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Supporting Information

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1) Experimental Methods

Materials

Ammonium chloride (Fisher, ACS Grade) and lithium triflate [LiOTf] (Sigma-Aldrich, 99.995%) were used as received. Ethanol (Fisher Scientific, Absolute, ACS Grade), tetrahydrofuran [THF] (Sigma-Aldrich, anhydrous, inhibitor-free, 99.9%), diethyl ether (Fisher Scientific, anhydrous, ACS grade), hexane (Sigma-Aldrich, mixture of isomers, 98.5%), acetonitrile (Sigma-Aldrich, anhydrous, 99.8%), dimethylsulfoxide [DMSO] (Fisher Scientific, anhydrous, ACS grade), and propylene carbonate (Sigma-Aldrich, anhydrous, 99.8%) were used as received. Copper (II) sulfate pentahydrate (Fisher Scientific, 98%) and Ethylenediaminetetraacetic acid, disodium salt [EDTA] (Invitrogen, 99%, 'Ultrapure') were used as received. Water was obtained from a Millipore system (18.2 MΩ cm). 5 mm NMR tubes were used in all NMR experiments (Norell, Standard Series). 1 cm optical glass cuvettes (Starna Cells Inc., Atascadero, CA) were used in UV-Vis/colorimetric experiments. Sodium salicylate (Sigma-Aldrich, 99%), sodium nitroprusside (Sigma-Aldrich, 99%), sodium hydroxide (Sigma-Aldrich, 99.9%) and sodium hypochlorite (Sigma-Aldrich, 4-4.99% aqueous solution) were used as received. Final concentrations of sodium hypochlorite after dilution were calculated assuming 5% mass/mass initial concentration. Analytes for both the NMR and colorimetric method were prepared in the reported concentrations by the dissolution of NH₄Cl and/or LiOTf into the appropriate solvent. Some solvents (e.g. hexanes, diethyl ether, propylene carbonate) required the addition of a co-solvent (ethanol and/or water) in order to fully dissolve NH₄Cl and/or LiOTf.

NMR Method (Frequency-Selective Pulsed Gradient Spin Echo)

NMR samples were prepared by the addition of 500 μL analyte to an Eppendorf tube, followed by the successive addition of locking solvent (DMSO-d₆, unless otherwise noted), calibration standard (where needed), and acid (0.1 M H₂SO₄ unless otherwise noted). Care was taken to ensure complete mixing prior to the addition of the mixture to the NMR tube, which was necessary to observe sharp NH₄⁺ resonances.

NMR spectra were recorded on an Avance II Bruker NMR spectrometer operating at 900 MHz and at 25 °C except where noted. The instrument was equipped with a TCI cryoprobe and 16-sample sample changer. A frequency-selective pulse gradient spin echo sequence (See Figure S2) consisting of a hard 90° pulse followed by a gradient – selective 180° – gradient echo pulse sequence was employed except where noted.¹ This sequence is implemented in Bruker Topspin 3.2 as 'selgpse'. In a typical experiment 128 k complex points were recorded for each spectrum with the carrier frequency set to the hydroxyl resonance of ethanol (approximately 4.82 ppm) and the spectral width set to 16 ppm. The recycle and acquisition delays were 1.5 sec and 2.27 sec, respectively, for a total relaxation delay of 3.77 sec. The number of scans ranged from 16 for samples with ammonia at 100 μM concentrations to 1024 scans for samples with ammonia at near or sub-micromolar concentrations. The gradient pulses were applied as the positive half of a sine wave form defined by 100 points for 1 millisecond at a strength of 2.5 Gauss/cm. The 180 degree shaped pulse was applied as a Gaussian wave form (Bruker shape file Gaus1_180r.1000) defined by one thousand points for 1500 microseconds. The shaped

pulse was located near the ammonia and reference standard signals by shifting it 2.67 ppm downfield from the carrier frequency. Because of the non-uniform excitation profile, it was important to maintain the same carrier frequency between spectra compared quantitatively. The phase of hard 90° pulse and shaped 180° pulses were { x x y y -x -x -y -y } and { y, -y }, respectively and the phase of the receiver was { x x -y -y x x y y }.

