

Application of Ion Chromatography for the Reliable Quantification of Ammonium in Electrochemical Ammonia Synthesis Experiments: A Practical Guide

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Assessing novel electrocatalysts for the electrochemical ammonia synthesis (EAS) requires reliable quantitative trace analysis of electrochemically produced ammonia to infer activity and selectivity. This study concerns the development of an ion chromatography (IC) method for quantitative trace analysis of ammonium in 0.1 M sulfuric acid electrolyte, which is applied to EAS gas-diffusion electrode (GDE) experiments with commercial chromium nitride as electrocatalyst. The developed IC method is highly sensitive, versatile, and reliable, achieving a limit of quantification (LOQ) of $6 \mu\text{g l}^{-1}$ ($6 \text{ ppb}_{\text{mol}}$) ammonium. The

impacts of the sample matrix, dilution, and neutralization, as well as contamination, on the quantitative analysis by IC are analyzed. Experimental constraints result in an effective LOQ including dilution of $60 \mu\text{g l}^{-1}$ for the determination of ammonium in 0.1 M sulfuric acid electrolyte, owing to necessary sample dilution. The practical guide presented herein is intended to be very relevant for the field of EAS as a guideline and applicable to a broad range of catalyst systems and ion chromatography devices.

Introduction

Electrochemical ammonia synthesis (EAS) as prospective green alternative to the well-established industrial-scale Haber-Bosch process has gained much interest in science. Although there are many experimental reports on various different active materials, catalyst performance in general and broad reproducibility are lacking. Proof of genuine EAS by electrochemical nitrogen reduction reaction (ENRR) is challenging, because of especially low production rates, ubiquitous sources of contamination and, in turn, necessary, reliable trace analysis.^[1] Assessing a catalyst

material for the EAS based on the quantitatively determined amount of electrochemically produced ammonia requires reliable and reproducible detection of concentrations typically found in such experiments, which are in the range of $\mu\text{g l}^{-1}$ to mg l^{-1} depending on experimental setup.


Ammonia is a colorless, corrosive and toxic gas with pungent smell. It easily forms ammonium ions in aqueous solution depending on pH as it reacts as weak base. There are several methods used to quantitatively determine ammonia or ammonium, depending on the respective scientific field, application, and range of concentration. Two photometric assays, Nessler's reagent method (NR) and the Indophenol blue method (IB), are commonly used in the field of ENRR and photo(electrochemical) NRR.^[2] A related spectrophotometric method is the *o*-phthalaldehyde fluorometric detection (OPA-FD) of ammonia often used in marine research.^[3] Other methods used but not limited to (this application) are ^1H nuclear magnetic resonance spectroscopy (^1H NMR) and ion chromatography (IC).^[4] All these methods inherently vary in their sensitivity, reproducibility, resilience, applicability and equipment requirements. NR and IB are easy to adapt, sensitive, and require little equipment, but are susceptible to environmental factors such as reaction time or temperature, owing to indirect detection (i.e., necessary quantitative chemical reaction).^[2,5] Consequently, precise control of the reaction conditions is required for reliable and reproducible results using NR, IB and OPA-FD. OPA-FD is highly sensitive, achieving ammonium detection limits of nmol l^{-1} using flow injection, but requires special instrumentation.^[3] ^1H NMR is a powerful method that can quantify ^{15}N -ammonium isotope-selectively by the characteristic shift from a triplet to a doublet peak, but requires expensive instrumentation and specialist knowledge.^[4] It is mostly used for isotope-specific detection in isotope-labelled


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ENRR experiments. Easy access to the necessary NMR equipment by utilization of less sophisticated equipment and guidelines on the appropriate application was recently published by Martín et al.^[4] IC is highly sensitive and reproducible, enabling direct concurrent detection of ammonium and other ions, but requires dedicated instrumentation. All these methods are well established and possibly suitable, but in practice operational constraints of the method and application have to be considered. Furthermore, all of the above-mentioned methods used for the quantification of ammonium are more or less affected by the sample matrix, for example pH, ions, solvents, and impurities.^[2] These matrix constituents can influence the method-accuracy adversely. These experimental and analytical necessities in conjunction with to date low experimental ammonia production rates make investigating novel electrocatalysts for the EAS especially challenging and illustrate the need for feasible, suitable, and reproducible practical ammonium quantification. To this end, a method has to be evaluated and tested in a real-world application.

Ion chromatography has been used to determine trace amounts of ammonium in natural waters.^[2,6] Recently, Duan et al. evaluated the reliability and accuracy of an ion chromatography method for the quantification of ammonium in sample matrices of different pH by suppressed conductivity detection.^[7] The possible interference of common transitional metal cations and organic compounds on the quantification was explicitly investigated. Additionally, Duan et al. examined ammonium contamination of commonly-used reagents and ionomer membrane material, a commonly-known potential source or sink of ammonium.^[7] Although the ammonium quantification in sample matrices of different pH was investigated for reliability and accuracy, neither the method development nor the detection and quantification of ammonium in trace amounts by IC were considered isolated. Both are required for comparative evaluation of the method and application, which is essential for reliable results. Generally, IC provides several advantages for the trace analysis of ammonium, especially the high sensitivity, reproducibility, direct detection, and automatization. Automated IC analysis of samples makes routine analysis of many samples at trace levels feasible. A routine analysis of not only samples of interest, but also stock solutions and similar, allows for tight control on a variety of possible sources of contamination. Consequently, the reliability of experimental results is improved.

In this study, we aim to develop and implement an ion-chromatographic method for the detection of ammonium in the concentration range of low ppb to ppm [i.e., $\mu\text{g l}^{-1}$ to mg l^{-1} ; Eq. (1)]:

$$\frac{\mu\text{g}}{\text{l}} \cdot \frac{M_{\text{H}_2\text{O}}}{M_{\text{NH}_4^+}} \cdot \frac{1}{\rho_{\text{H}_2\text{O}}} = \frac{\text{g}}{\text{l}} \cdot 10^{-6} \cdot \frac{18.015}{18.0387} \cdot \frac{1}{998.2067} \text{ g} \quad (1)$$

$$\cong 1.0007 \text{ ppb}_{\text{mol}}$$

The method, as well as the application thereof, for EAS experiments will be investigated in regard to suitability and reproducibility. To this end, an ion-chromatographic system will be characterized and optimized for fast and reliable detection

at a low limit of quantification (LOQ). Sample contamination by environmental ammonia and ammonium pollution is investigated at method level. Additionally, methods are developed to prepare samples and analyze the ammonium concentration in a typical sample matrix by appropriate preparation. The developed method is applied to real-world EAS-samples for the quantitative detection of ammonium in 0.1 M sulfuric acid electrolyte using commercial chromium nitride. Nash et al. described chromium nitride as potentially active for the ENRR.^[8] However, it is important to note that the results presented herein do not prove genuine ENRR activity, owing to possible noncatalytic decomposition of vanadium and niobium nitride catalysts.^[9] Thus, electrochemically produced ammonia detected by IC might not originate solely in a complete catalytic cycle of the ENRR (via supposed Mars-van-Krevelen mechanism).^[10] The chromium nitride was depicted here as a case study in reference to literature to demonstrate real-world application of the developed IC method. The used commercial GDE-setup is fed with gaseous nitrogen as educt, which realizes mass transport conditions close to the application and circumvents low nitrogen saturation in liquid electrolyte. The electrolyte as reservoir for electrochemically produced ammonium is sampled several times over the duration of the experiment. The quantitative ammonium determination of these samples by IC resolves the time evolution of the concentration and allows to calculate the ammonia production rate. The setup and material are assessed based on the production rate in comparison to literature results of the used commercial chromium nitride in a different experimental setup.^[8] This practical guide will be very relevant for the field of EAS and ENRR and is applicable to both a broad range of catalyst systems and IC devices.

Results and Discussion

Selection of chromatographic conditions

In EAS research, reaction rates on the order of $\text{pmols}^{-1} \text{cm}^{-2}$ of currently studied catalyst candidates imply typical concentration ranges of ppb to ppm, depending on reactivity and selectivity of the catalysts, electrode size, electrolyte volume and experimental duration.^[4] Possibly necessary sample dilution sets the *effective* limit of quantification (LOQ*) in the application, determining the accumulation time in EAS experiment. Thus, quantification in the low ppb range needs to be reliably performed to ensure genuine EAS activity. Key to this is proven trace analysis. First, feasible and applicable chromatographic conditions were investigated to subsequently achieve sufficient detection of ammonium in 0.1 M sulfuric acid electrolyte, within an acceptable run time for the routine analysis in EAS experiments.

