Ion Chromatography Based Isolation and Quantitation of Chloronitramide Anion in Drinking Water

Jason A. Thornhill and Julian L. Fairey
Department of Civil Engineering, University of Arkansas, Fayetteville, AR 72701

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Chloronitramide anion (Cl–N–NO_2^-) is a recently identified decomposition product of inorganic chloramines

- Chloramines are used to disinfect tap water of ~113 M in the US alone
- Cl–N–NO_2^- forms at concentrations up to ~130 μg•L^{-1}
- Current analytical method for quantitation uses HILIC–UHRMS (Hydrophilic Interaction Liquid Chromatography–Ultrahigh Resolution Tandem Mass Spectrometry)
- Need simpler quantitation method for broad occurrence studies

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Chloronitramide anion is a decomposition product of inorganic chloramines

JULIAN L. FAIREY, JULIANA R. LASZAKOVITS, HUONG T. PHAM, THIEN D. DO, SAMUEL D. HODGES, KRISTOPHER MCNEILL, AND DAVID G. WAHMAN

Authors Info & Affiliations

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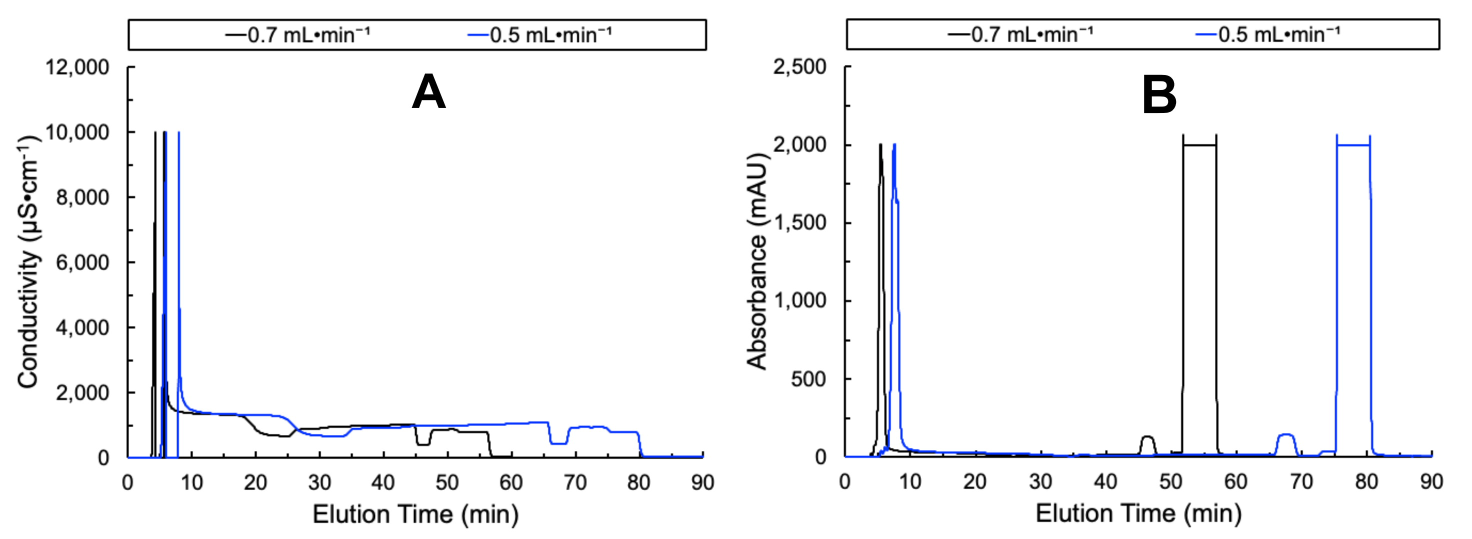
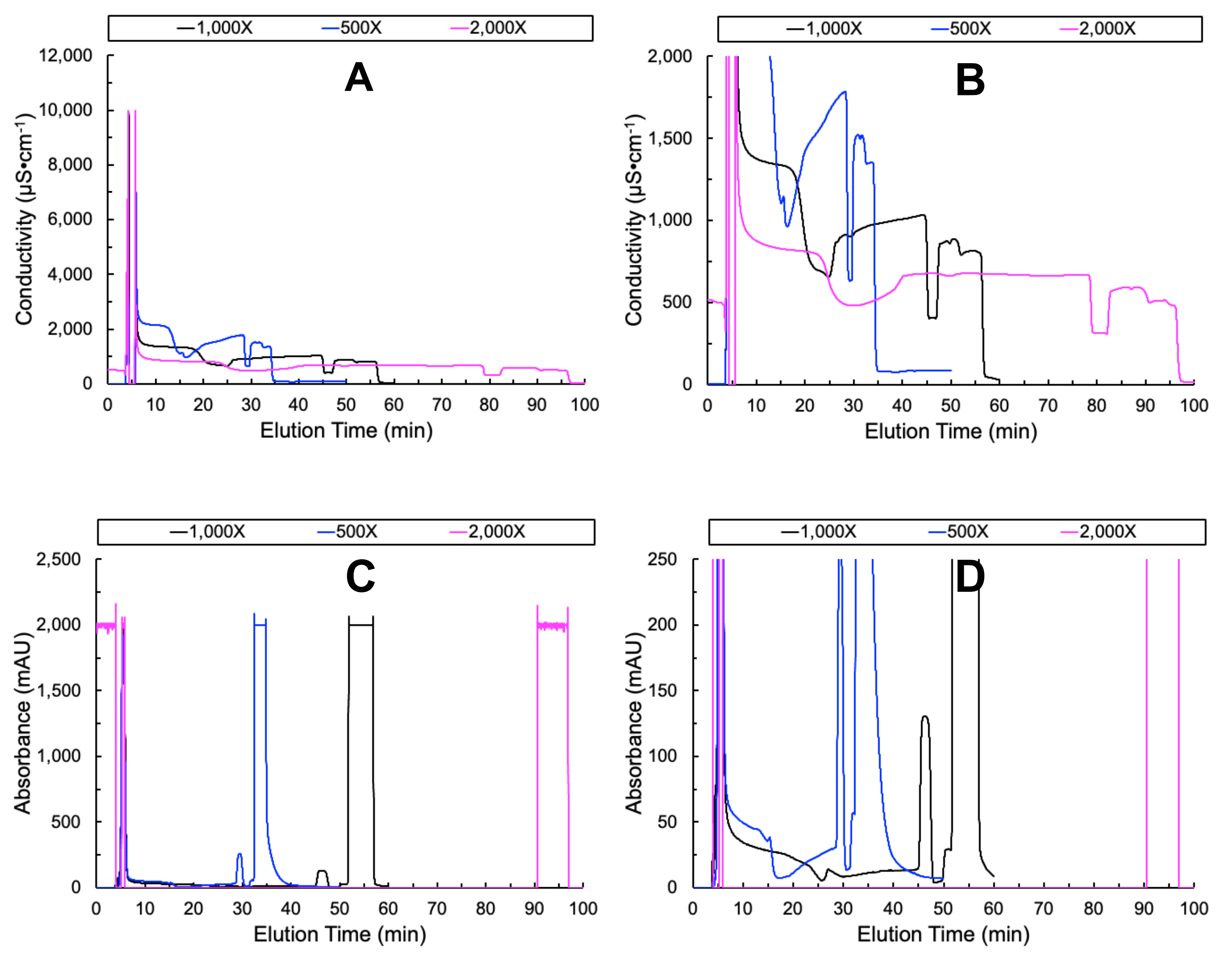
Incomplete Cl–N–NO_2^- Isolation at 0.5 mL•min^{-1}