The data were processed using either Topspin (version 3.2, Bruker Biospin Inc, Billerica, MA. USA) or MNova (version 12, Mestrenova Research S. L., Escondido, CA. USA) by baseline correction of the fid, line broadening (1 Hz), Fourier transformation, and phasing. In some cases, baseline distortions were observed. The distortions were corrected by converting the data from digital to analog form, re-creating the first twelve to thirty-two points by back linear prediction, and processing as described. Prior to integration, the baseline in the region that contained the signals of interest (8 – 6.8 ppm) was adjusted to zero using algorithms supplied within the processing programs. Chemical shifts were referenced to tetramethylsilane (TMS) in non-aqueous solvents and trimethylsilylpropionic acid (TSP) in water. For each sample, the concentration of the ammonium ion was determined by calculating the ratio of the area under the ammonium peak and that of the standards (a synthetic standard generated using the ERETIC2 routine; or chloroform, 1,3,5-trimethoxybenzene, or hydroquinone) and comparison to a standard curve. ERETIC refers to ‘Electronic REference To access In vivo Concentrations’, a method developed to generate a repeatable, synthetic, NMR signal for the purpose of calibration of analyte concentration.^{2,3} A version of this method, ERETIC2, implemented in Topspin 3.2 based on the PULCON method, was used herein.⁴ We note that the MNova qNMR package was also capable of efficiently quantifying NH₃ concentrations using a synthetic signal. Because the relaxation delay of 3.77 sec is less than the time needed for full recovery of the magnetization of the standards (usually 5 T1s), it was important to develop and compare the actual data to a standard curve developed under similar experimental conditions when using internal chemical standards. The effective measured T1 time of the NH₄⁺ resonance in EtOH was found to be 183 ms. Effective T1 time is reported because the measured T1 may be due to exchange with solvent. Use of the ERETIC2 standard was found to be advantageous because it did not require consideration of chemical calibration standard T1 time (measured CHCl₃ T1=5.72 s in 40 μM CHCl₃ in EtOH solution), particularly in light of the short NH₄⁺ T1 time, and is recommended where possible.

Electrochemical measurements (Figure 3c) were performed using an SP-300 potentiostat (Bio-Logic Science Instruments SAS) according to a previously reported method.⁵ Lithium triflate was used as a supporting electrolyte in lieu of lithium perchlorate as reported in reference 5.

NMR Method (Frequency-Selective Pulsed Gradient Spin Echo) (Tutorial Description)

The frequency-selective PGSE NMR method described herein can be readily applied via a simple chemical manipulation described below. After attempting N₂ electroreduction in an electrolyte, take a 500 μL aliquot of the electrolyte and add it to a clean glass container. Add 25 μL DMSO-d₆ to the electrolyte followed by 50 μL of an aqueous 0.5 M H₂SO₄ solution. If the electrolyte solvent is immiscible with H₂O, an additional small volume of ethanol can be added to promote miscibility. The addition of H₂SO₄ may also drive precipitation of the supporting electrolyte.

Avoiding precipitate transfer to the NMR tube is advantageous but not critical. Transfer the prepared electrolyte to an NMR tube. The recommended pulse sequence and selective 180° pulse shape are readily available in the Bruker TopSpin software ('selgspe' and 'Gaus1_180r.1000' respectively), but should be available on most modern NMR instruments. No internal chemical standard is required as both Bruker TopSpin and the and MNova 12 software have routines capable of determining an unknown analyte concentration after defining a reference spectrum with a known analyte concentration.