Development of a fast measurement method

An analytical method must be able to detect, identify and quantify the analytes of interest. Unspecific conductivity

detection of cations by IC is only possible after sufficient separation of the constituent cations in the specific sample matrix for identification by the specific analyte retention time. Separation column, eluent, and process parameters, flow rate, and column temperature determine the separation efficiency and analysis duration. Further theoretical details of IC method and used terms are given in the Supporting Information section S1. The manufacturer's recommended standard conditions for the used high-capacity separation column were used as starting point to assess the initial separation efficiency (capacity factor k , resolution R , etc.). The manufacturer's recommended standard conditions are an eluent consisting of 1.7 mM nitric acid and 1.7 mM dipicolinic acid, a flowrate of 0.9 ml min^{-1} and a column temperature of 30°C .^[11] Dipicolinic acid is used as complexing agent accelerating the elution of some cations.^[12] Standard conditions resulted in excellent separation of the six standard cations lithium Li^+ , sodium Na^+ , ammonium NH_4^+ , potassium K^+ , calcium Ca^{2+} magnesium Mg^{2+} , (see the Supporting Information, Figure S1), but elution of magnesium required close to 40 min. The last eluted cation determines the chromatogram's duration to prevent carryover of cations still retained on the separation column. All six cations but lithium occur naturally in water.

Separation can be sped up at the expense of the separation efficiency by using a higher ionic strength eluent that is, by using an increased nitric acid concentration.^[12] Additionally, a smaller difference in ionic strength of the eluent and sample matrix results in a smaller matrix-effect, which is discussed later. To this end, the eluent composition was changed to neat 6 mM nitric acid to accelerate separation. The increased nitric acid concentration of 6 mM results in overall faster elution with consequently reduced, but sufficient separation (Figure 1, black line) compared to the standard eluent concentration of 1.7 mM nitric acid (Figure S1). Notable consequence is magnesium (4) eluting before potassium (5). The total chromatogram duration

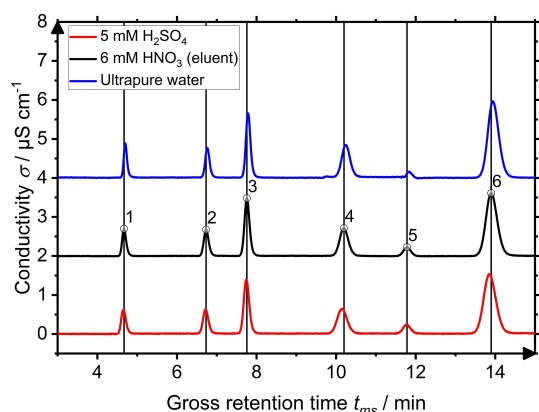


Figure 1. Matrix effect of ultrapure water, eluent, and 5 mM sulfuric acid on the separation of a multi-cation standard. Other conditions: Column: Metrosep C6 250/4.0, eluent: 6 mM nitric acid, flow rate: 0.9 ml min^{-1} , sample loop: $50 \mu\text{l}$, unsuppressed conductivity detection, blank correction, analysis by MagICNet software. Multi-cation standard 1, 1:999 in ultrapure water/eluent/5 mM sulfuric acid, Li^+ $50 \mu\text{g l}^{-1}$ (1), Na^+ $200 \mu\text{g l}^{-1}$ (2), NH_4^+ $400 \mu\text{g l}^{-1}$ (3), Mg^{2+} $200 \mu\text{g l}^{-1}$ (4), K^+ $200 \mu\text{g l}^{-1}$ (5), Ca^{2+} $1000 \mu\text{g l}^{-1}$ (6). Baselines have been shifted to $0/2/4 \mu\text{S cm}^{-1}$ at the origin.

is reduced to 15 min (Figure 1 cf. Figure S1), which is feasible for the routine analysis of 15+ samples (see below).

Adaption of the sample matrix

The prerequisite for the analysis of samples is material compatibility of the analyzed sample with the used analytical device. The material compatibility of the used separation column requires a pH of 2–10 for separation.^[11] This limits the acidity of analyzed samples accordingly and prevents the direct analysis of sulfuric acid electrolyte at the used concentration of 0.1 M. To later avoid detrimental necessary sample dilution of 0.1 M sulfuric acid electrolyte, the direct use of diluted 5 mM sulfuric acid within the acceptable pH range as electrolyte was tested first. An electrolyte concentration of 5 mM sulfuric acid was insufficient for direct use as electrolyte. The resulting electrolyte resistance in the EAS experiments proved to be too high for electrochemical measurements, despite tested in-situ compensation thereof. Thus, adequate sample processing of a 0.1 M sulfuric acid electrolyte sample matrix within the required material compatibility for analysis by IC was investigated.

An accessible sample processing of 0.1 M sulfuric acid sample matrix for material compatibility is dilution down to 5 mM, which results in a theoretical pH of 2.1 (see the Supporting Information, section S3). Still, the ionic strength of the sample matrix can affect separation, detection, and quantification of analytes by IC. This matrix effect occurs when matrix components alter the detector response to the target compound, affecting separation, detection and quantification.^[13] Methods of choice are removing or minimizing the matrix-effect.^[13] If the matrix effect is relevant and cannot feasibly be removed, a matrix-matched calibration can be necessary, where calibration standards are prepared in the same matrix as later samples to compensate for the matrix-effect within the calibration itself, requiring a different calibration design.^[13] Whether a matrix-matched calibration is required was tested by comparing separation (capacity factor k , resolution R), gross retention time t_{ms} and peak area A for ultrapure water, 6 mM nitric acid (eluent) and 5 mM sulfuric acid (prospective sample matrix) as sample matrix (Figure 1).

Although the separation is affected, all parameters are comparable and the estimated standard deviation of the peak areas is within the uncertainty of the concentration, the peak area is unaffected. The peak area is the true measure of the analyte concentration in case of a conductivity detector.^[13] An analyte concentration is later calculated from the measured peak area with the established calibration curve. As a consequence, a matrix-matched calibration, with 5 mM sulfuric acid as sample matrix of the used standard solutions, was not necessary to account for a matrix effect. A sample matrix of 5 mM sulfuric acid can readily be analyzed by the used device and method. Therefore, calibration was designed with eluent as sample matrix for the standard solutions.

Method calibration and reproducibility

An analytical method must be calibrated in the expected concentration range before detected analytes can be quantified. This calibration determines the limit of detection (LOD) and LOQ of the method. The LOD is the analyte concentration corresponding to the minimum signal that can (statistically) reliably be attributed to the presence of analyte. The LOQ is the minimum analyte concentration that can be quantified with satisfactory precision.^[14] The applicability of an analytical method for trace analysis is determined by the LOD and LOQ. A multipoint calibration is designed in regard to the expected concentration range and sample composition to ensure high method accuracy, precision, and reliability. Minimum analyte concentration is inherently limited by the device response and noise. A minimum signal-to-noise ratio (SNR) of 3 is commonly accepted as lower limit.^[12] The highest standard concentration should range between 100 to 150% of the expected analyte concentration.^[13] The calibration line should comprise five to ten standard concentrations. Two repetitions per standard suffice if peak area repeatability is within 2% of the relative standard deviation (RSD).^[13]

A minimum analyte concentration for a $\text{SNR} \geq 3$ was estimated based on the measured analyte peak area and baseline noise of 2–8 nS cm^{-1} for an injection volume of 100 μL . A minimum standard concentration of 2.5 $\mu\text{g l}^{-1}$ was chosen accordingly. The calibration was carried out with 11 standard concentrations, from 2.5 $\mu\text{g l}^{-1}$ to 1000 $\mu\text{g l}^{-1}$ for all 6 standard cations (Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}). The commercial single element cation standards were diluted in eluent. The estimated standard deviation (ESD) of concentration was inferred from the individual weight of commercial cation standard solution added to the standard stock solution. The stock solution was diluted with eluent to the desired concentration of the standard. A prior triple measurement of multi-cation standard showed an ESD in retention time, area, and resolution below 1% for all six cations at the injection volume of 100 μL . In consequence, each standard concentration was measured in triplicate for the calibration, as shown for ammonium in Figure 2a.