- Two flowrates
  - 0.5 and 0.7 mL•min^{-1}
- A: Baseline does not reach zero
  - Incomplete Cl–N–NO_2^- separation from common anions
- B: UV_{254} shows increasing elution time with decreasing flowrate by ~30 min
  - 0.7 mL•min^{-1} selected for isolation



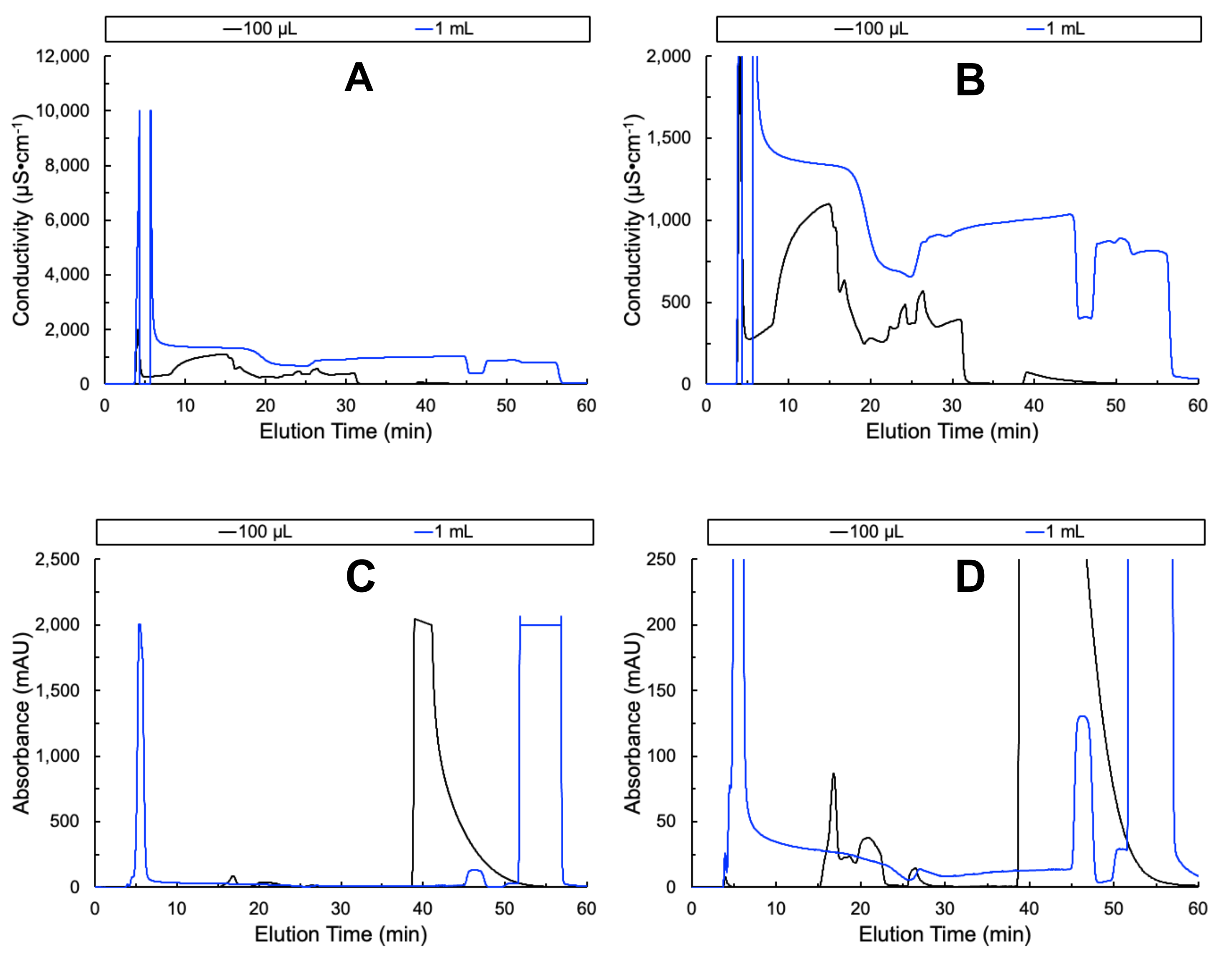
Incomplete Cl–N–NO_2^- Isolation with 1 mL Injection Loop

- Three eluent strengths
  - 1000X, 500X, 2000X
- B: Baseline does not reach zero
  - Incomplete Cl–N–NO_2^- separation from common anions
- C & D: UV_{254} shows increasing elution time with decreasing eluent strength by ~60 min
  - 1000X selected for isolation



