming sample preparation.

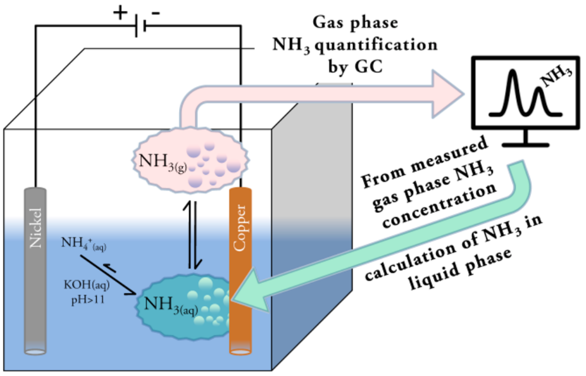

Figure 1. Representation of electrochemical ammonia generation device and equilibrium between dissolved ammonia ($NH_{3(aq)}$) and gas-phase ammonia ($NH_{3(g)}$) provided pH is basic. Gas-phase ammonia concentration is addressed directly by GC, while dissolved ammonia concentration is calculated from gas-phase ammonia concentration.

Ammonia Gas Chromatography and Calibration Curve. A few key aspects are fundamental to establish quantitative GC ammonia detection. Ammonia gas is well-known for its tendency to physisorb onto most materials, including stainless steel tubing, often used to connect experimental setups to the GC inlet and sometimes also for GC internal connections.[19] Physisorption onto tubing and valves becomes a very relevant issue when ammonia concentration approaches the sub-ppm range, as most analyte would be lost because of physisorption, with drastic implications for quantitative detection. In this regard, some other materials are used to minimize this issue. Stainless steel coated with an inert layer of SilcoNert 2000 (Sulfinert) minimizes ammonia physisorption to around 5.7 × 10^{12} molecules/cm^2.[20] In comparison, bare stainless steel adsorbs over 2 orders of magnitude more ammonia: 1.50 × 10^{14} molecules/cm^2. Among materials with low ammonia adsorption that can be useful for setup fabrication are PVDF (polyvinylidene difluoride), LDPE (low-density polyethylene), PTFE (polytetrafluoroethylene), and PFA (perfluoroalkoxy alkanes) ranging from 1 × 10^{12} to 14 × 10^{12} molecules/cm^2.[20] Care should also be taken to exclude any valve that might be present along the sample path as they are unlikely to be inert toward ammonia physisorption, including those within the GC instrument such as stop flow valves typically placed before sample loops. VICI diaphragm valves were used in our setup as their main body is inert and the sample comes in contact with only an inert membrane. The separation column chosen, Agilent Select Low Ammonia, is of primary importance to achieve good water/ammonia separation while maintaining a symmetric and sharp ammonia peak shape, important for sensitive quantification (Figure 2). The GC configuration and details of the method are presented in the Supporting Information.

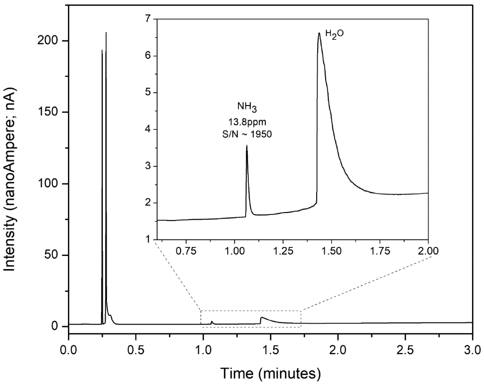

Figure 2. Example of full chromatogram obtained for a sample containing 13.8 ppm ammonia in N_2. Permanent gases are eluted at 0.25 min, ammonia at 1.1 min, and water at 1.3 min. The inset shows the nearly symmetrical ammonia peak and the excellent resolution between ammonia and water peaks. The slight background signal increase is due to temperature increase ramp.