The detector response, peak area A , is linearly dependent on the analyte concentration c with an increased deviation at the lowest concentrations of 2.5 and 5 $\mu\text{g l}^{-1}$ ammonium, where the SNR is close to or below 3 (Figure 2b).

Low-frequency fluctuation of the base line became relevant for the determined peak area at these concentrations, possibly similar to an analyte specific device offset (Figure 2a, inset). The divergence to higher determined areas can indicate background contamination, which becomes increasingly relevant at this concentration level. A background contamination of the eluent should be accounted for by the background correction. Furthermore, any form of accumulation of external ammonium is unlikely, because the sample vials were capped, and the lowest concentrations were measured first. A constant small-scale contamination of the standards with ammonium would not affect the slope. However, an increased error in dilution from the stock solution at low concentrations should affect all analyte cations identically. This is not the case, although lithium

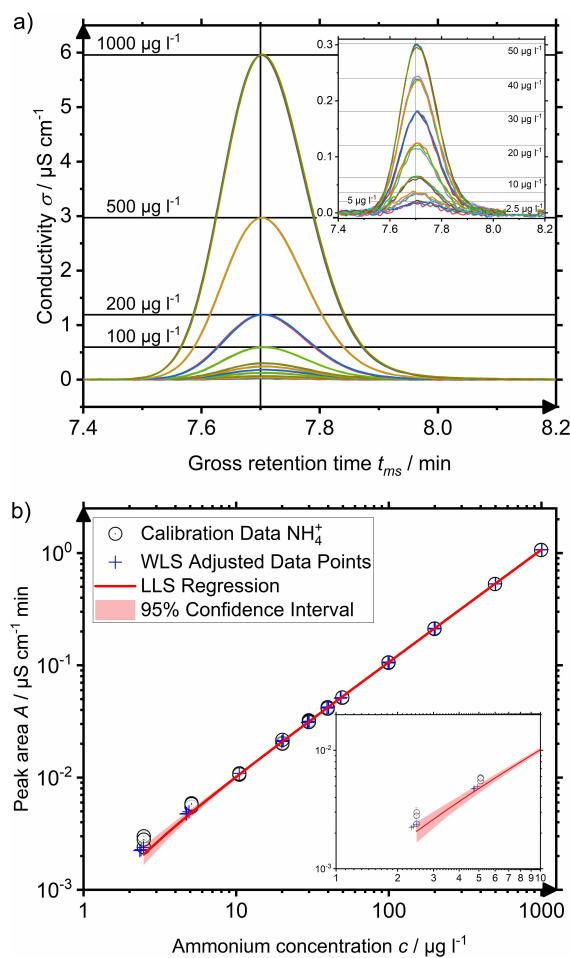


Figure 2. Ion chromatography method calibration for ammonium: a) Chromatographic peak of ammonium for all 11 standards. The chromatograms have been shifted to zero at 7.4 min. b) Ammonium method calibration. The raw data points are marked as black circles with central dots. The linear least-squares (LLS) regression curve is shown as a red line with corresponding 95% confidence interval. The weighted least-squares (WLS) regression-adjusted points by the method reported by York et al. are shown as blue crosses.^[15]

and magnesium show the same principal deviation, potassium and calcium show the opposite (cf. Figure S3). The most likely cause is the limiting SNR affecting determination of the peak area. Insufficient detection sensitivity limits reliable detection at even lower concentrations in this device configuration.

Calibration curve

A mathematical relationship must be established between the analyte content and detector response for quantitative analysis. A calibration curve of the analytical type used in quantitative analysis links the analyte quantity q ($q = c \cdot V_{\text{inj}}$) to the analyte peak area A . This calibration curve is calculated by regression analysis from the calibration data. An unweighted linear least-square (LLS) regression is often used. A weighted least-square (WLS) regression can give better results for low concentrations

and nonuniform variance (heteroscedastic). The coefficient of determination R^2 is one common quantity to assess the goodness of fit and should be higher than 0.96. A better indicator is the relative residual standard deviation s_{Res}/\bar{y} , which should not exceed a few percent, the lower, the better.^[13] First, the calibration curves were calculated by LLS regression (see the Supporting Information, section S5). The calibration curve for ammonium is shown as a red line in Figure 2b. Slope and intercept of LLS regression lines for all six cations are given in Table S1. The LLS lines of all six cations have a high R^2 of >0.9999 , the relative residual empirical deviations s_{Res}/\bar{y} are low, showing a very good fit. LOD and LOQ were calculated based on these LLS lines and are given in Table 1.

All achieved LODs are below $5 \mu\text{g l}^{-1}$ (Table 1), with the exception of potassium. The detection limit for the unexpressed conductivity detection of simple inorganic cations (Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+}) is given to be about $10 \mu\text{g l}^{-1}$ for an injection volume of $50 \mu\text{l}$.^[12] The herein developed method is at or slightly below this value of $5 \mu\text{g l}^{-1}$ accounting for the injection volume of $100 \mu\text{l}$. Further increasing the injection volume to reach even lower LOD is not expedient, especially with a complex sample matrix. A LOQ of $5 \mu\text{g l}^{-1}$ ammonium equals 28 pmol at the injection volume of $100 \mu\text{l}$, illustrating the high sensitivity of the method. The LOQ of $6 \mu\text{g l}^{-1}$ for the IC compares well to the ammonium quantification by OPA-FD with a LOQ of $10 \mu\text{g l}^{-1}$.^[16] The analyte cations lithium and ammonium are of greatest interest for the later application. Ammonium is the principal analyte cation to be quantified in the application. Since lithium does not occur naturally in relevant water, it can be used as internal standard. The low LOQs of lithium and ammonium are beneficial for that purpose. The achieved calibration is of high quality for trace analysis. A WLS regression as described by York et al. was tested for an improved fit at the lowest two standard concentrations,^[15] the effect overall was minor, the results can be found in the Supporting Information (section S6). Relevant for practical use is the accuracy and reproducibility of the method, that is, the exactness and precision of the measured analyte quantity.^[17] Both were practically examined briefly and found to be exact (see the Supporting Information, section S7).

To summarize, we have developed a fast, sensitive, precise, and exact quantitative analytical IC method for the trace analysis of ammonium with a LOQ of $6 \mu\text{g l}^{-1}$ (ppb). Investigating the application to quantify trace amounts of ammonium in 0.1 M sulfuric acid matrix was the next step.

Quantification of ammonium in 0.1 M sulfuric acid

Actual EAS production rate, electrolyte cell volume and feasible experimental duration determine the ammonium concentration in EAS samples. Ammonium concentration ranged from less than 20 to more than $500 \mu\text{g l}^{-1}$ in our experiments (see below). The sample matrix consists of 0.1 M sulfuric acid. As stated, this sample matrix cannot be directly injected into the used separation column, because of the required material compatibility (i.e., a minimum sample pH of 2). Possible ways to circumvent this are sample dilution, acid neutralization or analyte extraction. Analyte extraction has been demonstrated specifically for ammonium by purge-and-trap methods.^[18,19] These methods work by selectively purging ammonium from the sample matrix (donator solution) as gaseous ammonia and trapping it in a suitable solution (receptor solution). This can be done by a carrier-gas stream^[18,19] or membrane-contactor,^[16,20] but requires a known and reliable transfer efficiency for use in practice and in consequence automatization. Dilution and neutralization, either by alkaline solution or strong anion exchange (SAX) resin, were tested for feasibility in this work.

Dilution

Dilution is the easiest and quickest way to measure samples with a 0.1 M sulfuric acid sample matrix. Diluting 0.1 M sulfuric acid by a factor of 20 down to a concentration of 5 mM results in a pH of 2.1 (see the Supporting Information, section S3), enabling injection onto the separation column and analysis. The disadvantage of straight sample dilution is the proportionally reduced analyte concentration and in consequence effective LOQ (LOQ*). The LOQ* for ammonium is increased from 6 to $120 \mu\text{g l}^{-1}$ in comparison to the original sample composition. This accordingly affects the experimental design regarding necessary accumulation time, determinable reaction rates and contamination risks. All other parameters equal, a necessary sample dilution of 1:19 requires a 20 times higher accumulation time in EAS experiments to compensate for the dilution.