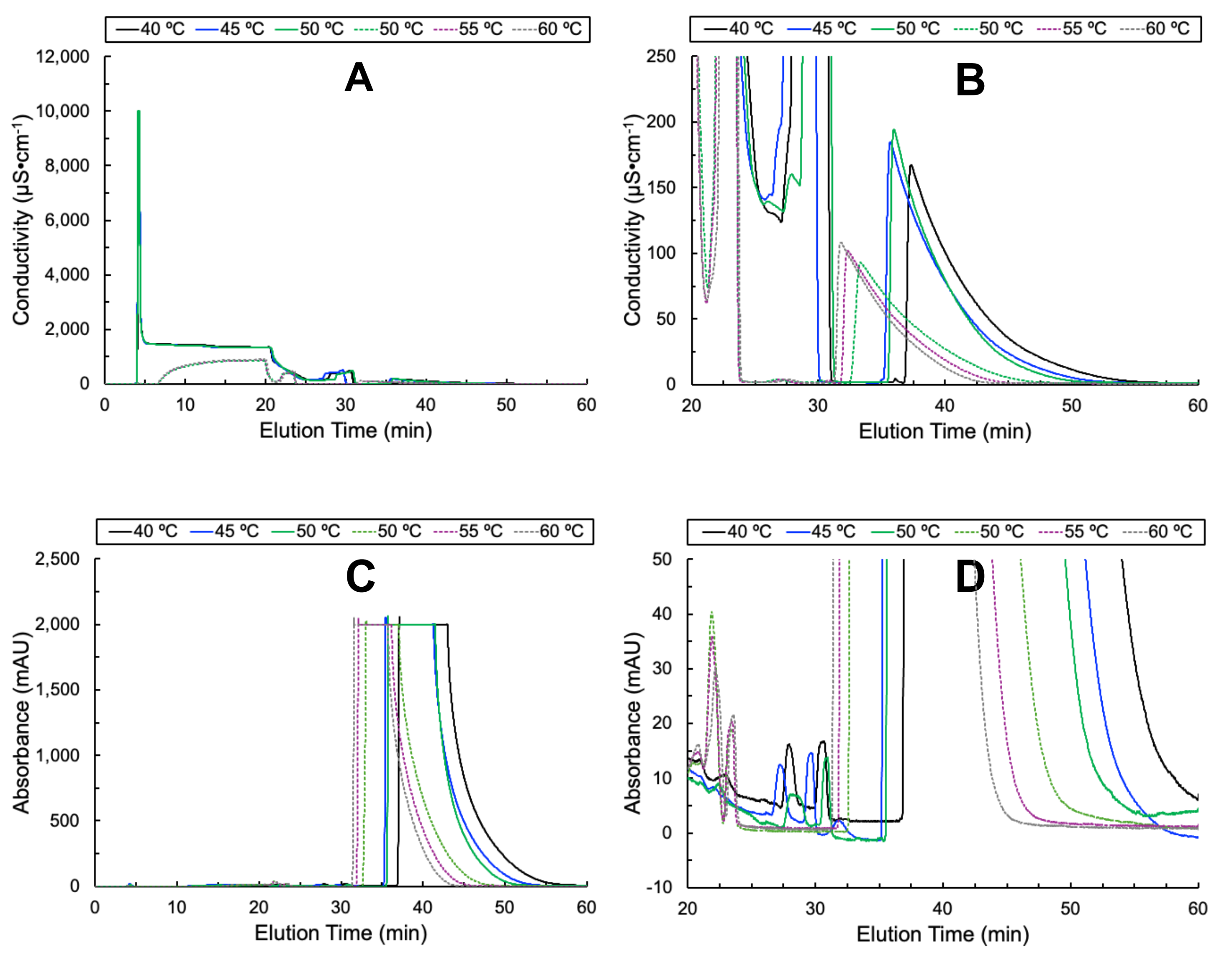
Complete Cl–N–NO_2^- Isolation with 100 µL Injection Loop

- C: Cl–N–NO_2^- elutes ~40 min with 100 µL injection loop
- B: Baseline reaches zero prior to 40 min with 100 µL injection loop
  - Complete separation
- B: 1 mL injection loop overloading column
  - 100 µL injection loop selected for isolation



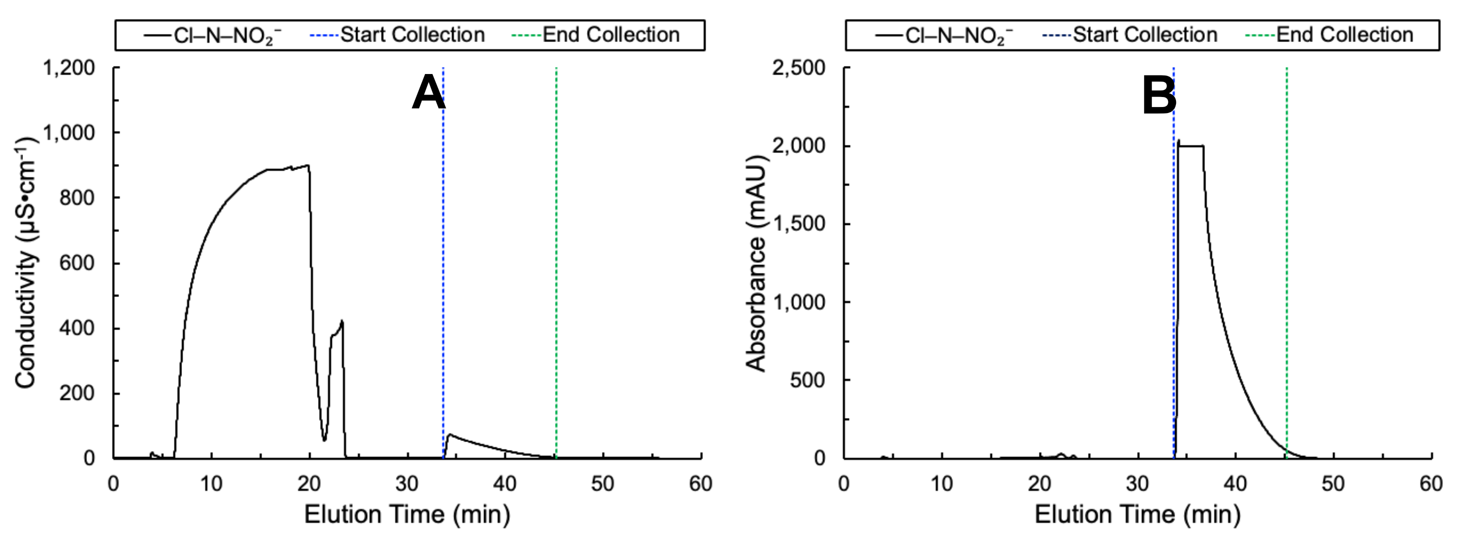
Decreased Elution Time with Increased Column Temperature