For the validity of the method it is fundamental to obtain an ammonia calibration curve, which was built by nitrogen dilution of ammonia-containing certified cylinders. The dilution was carried out with the aid of a mass flow controller (MFC) and a mass flow meter (MFM) as depicted in Figure S1. This simple set-up allows for choosing a nitrogen flow at MFC (dilution gas) while the ammonia-containing gas flow is tuned by a needle valve, positioned just after the NH_3 cylinder pressure reducer, to obtain the desired total flow displayed at MFM. With such a dilution setup, ammonia never passes through noninert surfaces such as that of valves or mass flow controllers, allowing for generation of ammonia-containing samples ranging from 13.8 ppm to 100 ppb. A good linear response between ammonia concentration and area under the NH_3 peak was obtained (Figure S2). A series of consecutive injections of samples with the same gas composition was used to calculate the standard deviation and determine the experimental error (Table S2).

Ammonia in Liquid Phase. As ammonia can be measured reliably in the gas phase, this method can be directly applied to those (electrochemical) systems that produce ammonia as a gaseous product without direct contact with electrolyte, e.g., gas diffusion electrodes or gas-phase heterogeneous catalytic systems.[21,22] However, most electrochemical systems do require aqueous electrolyte; thus, we set out to find a versatile method to correlate ammonia concentration in the electrolyte and ammonia concentration in the gas phase in equilibrium with it. We envision that this correlation can be easily found by plotting the concentration found in solution measured by the traditional indophenol method and the concentration in the gas phase measured by GC as described above.

Ammonia-containing solutions at different concentrations were analyzed by the Berthelot indophenol colorimetric method to accurately determine their concentration in the liquid phase by comparing their absorbance at 650 nm with a suitable UV−vis calibration curve obtained previously (Figure S3). Second, aliquots of the same solutions were individually placed in a closed cell having a nitrogen inlet gas stream blowing over the ammonia solution and an outlet line connected to the GC sample inlet. After allowing time for equilibration between the liquid phase and head space, the nitrogen carrier flow was activated and the ammonia concentration in the gas phase was evaluated by comparing the ammonia peak area measured to the calibration curve shown in Figure S2. Plotting the ammonia concentration in solution obtained by the Berthelot indophenol colorimetric method against the ammonia concentration in the gas phase obtained by GC results in a linear relationship (Figure S4) that allows for quickly calculating ammonia concentration in solution by simply measuring the ammonia concentration in the gas phase above the liquid electrolyte. The authors note the method can be easily applied to any set of conditions experimentally needed, provided that the pH of the liquid phase is basic, in order to establish the NH_3/NH_4^+ equilibrium toward the NH_3 side according to Scheme 1, and that calibration curves are obtained with the experimental setup and conditions that are to be used for the experiment itself.

In Situ GC Quantification of Electrochemically Produced Ammonia. To showcase the validity of the method, nitrate reduction operated electrochemically in basic aqueous media was chosen as model reaction as this particular electrochemical reaction is sufficiently robust and widely studied in the literature.[23−28] For the purpose intended in this Viewpoint, our interest lies in showing the applicability of the *in situ* ammonia detection method; therefore, a simple one-compartment cell, two-electrode system without ion exchange membrane was used, and the array of possible reaction products compiled in Figure S5 was not investigated. Copper wire was used as working electrode, and a nickel wire was used as counter electrode in KOH aqueous electrolyte containing potassium nitrate as substrate. The electrodes were placed into a sealed Teflon cell equipped with a nitrogen carrier gas inlet line and an outlet line directly connected to the GC sample inlet, all controlled by MFC and MFM in a manner similar to that discussed previously.

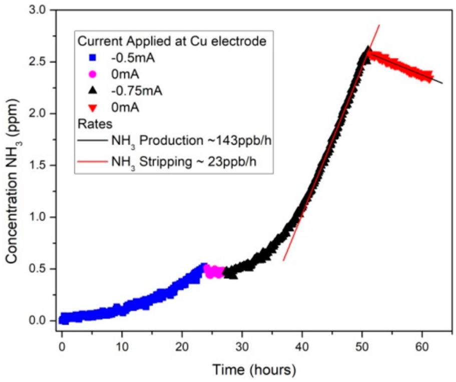

Figure 3. In-line ammonia detection from electrochemical nitrate reduction reaction at a copper electrode at different currents in basic aqueous electrolyte.