Neutralization by alkaline solution

Neutralizing the acidic sample matrix potentially reduces the resulting sample dilution and in turn the LOQ*. An acid-base reaction of a strong acid and strong base is quantitative. The sulfuric acid – a strong acid – is neutralized by potassium hydroxide, a strong base. The counterions of the acid, sulfate

Table 1. Overview of calculated limit of detection (LOD) and limit of quantification (LOQ) for the calibration of Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+} using the adjusted chromatographic conditions.

Cation	Li^+	Na^+	NH_4^+	Mg^{2+}	K^+	Ca^{2+}
s_{Res}/\bar{y} [%]	0.2	1.1	0.5	0.5	1.5	1.2
LOD ^[a] [$\mu\text{g l}^{-1}$]	0.76	4.14	1.97	1.76	5.81	4.52
LOQ [$\mu\text{g l}^{-1}$]	2.29	12.39	5.91	5.27	17.39	13.54

[a] Calculated based on an unweighted linear least square (LLS) regression with 99.5% significance level (Figure S3).

SO_4^{2-} , and base, potassium K^+ , remain in solution as part of the sample matrix. Although the pH is adjusted accordingly by the neutralization reaction to the added amount, the ionic strength is increased further by the added base. This is relevant for the separation, detection, and quantification by IC. To investigate whether neutralization of the acidic sample matrix by high-purity potassium hydroxide solution is practically feasible, neutralized 0.1 M sulfuric acid was measured with two dilutions, 1:4 and 1:9. 5 mM sulfuric acid was measured as reference for straight dilution without any neutralization of the sample matrix. All three sample types were spiked with $50 \mu\text{g l}^{-1}$ of lithium and ammonium (Figure 3). The recovery rate of these two analytes at the sample dilution was used as measure of the detection feasibility in this high ionic strength matrix. Potassium hydroxide was chosen over sodium hydroxide because it is commercially available in high purity and potassium elutes 5 min after ammonium with the investigated chromatographic conditions (Figure 1). The potassium peak will not overlap with ammonium at the order of magnitude higher concentrations necessary to neutralize the 0.1 M sulfuric acid sample matrix.

The high ionic strength of the neutralized 0.1 M sulfuric acid matrix had a pronounced effect on the separation. The baseline increased, progressively decreasing asymptotically until reaching potassium. This baseline drift affects peak quantification if not corrected.^[13] The baseline decreased sharply after potassium, levelling off close to the pre-injection level. The visible peaks of lithium (1), sodium (2) and ammonium (3) showed pronounced broadening. Sodium showed peak splitting at the lower dilution of 1:4. Although the peak form is heavily affected, the peak area of lithium is within margin at both dilutions compared to the 5 mM sulfuric acid. However, the peak area of ammonium is only 62% at the lower dilution. Moreover, sodium and ammonium were not baseline separated

anymore (red curve in Figure 3, vertical line at 7.6 min), thus requiring a higher dilution for this matrix.

The sulfate anion is not ionically retained on the cation separation column but can interact with cations in the sample matrix. The added potassium was retained and correctly quantified, albeit the concentration is orders of magnitude outside the region of calibration. Complex formation of sulfate with lithium, sodium and ammonium can affect their separation, detection, and quantification. An ion-exchange displacement effect of sulfate as dominant matrix ion likely led to the peak broadening and reduced separation efficiency.^[21] Cation separation by the equilibrium interaction with the functional anion groups of the stationary phase is possibly reduced by the competitive interaction with sulfate anions. Although lithium was quantified correctly at a sample dilution of 1:9 and 1:4, ammonium was not quantified correctly at the lower dilution. Direct analysis and quantification of analyte cations at $\mu\text{g l}^{-1}$ concentration in 0.1 M sulfuric acid is possible after neutralizing with high purity potassium hydroxide in the used setup, but a minimum dilution of 1:9 is necessary owing to the high ionic strength of the resulting sample matrix. Although quantification is possible at this dilution for ammonium, analysis quality is reduced by peak broadening, worse SNR, and baseline drift. Nonetheless, neutralization is a twofold improvement over straight dilution regarding the LOQ* of $60 \mu\text{g l}^{-1}$. A deliberated choice of a pH-neutral electrolyte, like K_2SO_4 , is in principal possible to avoid this operational constraint, but only if the catalyst system is active in such. Moreover, the high ionic strength remains problematic, especially in regard to deterioration of the separation column.

Neutralization by solid-phase-extraction

A feasible practical alternative to remove interfering constituents of the sample matrix, like 0.1 M sulfuric acid, is the use of ion exchange solid-phase extraction (SPE).^[22] Analytical grade particulate strong anion exchange (SAX) resin can be used to neutralize an acidic sample matrix and selectively extract constituent anions. The activated SAX sorbent in hydroxide form exchanges hydroxide ions OH^- for sulfate ion SO_4^{2-} in contact with the sulfuric acidic sample matrix. Ion exchange capacity (IEC), selectivity and local equilibrium determine the degree of ion exchange. Removal of the sulfate from the sample matrix is beneficial for the separation and detection (Figure 4). SPE is superior to dilution and neutralization by alkaline solution in regard to resulting dilution and ionic strength of the remaining sample matrix. Practical implementation of the ion exchange SPE is of relevance for the analyte recovery. An exceeding ion exchange capacity of the SAX packing can result in undesired exchange of the counter ions of the analyte cations and loss of analyte cations. Precise knowledge of the analyte recovery after treatment is required for use in practice. Multi-cation standard diluted 1:999 in a 0.1 M sulfuric acid sample matrix was measured diluted 1:19 and treated by a SPE cartridge with an IEC of 1.1 equiv. (Figure 4).

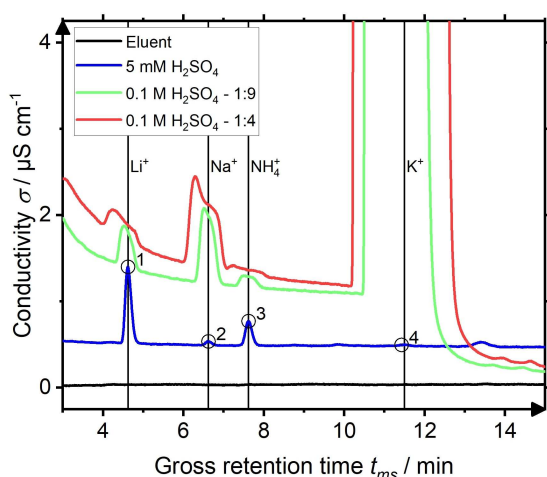


Figure 3. Recovery of $50 \mu\text{g l}^{-1}$ lithium (1) and ammonium (3) in 5 mM sulfuric acid as well as 0.1 M sulfuric acid neutralized with potassium hydroxide and diluted to 1:4 and 1:9. Other conditions: Column: Metrosep C6 250/4.0, eluent: 6 mM nitric acid, flow rate: 0.9 ml min^{-1} , column thermostat: 30°C , sample loop: $100 \mu\text{l}$, unsuppressed conductivity detection, no blank correction, analysis by MagICNet software. $50 \mu\text{g l}^{-1}$ lithium (1), sodium (2), $50 \mu\text{g l}^{-1}$ ammonium (3), potassium (4).

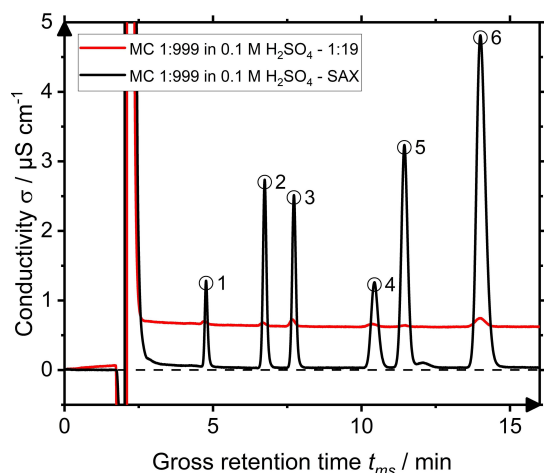


Figure 4. Comparative measurement of multi-cation standard diluted 1:999 in 0.1 M sulfuric acid and measured either diluted with ultrapure water 1:19 (red line) or neutralized with SPE by SAX-packing (black line). The chromatograms have been shifted to zero at 0 min (injection). Other conditions: Column Metrosep: C6 250/4.0, eluent: 6 mM nitric acid, flow rate: 0.9 ml min⁻¹, column thermostat: 30 °C, sample loop: 100 μl, unsuppressed conductivity detection, no blank correction, analysis by MagICNet software. Multi-cation standard 1, 1:999 in 0.1 M sulfuric acid, Li⁺ 50 μg l⁻¹ (1), Na⁺ 200 μg l⁻¹ (2), NH₄⁺ 400 μg l⁻¹ (3), K⁺ 200 μg l⁻¹ (5), Mg²⁺ 200 μg l⁻¹ (4), Ca²⁺ 1000 μg l⁻¹ (6).