Colorimetric Method

UV-Visible spectra were taken using a Cary 300 BIO instrument. Spectra were obtained between 800nm and 400nm with a scan rate of 300 nm/min. Analytes were prepared variously by dilution of the electrolytes by volume with pure ethanol or water to a total volume of 2 mL in order to promote homogenous mixing of all solution components and color development (see Table S1, 'Solvent Conditions'). For example, a propylene carbonate-based standard analyte (e.g. 10 μ M NH₄Cl + 0.1 M LiOTf in propylene carbonate solution) was prepared by the addition of 1 mL propylene carbonate analyte to 0.5 mL water and 0.5 mL EtOH (50% electrolyte, 25% EtOH, 25% H₂O). The necessary solution volumes of each reactant were added to a 2 mL analyte sample volume in order to achieve the reactant concentrations reported in Table S1. Suggested concentrations of reactant solutions are as follows: sodium salicylate (2.5 M), sodium hydroxide (1.0 M), sodium nitroprusside (0.2 M), sodium hypochlorite (5% mass/mass in solution). Samples were collected in cuvettes made of optical glass to minimize incompatibilities with polymer-based, disposable cuvettes. Absorbances were reported at the λ_{max} (between 660nm-670nm) associated with the dicarboxylated indophenol product. Absorbance values were corrected with respect to a background spectrum composed of identical electrolyte and reaction conditions, but no measurable NH₃.

2) 1D NOESY Suppression Method

Although the frequency-selective pulsed gradient spin echo method offers unparalleled ease-of-use and versatility, the acquired spectra only identifies a small part of the compounds present in the sample. From a quantification point-of-view, this may be sufficient, but nevertheless suppressing only the solvent peaks offers more information about the sample composition, which can potentially be useful for studies into degradation and reaction processes taking place during the synthesis of NH_3 . For suppression of three solvent peaks (e.g. ethanol) the 1D NOESY pulse sequence needed minor modifications as severe baseline distortions is introduced when saturating three signals with one shaped pulse. Using a two-channel systems we found that the best option was to discard ^{13}C decoupling and applying a double-selective shaped pulse (around 50 ms) on one channel saturating both the CH_2 (on-resonance) and CH_3 (off-resonance) multiplets, while the other channel employs a standard cw-presaturation at the OH resonance. For a three-channel system the ^{13}C decoupling is included and offers a small but significant improvement in the overall solvent suppression. With this method, reduced signal-to-noise as compared to the frequency-selective gradient spin echo method in the same duration were observed (approx. 20% S/N improvement for frequency-selective PGSE compared to suppression), but minor signals originating from secondary compounds in the sample were still observed. Only minor J-modulation is introduced during the saturation pulse and reliable integrals can be extracted for both NH_4^+ and an added internal standard. Thus, a quantitative analysis is still possible. The pulse sequence can be used both manually and in automation, although it ultimately requires (considerably) more setup time as compared to the frequency-selective PGSE method.

Spectra obtained using the NOESY method were collected on a Bruker Avance III spectrometer operating at a ^1H frequency of 600.165 MHz equipped with a Bruker broadband Smart Probe (BBFO) to compare the frequency-selective pulsed gradient spin echo and the 1D NOESY suppression techniques (Figure S1) reported previously.⁶ In this comparison, the frequency-selective PGSE used the following parameters: ns=256, d1=0.8 s, AQ=1.36, TD=32K, p12(refocus) = 1500 μs centered at 7.46 ppm, o1p=5.242 ppm. The 1D NOESY suppression technique used the following parameters: ns= 256, d1 = 0.8 s, AQ = 1.36 s, TD = 32K. In THF, p23 was set to affect both THF-signals (3.56 ppm and 1.71 ppm), while also applying cw-presaturation (using F2) at 1.71 ppm. O1p = 3.56 ppm.

Figure S1. NMR spectrum of a 0.1M LiClO₄ in 1% EtOH/THF electrolyte after executing previously reported electrochemical N₂ reduction technique using ¹⁵N₂.⁵ (blue) NMR spectrum obtained using 1D NOESY suppression technique (NH₄⁺ S/N Ratio: 432). (red) NMR spectrum obtained using a frequency-selective pulsed gradient spin-echo pulse sequence (NH₄⁺ S/N Ratio: 561).