- B: $Cl–N–NO_2^{-}$ elutes ~32 & 38 min, depending on concentration
- B: Peak height increases with increasing column temperature
- B: Elution time decreases with increasing column temperature
- Higher temperature increases IC equilibration time by 30–60 min
- 50 °C selected for isolation



Collection Interval of Cl–N–NO_2^-

- A: IC–EC
  - Complete isolation from common anions
  - Start = 34 min
  - End = 45 min
- B: IC–UV_{243}
  - Collection start at peak front
  - Collection end after signal < 50 mAU

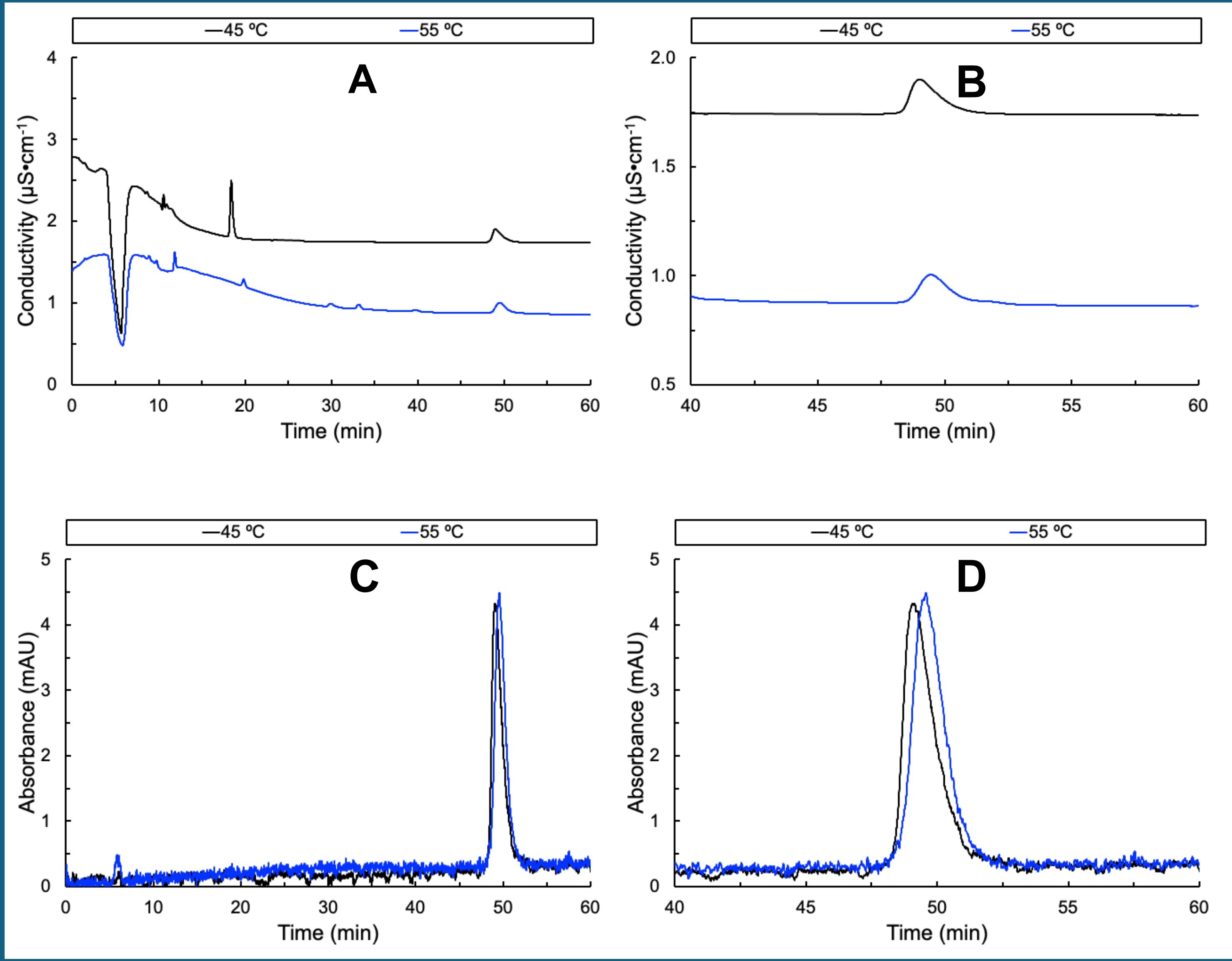


Cl–N–NO_2^- Isolation: IC Method

Isolation		
Model	Metrohm 850 Professional IC	
Injection Loop	100	μL
Column	Metrosep A Supp 7 – 250/4.0	
Temperature	50	°C
Flow Rate	0.7	mL•min^{-1}
Eluent	Metrohm A Supp 7 Eluent	
Eluent Strength	1000X	
Detectors	Metrohm IC Conductivity Detector	
	Metrohm 887 Professional UV/Vis Detector	
UV Wavelength	243	nm
UV Bandwidth	2	nm