The multi-cation standard in 0.1 M sulfuric-acid matrix diluted to 1:19 with ultrapure water showed an increased offset of the baseline characteristic for the matrix and concentration (i.e., 5 mM sulfuric acid; Figure 4, red line). The analyte peaks are appropriately small for the high dilution of 1:19 compared to the sample concentration of the sample treated by SPE (Figure 4, black line). Recovery ranges from less than 90 to more than 120% for the diluted sample. The relative uncertainty in measured concentration is high at these low concentrations (lithium 2.5 μg l⁻¹, ammonium 20 μg l⁻¹) and is the likely cause for the larger range in the recovery rate. In contrast, the SPE-neutralized sample shows appropriately large, well-separated, and formed peaks (Figure 4, black line). The sodium and potassium concentration are compared to the nominal value increased by a factor of more than 2 and 8 respectively. Sodium was found before analyzing neat high purity sulfuric acid and could be a constituent of the acid stemming from the production process of the sulfuric acid. The increased concentration of potassium was likely caused by residual potassium hydroxide solution from the activation of the SPE SAX-packing despite rinsing. The undesired sample dilution was likely caused by water and sample retention inside the void volume of the particulate SAX packing, as only gravity driven percolation of the resin bed was used. Ammonium recovery was 99.3 ± 0.8% accounting for sample dilution by the concentration ratio of ammonium to lithium of 8 ± 0.1 in the multi cation standard. The sample pH was approximately 2.6 after SPE, theoretically equaling a remnant sulfuric acid concentration of less than 1.4 mM (i.e., removal of 98.6% of sulfuric acid). When an increased IEC of the SPE cartridge of 2.2 equiv. was used instead of 1.1 equiv., it resulted in sample pH of > 10.1 after passing the

SAX packing. Although this sample was acidified before measurement, the recovery of ammonium was only 89.8 ± 0.8%, accounting for sample dilution by the concentration ratio of ammonium to lithium. Sample preparation by SPE for the removal of the 0.1 M-sulfuric-acid sample matrix is possible without loss of analyte (ammonium), if the IEC is chosen accordingly and undesired sample dilution is either prevented or accounted for, for example, by an internal standard (lithium). The resulting LOQ* including minimal dilution would be close to the LOQ.

All three investigated methods allow to quantify trace amounts of ammonium in 0.1 M sulfuric acid electrolyte under the prerequisite of a sample pH between 2 and 10. Dilution is the easiest to apply but has the largest reduction in LOQ*. Neutralization and dilution by alkaline solution requires overall less dilution, but the high ionic strength of the resulting sample matrix is detrimental to the detection and quantification of the analyte cations. Solid-phase extraction of anions is the best method to neutralize the acidic sample matrix without introducing ions, but precise control or knowledge of the occurring sample dilution is necessary and reliable practical implementation requires extensive experimentation, especially for low amounts of sample and therefore not used for the small amount of sample (i.e., 0.5 ml) drawn in electrochemical measurements. Sample preparation by SPE could be implemented in future studies.

Ammonium contamination

There are many possible sources of ammonia and ammonium contamination reported in literature. Among them are atmospheric pollution, nitrile gloves and the human breath. False positive results for the EAS activity by environmental contamination are an important relevant aspect in literature.^[1,23] Commonly used acidic ionomer material (Nafion) can be a source of ammonium through contamination. Therefore, their use had to be avoided. Hanifpour et al. specifically investigated protocols for the removal of ammonium contamination from Nafion membrane material prior to use in EAS experiments.^[20] These aspects regarding contamination are of specific relevance for the field of ENRR. The fundamental requirements for quantitative trace analysis regarding contamination are of general concern and will be studied here for the established IC method in conjunction with EAS experiments. The purity of labware and cleaning thereof is integral to the quality of the developed methodology.^[24] Consequently, cleaning of the used labware and measurement cell was tested (Figure S5). Simple rinsing with fresh ultrapure water to at least three times the vessel's volume was found to be sufficient and practicable. Carryover between sample vials was not observed (see the Supporting Information, section S9).

Contamination by environmental ammonia pollution

Contamination by environmental ammonia pollution was observed and examined in practice. Atmospheric ammonia pollution from environmental ammonia sources was found to be practically present and noticeable in quantification. Suitable air quality monitoring data for the geographic region reports an annual average ammonia air pollution of 2.9 to 10.1 $\mu\text{g m}^{-3}$ in 2020, which is equivalent to an ammonium concentration of 4.4 to 15.4 $\mu\text{g l}^{-1}$ (see the Supporting Information, section S10).^[25] This expected ammonium concentration by sustained atmospheric ammonia pollution is consistent with the observed accumulation of ammonium in initially ammonium-free open-vessel high-purity water blanks measured between samples, which ranged from initially none to up to 10 to 15 $\mu\text{g l}^{-1}$ after a long run. Contamination by ingress of environmental ammonia pollution was effectively prevented by capping sample vessels and proved to be a necessity.

In one isolated incidence, a noticeable short-lived smell of manure inside the laboratory space coincided with a field across the building being manured with liquid manure and was linked to a substantially increased accumulation of ammonium in initially ammonium-free ultrapure water blanks over a duration of several hours (Figure 5).

The change of concentration over time shows the typical asymptotic form of equilibrium driven mass transport processes. This shows the relevance of continuous atmospheric background ammonia pollution in general and specifically the impact of localized high-intensity sources of ammonia pollution. Atmospheric background ammonia pollution can be assessed well on basis of data as shown, if available. High-intensity sources of ammonia pollution can occur, and their impact is measurable above the background atmospheric ammonia pollution. Most importantly, contamination of samples by atmospheric pollution, continuous or localized, can effectively be excluded by preventing prolonged contact with the atmosphere.

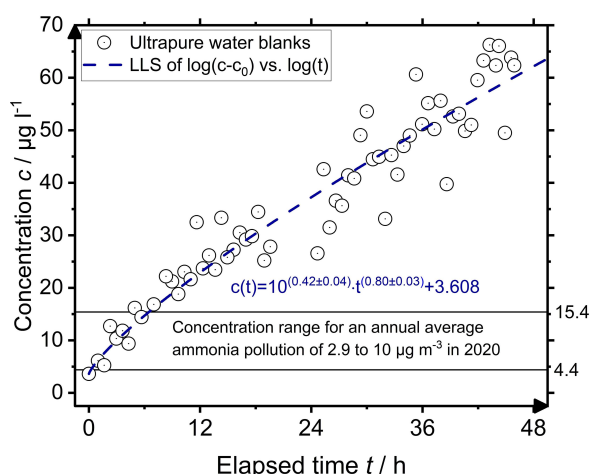


Figure 5. Ammonium concentration in ultrapure water blanks measured between samples as a function of time for a strong short-lived smell of manure inside the laboratory on the day of the experiment.

Application of IC for EAS experiments

Advancements in the field of EAS and ENRR not only require novel highly active and selective electrocatalysts, but also a broad and reliable data basis on found catalysts. This extends to a key aspect of scientific research, reproducibility, and reproduction of results, especially in light of likely false-positive results of earlier research, owing to contamination. The sampling procedure depicted in Figure 6 was adopted for this reason. A routine analysis of not only the samples (5–9, 10, 11), but also the stock solutions (2, 3) from which they are derived, allows accounting of contamination at these points of the experiment, improving reliability. Sampling the electrolyte at different points in time (5–9), enables to resolve the time evolution of the ammonium concentration, providing additional insight. Analyzing the gas scrubbers, which account for gaseous ammonia in the up- and down-stream, and acid-leached spent GDE and Nafion membrane type 212 (NM212) covers additional possible ammonium reservoirs. Automated processing of these prepared samples by IC made the reliable routine analysis of that many samples feasible.