3) Pulse sequence diagram

Figure S2. Frequency-selective PGSE sequence used to selectively observe NH_4^+ resonance in non-deuterated electrolytic solutions. A hard 90° pulse followed by a gradient – selective 180° pulse – gradient echo pulse sequence was employed. ¹H refers to the observed channel and G_x refers to the gradient channel. *Selective 180° pulse shape defined as a Gaussian wave form using Bruker shape 'Gaus1_180r.1000'. The phase of hard 90° pulse and shaped 180° pulses were { x x y y -x -x -y -y } and { y, -y }, respectively and the phase of the receiver was { x x -y -y x x y y }.

4) Various pulse sequences NMR spectra

Figure S3. NMR spectrum of 100 μM NH_4^+ /0.1 M LiOTf in EtOH using various pulse sequences. The entry for each pulse sequence in the Bruker Pulse Program Catalogue is listed in parentheses. A) Standard hard 90° pulse. No NH_4^+ resonance observed. B) Frequency-selective PGSE. NH_4^+ resonance and chemical standard resonance readily observed. C) Simple selective excitation pulse. NH_4^+ resonance observed, but phase information degraded and demonstrated by inverted chemical standard reference at 7.7ppm. D) Presaturation pulse. No NH_4^+ resonance observed, artifacts present in region of NH_4^+ chemical shift. *Note that a presaturation pulse was applied to each of the three EtOH resonance peaks in turn while using this pulse sequence instead of the multichannel 1D NOESY suppression demonstrated in previously reported work. E) Jump and return pulse. No NH_4^+ resonance observed, artifacts present in region of NH_4^+ chemical shift.

5) 1 μM NH_4^+ in EtOH, 1 hr acquisition, NMR detection, 900 MHz NMR

Figure S4. NMR spectrum of 1 μM NH_4^+ in EtOH detected using a 900 MHz NMR instrument equipped with a cryocooled probe. Total spectrum acquisition time was 59 minutes and 59 seconds. Acquisition time and recycle delay (D1) were each reduced to ~ 1 second in order to maximize the rate of data collection. Peaks seen to the left of the NH_4^+ resonance were assigned as impurities and were consistently present in spectra in which 1 μM NH_4^+ was resolved.

6) 10 μM NH_4^+ in EtOH, 25 min acquisition, NMR detection, 600 MHz NMR

Figure S5. NMR spectrum of 10 μM NH_4^+ in EtOH detected using a 600 MHz Varian INOVA NMR instrument equipped with a room temperature probe (5mm HCN) using frequency-selective PGSE. NMR parameters were as follows: TD=64K, AQ=2.0 s, ns=128, gain=40, d1=1 s, pw=8.3 μs , transmitter offset from EtOH OH resonance: 2.43ppm. Total spectrum acquisition time was ~25 minutes.

7) Frequency-selective PGSE pulse sequence solvent compatibility

Figure S6. NMR spectra of $100\ \mu\text{M}\ \text{NH}_4^+$ in THF, Et₂O, DMSO, Propylene carbonate, hexanes, acetonitrile, ethanol, and water.

8) Calibration curve for NH_4^+ in H_2O

Figure S7: Calibration curve generated via NMR for the determination of NH_4^+ concentration in water. Measurements of the ratio of a NH_4^+ :standard integral were taken in triplicate at 183, 91, 44, and 9 μM concentrations. The dotted black line represents the fitted curve. The standard deviation for each triplicate measurement was less than or equal to 3% of the mean value observed. The standard was generated synthetically using the ERETIC2/PULCON method. Note that the slope of the calibration line depends on the concentration of the chosen NH_4^+ standard.

9) Shaped Pulse Frequency Dependence

Figure S8. NMR spectrum of 100 μM NH_4^+ and $\sim 50 \mu\text{M}$ CHCl_3 in EtOH detected using various shaped pulse center frequency parameters in the frequency-selective pulsed gradient spin echo pulse sequence routine.

10) Effect of paramagnetic ion on NH_4^+ signal

Figure S9: NMR spectra of analytes composed of A) 100 μM NH_4^+ in H_2O , B) 100 μM NH_4^+ and 1 mM CuSO_4 in H_2O , C) 100 μM NH_4^+ , 1 mM CuSO_4 , and 1 mM EDTA in H_2O . Panel D) is each of the spectra in panels A), B), and C) overlaid.