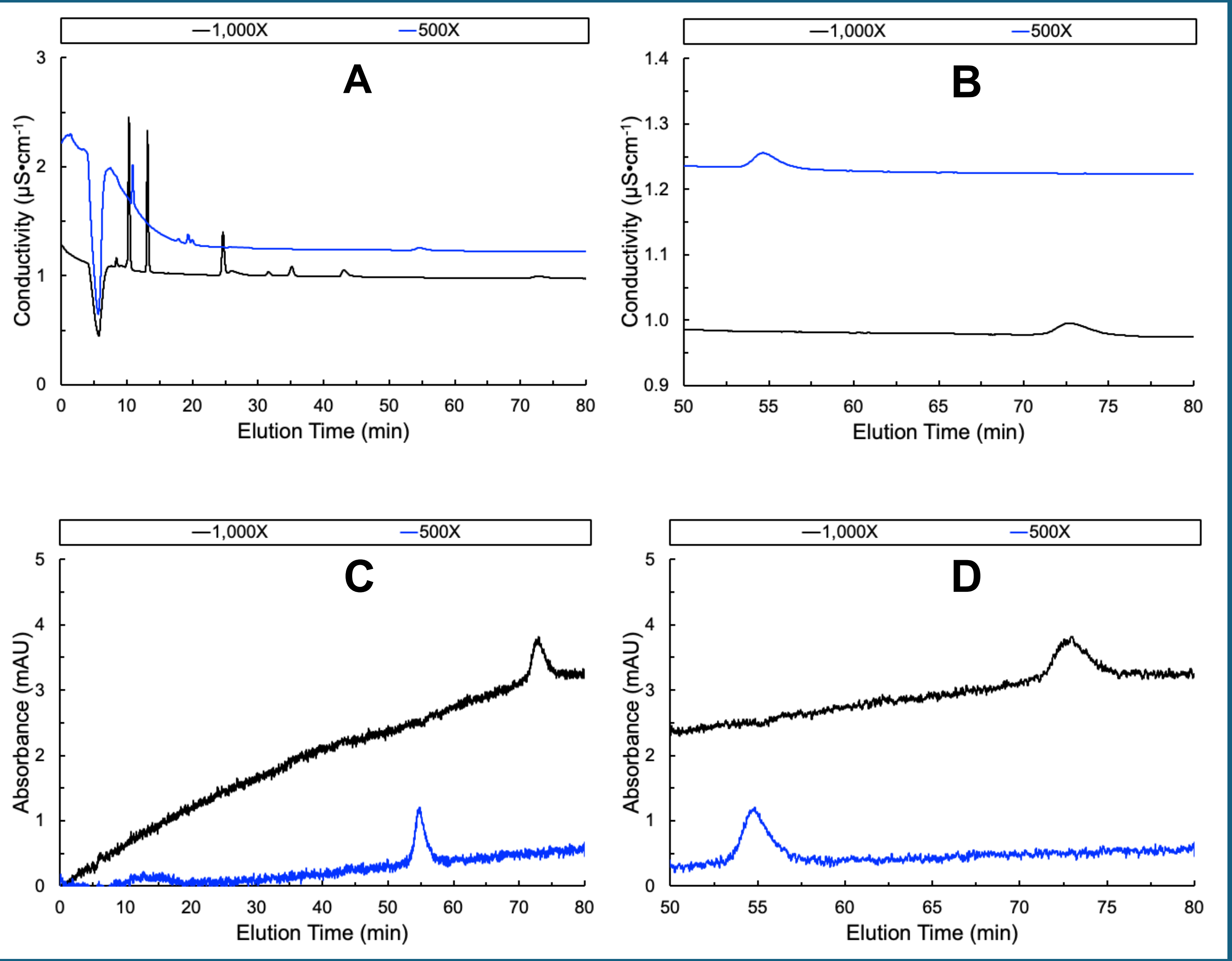
Cl–N–NO_2^- Quantitation: Minimal Impact of Column Temperature

- A & C: Cl–N–NO_2^- elution ~50 min with 1 mL injection loop
  - 1 mL injection loop used to maximize detection
- B & D: Cl–N–NO_2^- eluted ~50 min at 45 and 55 °C
- Column temperature does not impact elution time or peak height



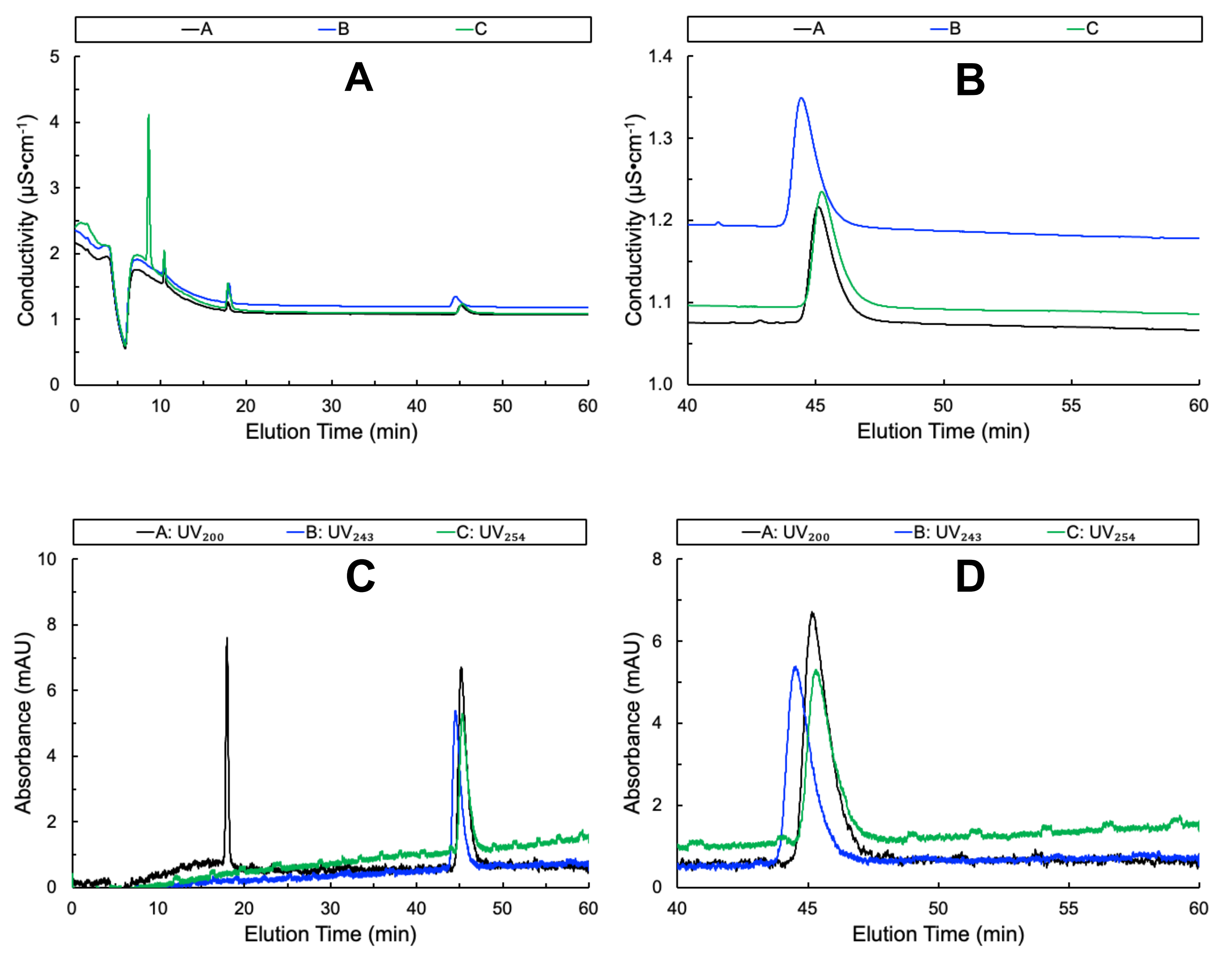
Cl–N–NO_2^- Elution Decreases with Increasing Eluent Strength