Chromium nitride has been described as an active electrocatalyst for the ENRR as shown by the results of Nash et al., who used a commercially available chromium nitride material for experiments in membrane electrode assemblies (MEA).^[8] However, noncatalytic decomposition of vanadium and niobium nitrides have been reported by Du et al. which makes the previous reports doubtful in regards of proving genuine NRR activity.^[9] Impact of different experimental conditions and setups as well as catalyst materials between both studies hampers obtaining a conclusive picture and further research is needed to differentiate between both processes. Its commercial availability allows the use of this commercial chromium nitride material to examine the developed IC methodology for the quantitative trace analysis of ammonium on a real-world sample, without intending to prove genuine ENRR. We deliberately conducted the experiments in a commercial GDE measurement cell (Figure S7), which allows to focus on the cathodic half-cell reaction, instead of both half-cell reactions. Furthermore, a GDE setup provides liquid electrolyte for analysis, which can be sampled during the experiment's duration. GDE measurements are a logical next step after classical electrochemical three-electrode measurements, realizing realistic mass transport conditions and avoiding saturation of the electrolyte with gaseous educt prior to reaction as in commonly used H-cell setup.^[26] Additionally, a relatively cheap commercial GDE measurement cell allows easier and broader adoption, which is beneficial for research.

Time evolution of the ammonium concentration

The time evolution of the ammonium concentration as end product of the ENRR can be informative about aspects such as possibly occurring activation, deactivation, decomposition, ingress of contamination and ammonium transport through the catholyte and anolyte separating Nafion ionomer membrane.

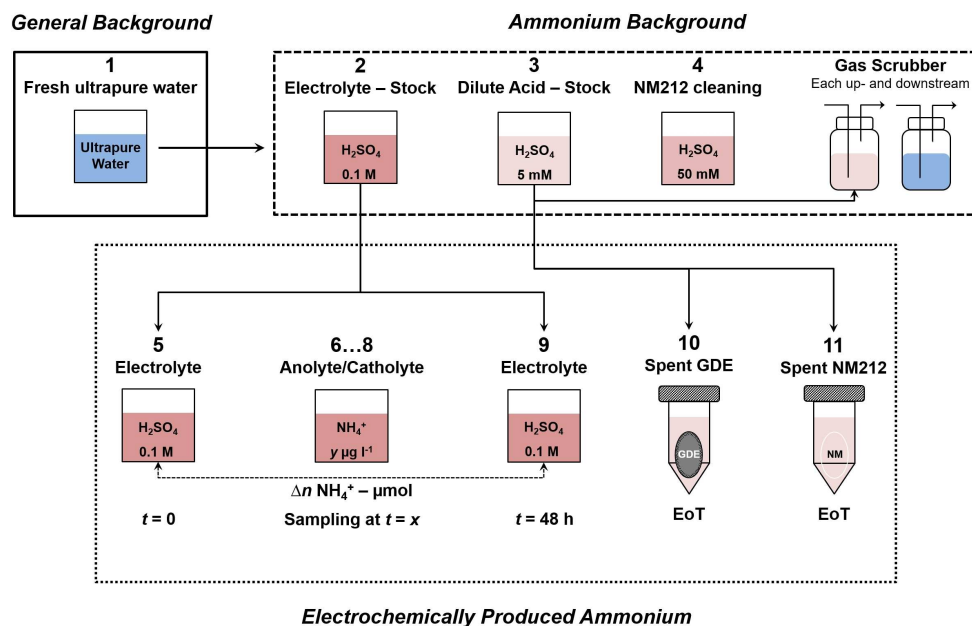


Figure 6. Sampling procedure and sample overview: All stock solutions, 0.1 M sulfuric acid electrolyte (2) and dilute sulfuric acid (2, 3), were prepared fresh on the day of the experiment from freshly taken ultrapure water (1), which was also sampled. All stock solutions and derived samples (5–11, 4, gas scrubbers) were measured by IC to determine the ammonium concentration. The sampled ultrapure water (1) was used as general background for possible ammonium contamination in all derived solutions. Stock solutions 2 and 3 were used to account for any ammonium contamination present at time of the analysis for derived samples (2; 5–9, 3; 10, 11). Sampling the electrolyte immediately before and after the chronoamperometric (CA) measurement (5, 9) enables derivation of the amount of electrochemically produced ammonium, excluding any ammonium already present or lost between end of the chronoamperometry (EoCA) and taking a final electrolyte sample after disassembling the measurement setup (end of test, EoT).

The time evolution of the determined ammonium concentration in an EAS experiment with an applied potential of -0.2 V vs. RHE at 25°C is shown in Figure 7. A rather high potential was chosen here compared to the respective literature to avoid

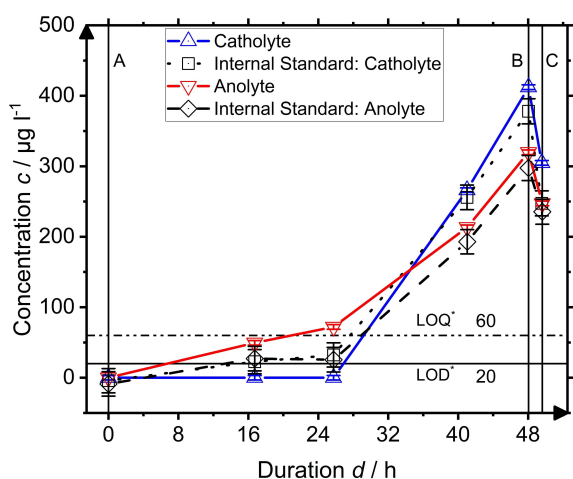


Figure 7. Ammonium concentration in catholyte and anolyte samples at different times over the total duration of 48 h chronoamperometric measurement (CA) with an applied potential of -0.2 V vs. RHE at 25°C . The given concentrations are the determined sample concentrations multiplied by the necessary sample dilution for analysis of 1:9. The effective LOD and LOQ, LOD* and LOQ*, containing the necessary sample dilution of 1:9, are shown accordingly as solid and dashed line. The shown error bars were derived by linear error propagation in volume, concentration, and dilution.

possibly accelerated noncatalytic decomposition at lower negative potentials.^[8]

There was no detectable ammonium in either catholyte or anolyte at the beginning of the chronoamperometric (CA) measurement (BoCA; Figure 7, line A). An ammonium concentration above the LOQ including dilution (LOQ*) was detected for the first time in the anolyte after more than 25 h. The ammonium concentration in the catholyte was higher than in the anolyte for all later samples taken. The highest concentration was measured at the end of CA (EoCA; Figure 7, line B). The measured concentrations were lower at the end of test (EoT; Figure 7, line C), after additional electrochemical measurements [i.e., cyclic voltammetry (CV)]. The electrolyte accounted for more than 94% of the calculated total amount of ammonium (Table S6). Small amounts of ammonium were liberated from the spent GDE and ionomer membrane.

The catalyst material is assessed for the EAS by quantitatively determining the amount of electrochemically produced ammonia, that is, the amount of ammonium dissolved in the electrolyte and other potential reservoirs (GDE, ionomer membrane). An experimental production rate is inferred from this net amount of product for the applied experimental conditions (i.e., active electrode area and experimental duration). A production rate of 1.7 ± 0.1 $\text{pmols}^{-1} \text{cm}^{-2}$ was calculated from the total amount of ammonium measured in the electrolyte at EoCA (line B) as well as GDE and ionomer membrane at EoT (line C and Table S6). This uncorrected production rate measured at 25°C is comparable with the results of Nash et al. of

$2.3 \text{ pmols}^{-1} \text{ cm}^{-2}$ at -0.2 V vs. RHE at 80°C in a membrane electrode assembly for unmodified catalyst material.^[8]

Three additional reference measurements and an isotope labelled experiment would be necessary to satisfy a quantitative proof of genuine ENRR activity according to current protocols in literature, which was out of scope of this study.^[1,23] This exemplary result is a qualitative proof of EAS in reference to the literature reproduced in the herein-used measurement setup. It proves the measurement setup and quantitative trace analysis by IC suitable.