When no current is applied to the electrodes, no ammonia is detected at the GC, but as soon as the current is switched on, the corresponding ammonia peak appears in the chromatograms. As shown in Figure 3, this peak increases in time, indicating that ammonia is generated electrocatalytically in solution and it quickly equilibrates with its gaseous head space as the high pH ensures that NH_3 is present in solution rather than NH_4^+. As an example, when a −0.75 mA current was applied, the ammonia production rate in the gas phase reached about 143 ppb/h. When the current is stopped while maintaining the nitrogen carrier gas flow active, the ammonia concentration slowly decreases because of the stripping effect of the carrier gas which slowly depletes the NH_3 from solution at a rate of 23 ppb/h.

Calculation of faradaic efficiency is straightforward as the ammonia concentration in solution can be derived from the concentration measured in the gas phase at the end of the experiment while integration of the plot in Figure 3 gives direct access to the amount of ammonia lost because of stripping effects from the N_2 carrier gas. Thus, ammonia present in the liquid phase at the end of the experiment is calculated to be 5.66 μmol NH_3 while stripped ammonia amounts to 9.70 μmol; roughly 60% of the total ammonia produced is lost because of stripping effects. The capability to measure the NH_3 stripping from the system is an illustration of the directness and strength of this method. The amount of charge passed though the electrodes is easily obtained from the electrochemical experiment done at constant current and, as such, faradaic efficiency can be calculated (detailed calculations are compiled in the Supporting Information). When all parameters of the system under investigation are known, other relevant information is easily calculated, such as catalytic turnover frequency, turnover number, and rate constants.

This set of experiments shows that electrochemically produced ammonia in basic aqueous solution quickly equilibrates with its head space and that its concentration can be monitored with *in-line* GC, rendering this method a valuable tool for sensitive real-time ammonia detection under a wide variety of experimental conditions. Calibration plots are still necessary for quantitative ammonia analysis, but their preparation requires only a limited amount of time as compared to the time requirements for sample handling and preparation for other quantitative ammonia analytical techniques.

Impact and Future Work. This fast and reliable method has the potential to speed up catalyst screening and development of novel sustainable ammonia evolution devices as it requires significantly less effort in sample handling and preparation in comparison to other reported methods. The method is unique as it allows for *in situ* monitoring of ammonia evolution from (electrochemical) devices as showcased by electrochemical nitrate reduction reaction. Furthermore, provided proper calibration curves are obtained for the set of experimental

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conditions employed, a simple 5 min gas chromatogram provides information on ammonia concentration both in the gas phase and in the liquid phase in equilibrium with it. We will shortly show an example of this method in a relevant nitrogen reduction to ammonia application that is currently under study in our laboratories.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.0c02219.

Materials and methods, experimental details, calibration curves for UV−vis and GC, and Faradaic efficiency calculations (PDF)

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https://pubs.acs.org/10.1021/acsenergylett.0c02219

Notes

Views expressed in this Viewpoint are those of the authors and not necessarily the views of the ACS.
The authors declare no competing financial interest.

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(18) It must be acknowledged that quantitative ^{1}H NMR and UPLC-MS not only allow sensitive ammonia detection but also allow for resolution and identification of nitrogen-labeled species, providing extremely useful information for detailed mechanistic investigations. We note that the method described here could also achieve such a level of analysis when the gas chromatographer is coupled with an MS detector. Direct NH_3 detection at MS detectors is notoriously challenging as the couples $^{14}NH_3/OH^-$ and $^{15}NH_3/H_2O$ share the same m/z ratio. However, the chromatographic method described here allows for excellent water−ammonia separation, as shown in Figure 2, thus minimizing MS detectability issues of the mentioned species as NH_3 and water reach the MS detector at different times. Water background at the MS detector from water present in the system, such as trace amounts in the He carrier gas, should not cause detection issues as they will be constant and, as such, cause only a time-independent baseline increase.

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