- A & C: Cl–N–NO_2^- elutes ~75 min with 1000X eluent and ~55 min with 500X eluent
- B & D: 500X eluent selected to increase throughput during quantitation



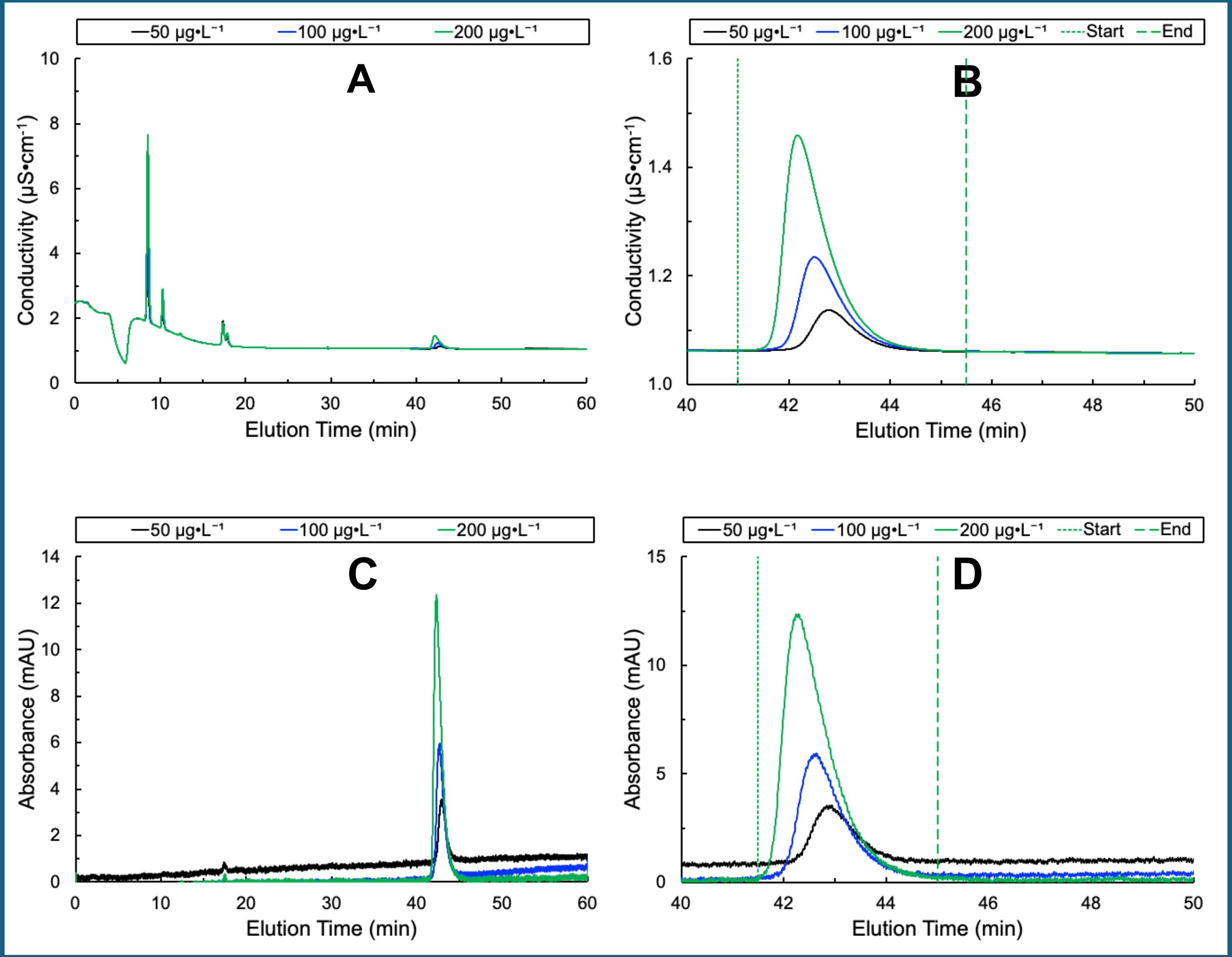
UV_{243} Selected for Cl–N–NO_2^- Quantitation

- A & C: Cl–N–NO_2^- elutes ~45 min
- B: No variation in peak height with triplicate injection
- C: UV_{200} excluded due to detection of other constituents (nitrate)
- D: Cl–N–NO_2^- UV molar absorptivity maxima at 243 nm selected for quantitation because S/N > 254 nm



Cl–N–NO_2^- Peak Tailing Necessitated Peak Area for Quantitation

- A & C: Cl–N–NO_2^- elutes ~43 min
- B & D: As concentration increases, peak tailing becomes more apparent
- B: IC–EC area taken 0.5 min prior to and following due to flat, noise-free baseline
- D: IC–UV_{243} taken at start and end of peak due to baseline noise