Assessment of novel catalyst materials for the EAS solely relies on the experimentally determined production rate. But the unknown production rate, experimental duration, electrolyte volume and LOQ* are experimentally interdependent. The production rate is calculated from the product quantity. Quantifying the product requires sufficient product concentration. This in turn requires a sufficient production rate, experimental duration, or electrolyte volume. The experimental duration can be increased, and the electrolyte volume can be reduced to increase the product concentration. Neither can be adjusted beyond practical limits. A LOQ* of $60 \mu\text{g l}^{-1}$ was achieved by the optimized IC methodology and partially neutralizing the 0.1 M sulfuric acid sample matrix. The measured concentration in either catholyte or anolyte should have theoretically exceeded the LOQ* after 10 h of elapsed time at the inferred production rate of $1.7 \text{ pmols}^{-1} \text{ cm}^{-2}$. This is not the case; the concentration apparently shows a nonlinear trend. There are several possible explanations for the observed nonlinear time evolution of the production rate. On one hand, the production rate might actually be linear, but the trend was either not observed, owing to inadequate resolution, or possible hidden ammonium sinks. On the other hand, the production rate might actually not be linear.

Possible causes for an apparently nonlinear production rate

Insufficient analytical resolution can obscure an in practice linear trend of the ammonium concentration. However, the resolution was sufficient for the time between samples to distinguish concentrations at the calculated production rate (see the Supporting Information, section S16). Similarly, sample concentrations below the LOD* would not have been registered, showing a nonlinear trend. All samples were also measured spiked with $50 \mu\text{g l}^{-1}$ lithium and ammonium (internal standard), allowing to determine concentrations below LOQ*, although with a methodologically higher standard deviation. The concentrations determined by this internal standard method are consistent with the directly measured concentrations (Figure 7). The electrolyte accounted for more than 94% of the calculated total amount of ammonium (Table S6). Small amounts of ammonium were liberated from the spent GDE and ionomer membrane.

A significant measurable increase of the ammonium concentration did not occur until after 25 h of measurement. This could have been caused by hidden ammonium sinks. There are two possibly relevant ammonium sinks, the ion conducting

polymer membrane (ionomer) and oxidation of ammonium at the counter electrode. The sulfonic acid functional-groups of the Nafion ionomer membrane can bind ammonium, retaining it. Although the ion exchange capacity of the used ionomer membrane piece exceeds the total amount of ammonium quantified, the amount of ammonium acid-leached from the used membrane (10 nmol) was negligible, about 1% of total amount quantified ($0.9 \mu\text{mol}$; Table S6). The fraction of negatively-charged sulfonic acid groups neutralized by ammonium is a function of the ammonium and proton concentration in solution.^[27] In consequence, the amount of ammonium retained is a function of the ammonium concentration in solution for a given acid concentration. The highest ammonium concentration encountered in the 0.1 M sulfuric acid anolyte was $320 \mu\text{g l}^{-1}$ including the sample dilution. Ammonium was extracted from the used Nafion membrane with 20 ml of 5 mM sulfuric acid. The concentration of liberated ammonium is $11.4 \mu\text{g l}^{-1}$ calculated based on the equilibrium absorption data of Hongsirikarn et al. (see the Supporting Information, section S17).^[27] This theoretical concentration is consistent with the determined concentration of $9 \mu\text{g l}^{-1}$ (10 nmol) and concurs with Cai et al. in regards to the accumulation of ammonium in Nafion ionomer membranes.^[28] In consequence, the ionomer membrane was not a significant sink of ammonium in this case and cannot explain the nonlinear trend by binding ammonium overall. This was also the case for the spent GDE (Table S6). However, the measurable accumulation of ammonium in the anolyte, which lagged behind the catholyte ammonium concentration, is in contrast to the model experiments of Cai et al.,^[28] but concurs with similar model experiments by Ren et al.^[29] This indicates a concentration driven mass transport of ammonium through the ionomer membrane occurs and the Nafion membrane does not pose a barrier to ammonium. This transport process can be the cause for the initially higher concentration in the anolyte.

The occurrence of oxidation of ammonium at the counter electrode has been described by Andersen et al.^[23] In contrast to alkaline conditions, the electrochemical oxidation of ammonium is not well understood in acidic solution. Some form of slow oxidation of ammonium occurs on platinum in sulfuric acid at 0.66 V vs. RHE.^[30] An oxidation of ammonium is possible under experimental conditions depending on the resulting potentials at the counter electrode as shown by Ren et al.^[29] A loss of ammonium was observed between EoCA (B) and EoT (C). Cyclic voltammetry (CV) measurements were performed between EoCA (B) and EoT (C), which likely resulted in the observed loss of ammonium by partial oxidation of ammonium. Similarly, a slow small-scale oxidation could have occurred at the counter electrode during the CA, causing or enhancing a nonlinear trend of the measured concentration over time, although it is unlikely at the low potential of -0.2 V vs. RHE applied to the working electrode. Lastly, although progressive contamination during the experiment causing a false-positive cannot be ruled out completely, it is unlikely for the analysis of the used stock solutions and taken steps to prevent contamination and carryover (Figure S5). The generally observed level of environmental ammonia pollution is insuffi-

cient in magnitude for the concentrations determined in electrolyte. Furthermore, consequently limited contact with the atmosphere should have limited this possibility. Most importantly, the nonlinear time evolution of the concentration is entirely different to a concentration driven accumulation from atmospheric pollution, as clearly visualized by the experimentally observed accumulation of ammonium caused by a localized high-intensity source of ammonia pollution (cf. Figure 5).

Possible causes for a nonlinear production rate

There are several possible causes for a nonlinear time evolution of the ammonium concentration. First and foremost is a nonlinear production rate. A possible cause is the necessary activation of the catalyst material or catalyst layer. A GDE measurement generally shows real-world results, because of the realistic experimental mass transport conditions. In consequence, a GDE measurement shows the activity of the catalyst layer/GDE, not solely the isolated material intrinsic catalytic activity.^[26] The increased production rate over time supports some form of activation process of either the GDE or catalyst material. However, this observation is also readily explained by an increasing noncatalytic material decomposition alongside or instead of a catalytic process. Distinguishing between catalytic production of ammonia from gaseous nitrogen and noncatalytic decomposition of the nitrogen-containing nitride forming ammonia requires more sophisticated examination, such as isotope-labeling experiments with isotope-sensitive quantification.^[1,10] A genuine proof of ENRR is generally challenging, but especially for nitrogen-containing materials like nitrides. This is reflected so far in published results using transition metal nitrides (TMN) as novel catalyst materials for the ENRR. The group of Yang et al. found vanadium nitride and chromium nitride to be active catalyst materials.^[8,31] In contrast, Du et al. found no electrocatalytic activity for vanadium nitride or niobium nitride, but noncatalytic decomposition of the nitride releasing ammonia.^[9] Similarly, the group of Skuláson recently determined niobium oxynitride to not to be catalytically active but to noncatalytically decompose.^[16] Theoretical catalyst screening by quantum-mechanical simulation by Skuláson et al. had identified all of these TMN as potentially highly active for ENRR in some form.^[32] The lacking realization in experimental studies and contradicting results illustrate the discrepancy between theoretical prediction and real-world application. This emphasizes the need for further research to elucidate whether kinetic barriers, general noncatalytic decomposition, or fundamental material limitations are the cause.

Conclusion

Detection and quantification methods for ammonium are fundamental for any current EAS and ENRR research. In this study, ion chromatography, as a sensitive, reliable, and automated analysis method, was adapted for the detection and

quantification of ammonium in trace amounts. Method conditions were investigated to achieve fast and reliable quantification. The applied calibration resulted in precise and exact quantification over more than two orders of magnitude, over a range of ammonium concentrations from ppb to ppm ($\mu\text{g l}^{-1}$ to mg l^{-1}) and a LOQ of $6 \mu\text{g l}^{-1}$. Analysis of real samples requires specific sample preparation because the electrolyte represents a complex sample matrix, not only for analysis by IC. Different methods with varying practicability and performance were successfully used to quantify ammonium in 0.1 M sulfuric acid as electrolyte. Although reliable quantification is required for ENRR research it is not sufficient. Potential contamination is of general concern for trace analysis and currently of special relevance for the field of ENRR research.

Contamination was examined not only at method level with regards to cleanliness of labware and carryover, but also at experimental level with regards to atmospheric ammonia background pollution. Sufficient cleanliness was ensured by repeated rinsing with ammonium-free ultrapure water and drying of all used labware at elevated temperature. Carryover between samples in routine analysis was not observed. The automatized routine analysis of samples by IC showed progressive accumulation of ammonium in ultrapure water open to atmosphere consistent with the known yearly-average range of geographically relevant atmospheric ammonia pollution. This shows the possibility to derive possible ammonium contamination on basis of available atmospheric ammonia background pollution data. The relevance and impact of atmospheric ammonia background pollution was further exemplarily shown for a closely-localized high-intensity source of ammonia, whose impact was measurable above the continuous background pollution. Most importantly, contamination of samples by atmospheric contamination, continuous or localized, can effectively be excluded by preventing prolonged contact with the atmosphere, especially during the quantitative trace analysis.