In order to determine the effect of paramagnetic species on the quality of the NH_4^+ signal using the frequency-selective PGSE NMR method, we added a Cu(II) species (1 mM CuSO_4) to a solution containing 100 μM NH_4^+ in H_2O . We observed no significant difference in the spectra between these two analytes upon addition of CuSO_4 (Figure S9a and S9b). We additionally collected the NMR spectrum of an analyte containing 100 μM NH_4^+ , 1 mM CuSO_4 , and 1 mM EDTA. EDTA can be used to sequester paramagnetic species in solution to improve NMR spectra, and while EDTA was ultimately not needed to improve the NH_4^+ signal in Figure S9, it may be valuable for other paramagnetic impurities and did not reduce the spectrum quality (Figure S9c). If paramagnetic species are a significant concern for an analyte, we suggest adding a small amount of NH_4^+ to the analyte to confirm that the NH_4^+ signal can be observed in the presence of the paramagnetic species.

11) H₂SO₄ concentration/'pH' dependence

Figure S10. NMR spectra of 100 μ M NH₄⁺ in EtOH at various H₂SO₄ concentrations. Linewidth at half max for 0.1M H₂SO₄ = 5.9 Hz. Linewidth at half max for 0.0001 M H₂SO₄ = 13.0 Hz. No NH₄⁺ resonance was observed when no H₂SO₄ was added.

12) NH_4^+ resonance peak shape dependence on locking solvent

Figure S11. NMR spectra of $10 \text{ mM } \text{NH}_4^+$ in EtOH using (A) $0.5 \text{ M } \text{D}_2\text{O}$ as a deuterated locking solvent and (B) $0.5 \text{ M } \text{CD}_3\text{CN}$ as a deuterated locking solvent. The smaller 1:1:1 triplet downfield of the larger triplet in (A) was assigned to a NH_3D^+ isotopologue formed via H/D exchange. The broadening of the ammonium resonance in the presence of exchangeable deuterium sources demonstrated the value of selecting locking solvents that did not have exchangeable deuterium. Spectra were taken on 600 MHz Varian INOVA equipped with a room temperature probe. We also note here that the use of a cryoprobe may be advantageous in promoting use of various deuterated locking solvents as the concentration of deuterium needed to generate adequate signal locking is reduced.

13) Colorimetric (Berthelot) NH_3 detection characterization

The extinction coefficient, reaction rate, color stability, salt dependence, and illumination dependence of the salicylate-based ammonia detection reaction were studied in four common electrochemical solvents (See '*Colorimetric Methods*' section of the SI for experimental details). Table S1 displays the reactant conditions applied in each solvent (THF, propylene carbonate, ethanol, and water) as well as comparisons of the analyte responses under various reaction conditions.

Table S1: Reaction conditions and results for the salicylate-based ammonia detection method executed in THF, propylene carbonate, ethanol, and water-based electrolytes. Each electrolyte solution contained 100 μM NH_3 and 0.1M LiOTf prior to dilution and were developed under lab illumination conditions except where noted.

^a Electrolytes were diluted percent by volume with H_2O or EtOH to promote rapid, reproducible, homogeneous reaction solutions. Each analyte solution was also diluted with a small amount of water as a result of using aqueous reactant solutions.

^b Reaction time is defined as the time point at which the maximum salicylate-based ($\lambda_{\text{max}}=660\text{-}670\text{ nm}$) absorbance was observed (A_{max}). Measurements were taken at 15 min, 30 min, 45 min, 60 min, 90min, 2 hr, 4 hr, 8 hr, 12 hr, and 24 hr.

^c Color stability was defined as the length of time after the observation of A_{max} that the measured absorbance was within 5% of that maximum value.

^d Extinction coefficient is reported at the λ_{max} for solutions containing 0.1M LiOTf and stored under laboratory illumination conditions.

^e Light sensitivity is defined as the percent difference in A_{max} between an analyte stored under ambient laboratory illumination conditions and one stored in the dark. Values are defined with respect to the illuminated analyte (e.g -10% suggests a 10% decrease in the dark sample A_{max} with respect to the illuminated sample).