Cl–N–NO_2^- Quantitation: IC Method

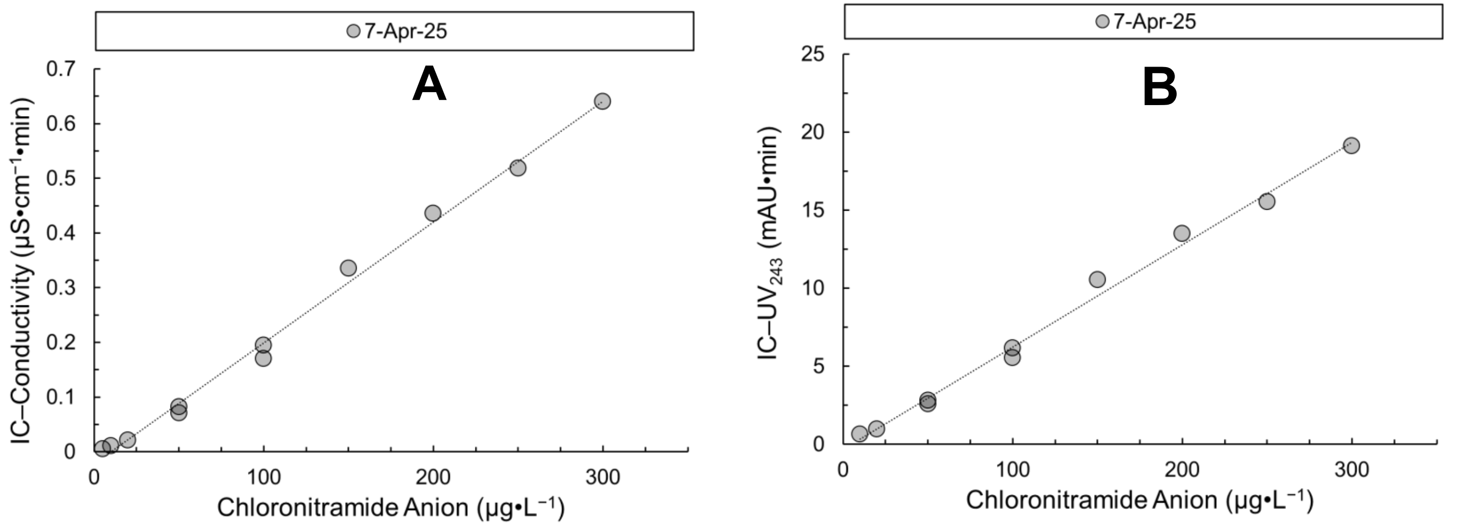
Quantitation		
Model	Metrohm 850 Professional IC	
Injection Loop	1	mL
Column	Metrosep A Supp 7 – 250/4.0	
Temperature	45	°C
Flow Rate	0.7	mL•min^{-1}
Eluent	Metrohm A Supp 7 Eluent	
Eluent Strength	500X	
Detectors	Metrohm IC Conductivity Detector	
	Metrohm 887 Professional UV/Vis Detector	
UV Wavelength	243	nm
UV Bandwidth	2	nm

Cl–N–NO_2^- Standard Curve by IC–EC and IC–UV_{243}

A. IC–EC
   - Standards range from 20–300 μg•L^{-1}

B. IC–UV_{243}
   - Standards range from 10–300 μg•L^{-1}

- Ten standard curves were made and those with $R^2 > 0.990$ averaged and used to determine concentrations



7-Apr-25	IC–EC	IC–UV_{243}
R^2	0.995	0.993
Slope	0.00226	0.0655
Y-intercept	-0.0313	-0.313