The quantitative trace analysis by IC of ammonium in 0.1 M sulfuric acid electrolyte was successfully applied to an EAS experiment using a hitherto proven, commercially available chromium nitride catalyst.^[8] Although the EAS experiment was implemented in a GDE measurement, in contrast to the work by Nash et al.,^[8] and at lower reaction temperature of 25°C instead of 80°C , the resulting production rate is in good agreement. A specifically cleaned Nafion NR212 membrane was used as separator in H-cell configuration for the GDE experiments. The amount of ammonium retained inside the membrane after experiments was found to be negligible at the encountered ammonium concentration. This is agreement with the equilibrium absorption as function of the ammonium concentration as described by Hongsirikarn et al.^[27] and the recent results of model experiments by Cai et al.^[28]

The time evolution of the determined ammonium concentration, and in turn the production rate, was nonlinear. Different possible explanations have been discussed. Although the catalytic activity of the used material has been shown by Nash et al.,^[8] a false positive activity in the performed experiment by contamination is possible, if doubtful, which could have caused the nonlinear trend. A purely noncatalytic decomposition of the

nitride releasing ammonia cannot be ruled out without reference measurements and isotope-labelled experiments.^[1,10] In general, theoretically promising novel transition metal nitride catalysts for the ENRR, like chromium nitride, require further basic research to elucidate the discrepancy between theoretical prediction and real-world results. The cause for this observed discrepancy in real-world results might lie within fundamental material limitations or kinetic barriers, for example a non-catalytic decomposition instead of catalyzing or the initial nitrogen activation limiting activity. This illustrates the need for further and deeper research in the field elucidating the mechanistic understanding of reaction paths and possible kinetic limitations in real world application.

Nevertheless, the presented results confirm the successful application of the developed quantitative analysis by IC for the use in real-world EAS experiments. The IC methodology proved to be highly sensitive, reliable, and reproducible. The automated measurement of prepared samples by IC enabled a feasible analysis of several samples including the stock solutions used in the experiments. This allowed to resolve the time evolution of the ammonium concentration and exclude environmental contamination, giving the desired sound basis for the generated results, regardless of the necessary deeper research into the causes of observed material and system behavior.

Experimental Section

Chemicals

All solutions were prepared from analytical reagent grade chemicals in ultrapure water (Merck Millipore, Milli-Q Synthesis, > 18.2 M Ω cm at 25 °C), if not specified differently. All chemicals used for ion chromatographic measurements were of a reagent grade made for IC, similar quality or higher (HNO₃, DPA, H₂SO₄, KOH). All elemental standards (lithium Li⁺, sodium Na⁺, ammonium NH₄⁺, potassium K⁺, magnesium Mg²⁺, calcium Ca²⁺) used for ion chromatography were of certified reference material quality (Sigma-Aldrich, Trace-Cert®) and stored refrigerated after opening. Working solutions derived by dilution were prepared fresh and stored refrigerated as well. Nafion™ membranes type NR212 (abbreviated with NM212) were procured from the German Ion Power store.

Instrumentation: ion chromatographic system

A Metrohm Ion Chromatography Professional 850 AnCat (Metrohm 2.850.3010) with Metrohm Sample Processor 863 (2.863.0010) was used for automated sampling, injection, and unsuppressed conductivity detection of cations. The sample-processor samples solution by a PEEK hollow needle attached to a turret and peristaltic pump. The IC system consists of a metal-free high-pressure pump with eluent degasser, six-way valve with sample loop (50/100 μ l), column compartment with thermostat and conductivity detector. Data processing, visualization and evaluation was done by MagICNet 3.2 software. Any additional data processing was done manually and will be mentioned at the appropriate point.

Stationary phase: separation column

Separation occurred on a high-capacity weak-acid Metrohm Metrosep C 6 250/4.0 (Metrohm 6.1051.430; 250 mm \times 4 mm) separation column for large volume injection with appropriate Metrosep C 6 Guard/4.0 precolumn (Metrohm 6.1051.500) at a recommended eluent flow rate of 0.9 ml min⁻¹. The packing of precolumn and separation column consists of 5 μ m spherical silica particles functionalized with polybutadiene maleic acid. The separation column has an ion exchange capacity of 50 μ mol K⁺. Material compatibility allows an eluent pH of 2–7 and sample pH of 2–10.^[11] The column thermostat was kept at 30 °C for all experiments.

Mobile phase: eluent

The standard eluent for the employed separation column consists of 1.7 mM nitric acid and 1.7 mM dipicolinic acid.^[11] The eluent was changed from the standard composition to neat 6 mM nitric acid, reducing the chromatogram duration to 16 min at 30 °C for the six standard cations Li⁺, Na⁺, NH₄⁺, Mg²⁺, K⁺, Ca²⁺ (order of elution). The eluent was generated from prediluted 3M nitric acid. This stock solution was stored refrigerated. Eluent was prepared freshly by adding 2 ml of 3M nitric acid to fresh ultrapure water in a 1 l polypropylene (PP) graduated flask.

Sample preparation/handling

All graduated flasks and beakers used were class A made of polymethylpentene (PMP) plastic. Flasks and beakers were cleaned by rinsing with fresh ultrapure water to at least three times their volume and dried at 60 °C. Prepared samples were stored in and drawn from 11 ml OEM polypropylene sample vials (Metrohm 6.2743.057) capped with pre-perforated lids (Metrohm 6.2743.077). Vials were reused, they were washed in a lab dishwasher and then additionally cleaned as described before.

Samples containing 0.1 M sulfuric acid as sample matrix were either 1:19 diluted with ultrapure water, partially neutralized 1:9 with 0.011 M potassium hydroxide solution or by use of solid-phase extraction (SPE). Neutralized samples were measured spiked with each 50 μ g l⁻¹ of lithium and ammonium as well (internal standard/addition method). SPE sample cartridges (Carl Roth, Chromabond®, Flash DL, empty columns, 8 ml, Art. No 8909.1) were packed with a strong anion exchange (SAX) resin (Carl Roth, Roti®Change 1 \times 8, 100–200 mesh, Art. No. 6855.1). The column packing was adjusted according to the desired ion exchange capacity (IEC) as multiple of the equivalent concentration (normality) of the treated sample volume.

Electrochemical ammonia synthesis experiments

Electrochemical experiments were carried out using manually spray-coated gas diffusion electrodes (GDE), a commercial Gaskatel FlexCell PTFE GDE measurement-cell and a Metrohm Autolab PGN128 potentiostat. A set potential of -0.2 V vs. RHE was applied to the working electrode for 48 h to quantitatively produce ammonia at a regulated electrolyte temperature of 25 °C. Electrolyte samples of 0.5 ml volume were collected at different intervals from the catholyte and anolyte compartment separated by a Nafion NR212 membrane (NM212). Electrolyte volume was filled back up with an equal amount of electrolyte stock solution. Drawn samples were prepared as described above before analysis by IC. The amount of electrochemically-produced ammonium was calculated from the determined ammonium concentration and total volume of the respective reservoir, for example electrolyte volume or washing solution (Table S6).

Small 50 ml PP narrow neck bottles were used as simplistic gas scrubbers (Figure S7). Two gas scrubbers each were connected in series in the up- and down-stream of the measurement cell. The first in line was filled with 5 mM sulfuric acid and the second with fresh ultrapure water. These gas scrubbers enabled accounting of gaseous ammonia (i.e., possible educt contamination as well as electrochemical product). Additionally, samples of all stock solutions and freshly drawn ultrapure water were analyzed for each EAS experiment (Figure 6). Nafion NR212 membranes were used as separator for anolyte and catholyte compartment. Membranes were pre-treated immediately before use as described by Hanifpour et al.^[20] Membrane and the spent GDE were stored overnight in 20 ml of diluted 5 mM sulfuric acid to leach out present ammonium. This diluted sulfuric acid was analyzed for leached ammonium.

Acknowledgements

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: electrochemistry · ion chromatography · nitrides · nitrogen fixation · trace analysis

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