^f Supporting electrolyte sensitivity is defined as the percent difference in A_{max} between an analyte composed of 100 μM NH_3 and 0.1M LiOTf against one composed of 100 μM NH_3 . No color development was observed for the propylene carbonate electrolyte when no supporting electrolyte was present. Values are defined with respect to the analyte containing 0.1M LiOTf.

	THF	Propylene Carbonate	Ethanol	H_2O
Sodium Salicylate	0.25 M	0.25 M	0.25 M	0.25 M
NaOCl	0.02 mM	0.02 M	0.02 M	0.02 M
NaOH	None	None	0.01 M	0.01 M
$\text{Fe}(\text{CN})_5(\text{NO})^-$	$8 \times 10^{-4}\text{ M}$	$8 \times 10^{-4}\text{ M}$	$4 \times 10^{-3}\text{ M}$	$4 \times 10^{-3}\text{ M}$
Solvent conditions ^a	50% electrolyte 50% H_2O	50% electrolyte 25% H_2O 25% EtOH	50% electrolyte 50% H_2O	100% electrolyte
Reaction time ^b	2 hr	4 hr	90 min	30 min
Color Stability ^c	>12 hr	>12 hr	>12 hr	>12 hr
Extinction coefficient ^d ($\text{M}^{-1}\text{ cm}^{-1}$)	4.4×10^3	3.4×10^3	1.47×10^4	1.45×10^4
Light sensitivity ^e	Minimal	~ 40%	Minimal	Minimal
Supporting ^f electrolyte sensitivity	~-50%	Critical	< -10 %	Minimal

Sodium salicylate was chosen over phenol as the phenolic precursor for the reaction after the observation of a penetrating odor when using phenol as the reactant in non-aqueous solvents. This is consistent with previous literature reports that suggest that ortho-chlorophenol can form during the reaction with phenol.⁷ The conditions needed to observe ammonia colorimetrically (indirectly as dicarboxylated indophenol) were similar but not identical between solvents, particularly with respect to the necessity of hydroxide addition, which was not useful in either THF or propylene carbonate. The color stability and illumination sensitivity varied between electrolyte and reaction conditions and the reaction time varied substantially between electrolytes. The salt sensitivity also varied, but did not preclude the use of electrolytes. It is interesting to note that the presence of supporting electrolyte was necessary to observe the development of color in propylene carbonate. The large extinction coefficient ($>500 \text{ M}^{-1} \text{ cm}^{-1}$) in each electrolyte is indicative of the high sensitivity of this method (See Figure S12 and S13).

The key conclusion is that ammonia is directly detectable in any of the four electrolytes using the Berthelot method, but that careful control of the reaction conditions must be executed if using as an analytical technique in non-aqueous electrolytes. Effectively all of the analytical parameters varied with changes in the reaction conditions, and thus calibration curves that reflect the exact electrochemical conditions under which the ammonia will be detected must be developed prior to using this method.

(A)

(B)

Figure S12. Absorbance at $\lambda_{\max}$ (660-670 nm) with respect to total reaction time for 100 μM NH_3 dissolved in various electrolytes and under various reaction conditions. Reaction conditions were varied with respect to the presence or absence of 0.1 M LiOTf in the analyte (salt/no salt) and with respect to analyte development under laboratory illumination or under dark conditions (light/dark). Data is reported for electrolytes/solutions in A) ethanol, B) propylene carbonate, C) THF, and D) water. Panels on the right are zoomed in versions of the panels on the left. Error bars represent the total standard deviation about the mean absorbance value. $\lambda_{\max}$ was observed to blue-shift slightly with addition of 0.1 M LiOTf when compared to salt-free solutions.

Figure S13. Calibration curves for the colorimetric detection (Berthelot method) of NH_3 in a 0.1 M LiOTf electrolytic solution developed under laboratory illumination in a) ethanol, b) propylene carbonate, c) THF, and d) water. Derived extinction coefficients are reported in Table S1 and can be seen. Absorbance values used herein were corrected with respect to a background spectrum composed of identical electrolyte and reaction conditions, but no measurable NH_3 .

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