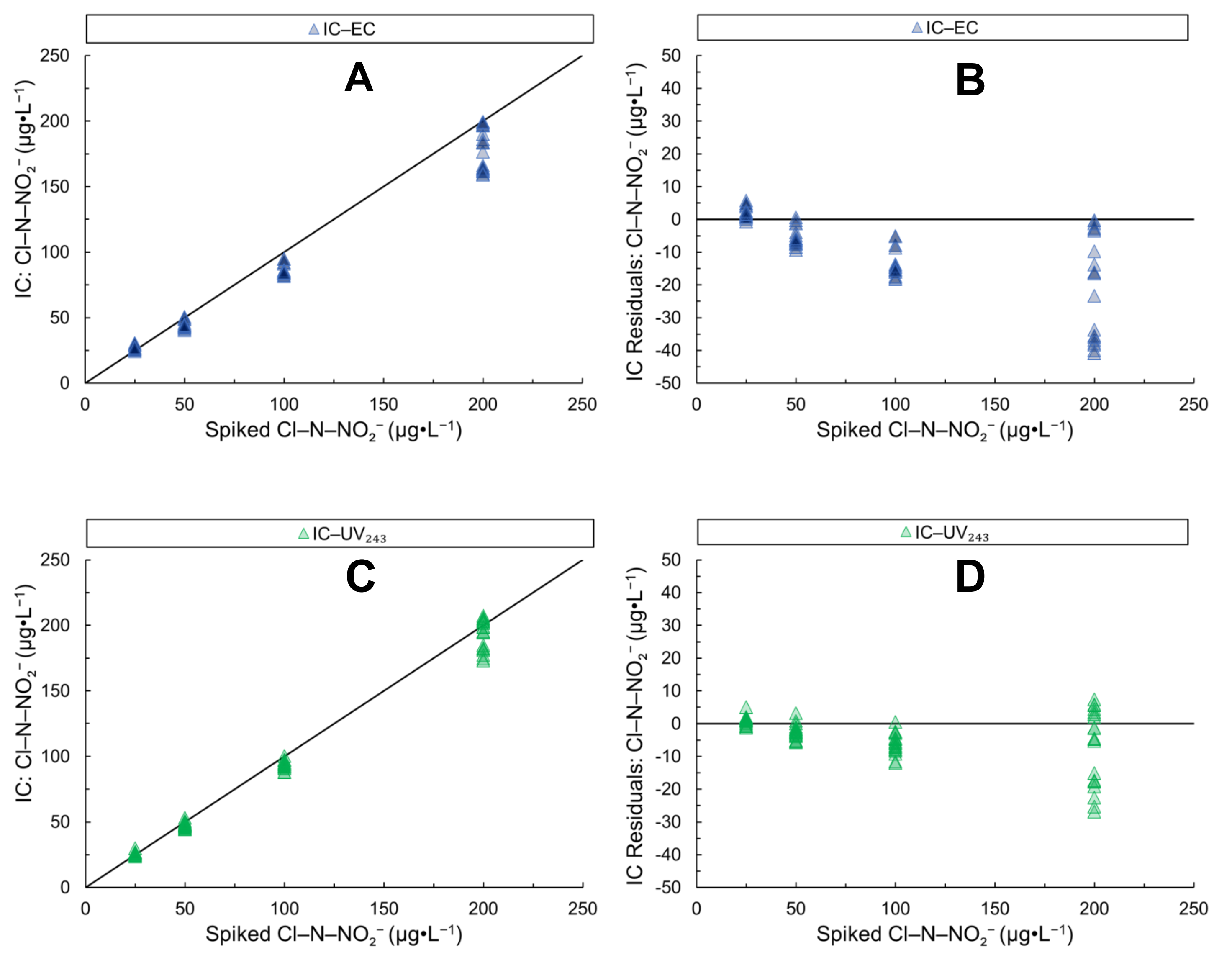
Cl–N–NO_2^- MDL, LOD, and LOQ

- MDL determined from EPA method
- IC–UV_{243} LOD and LOQ from blank determination
- IC–EC LOD and LOQ from linear regression
- IC based LOD and LOQ > HILIC–UHRMS
- IC–UV_{243} has lower MDL and LOQ than IC–EC

	MDL ($\mu g \cdot L^{-1}$)	LOD ($\mu g \cdot L^{-1}$)	LOQ ($\mu g \cdot L^{-1}$)
IC–EC	22.4	11.8	39.4
IC–UV_{243}	13.0	10.4	12.7
HILIC–UHRMS		0.17	0.58

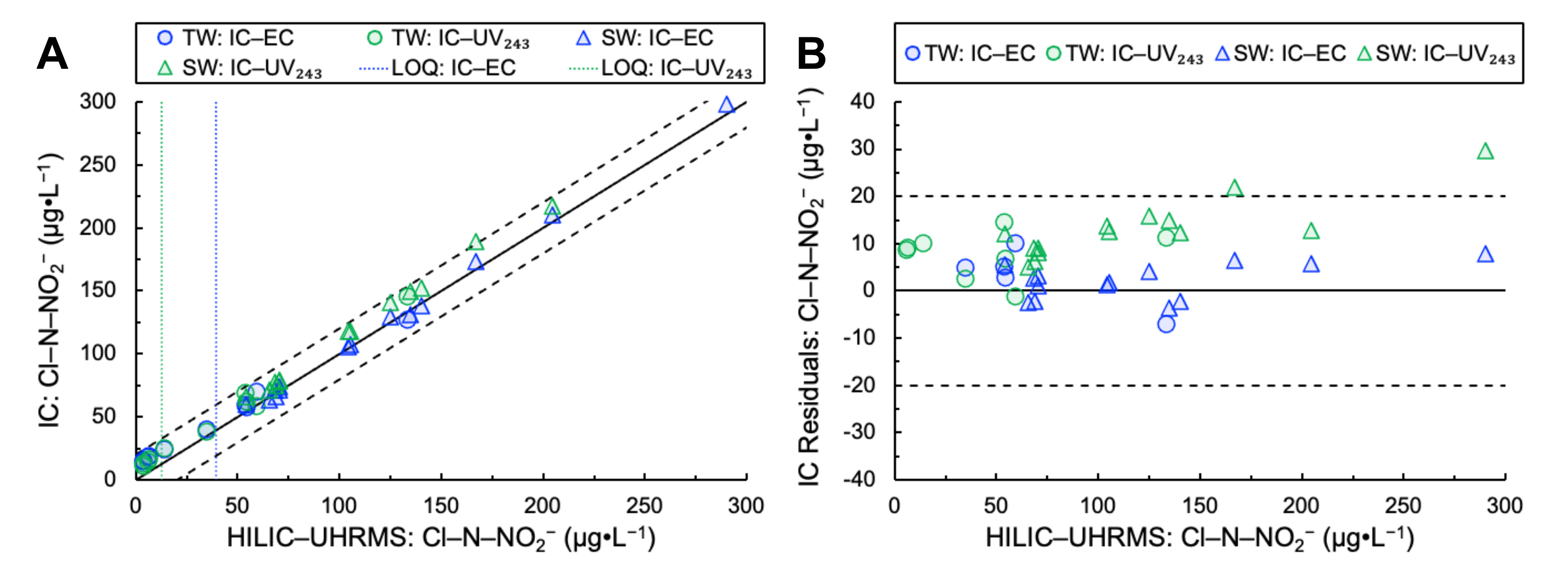
IC–UV_{243} has Lower Reproducibility Variation for Cl–N–NO_2^-

- Testing over 6 days
- A & B: IC–EC quantitation accurate at 25 & 50 µg•L^{-1} but had negative residuals at 100 & 200 µg•L^{-1} (< ~20 %)
- C & D: IC–UV_{243} quantitation like IC–EC, although residuals were lower at high concentrations (< ~15 %)



Cl–N–NO_2^- Quantitation in Tap Waters and Synthetic Waters

- A: Comparison between IC methods and HILIC–UHRMS
- B: Residuals calculated from IC minus HILIC–UHRMS
- Black line is 1:1 line and dashed lines are ± 20 μg•L^{-1}
- IC–EC residuals are closer to zero compared to IC–UV_{243}



Conclusions and Future Work

Conclusions:

- IC–EC LOQ = 39.4 µg•L^{-1} with reproducibility of 20% for lab-grade waters and within ~10 % of HILIC–UHRMS
- IC–UV_{243} LOQ = 12.7 µg•L^{-1} with reproducibility of 15% for lab-grade waters and within ~50 % of HILIC–UHRMS

Future Work:

- Repeatability testing with water matrices spiked with Cl–N–NO_2^- to determine matrix effects
- Formation conditions for Cl–N–NO_2^- in drinking water systems