

Analysis of Common Anions by Unsuppressed Conductivity

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This project was a cooperative effort between
Shimadzu Scientific Instruments, Inc., Columbia, MD
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Why Unsuppressed Ion Chromatography?

- Anions are typically analyzed by suppressed conductivity
- Suppressors are expensive and somewhat fragile
- Demand for anion analysis is limited in some markets
 - Ion Chromatograph (IC) sits idle at times
- Demand for HPLC analysis is limited in some markets
 - HPLCs sometimes sit idle for weeks in small labs
- Unsuppressed IC allows an HPLC to be a dual use instrument
 - Addition of a conductivity detector is less expensive than a dedicated IC
 - No need for dedicated instruments in small labs
- UV allows analysis of nitrite/nitrate in the presence of high chloride
 - Use of a UV transparent mobile phase
 - Connected in series with conductivity detected

Mobile Phase, Column, and Conditions

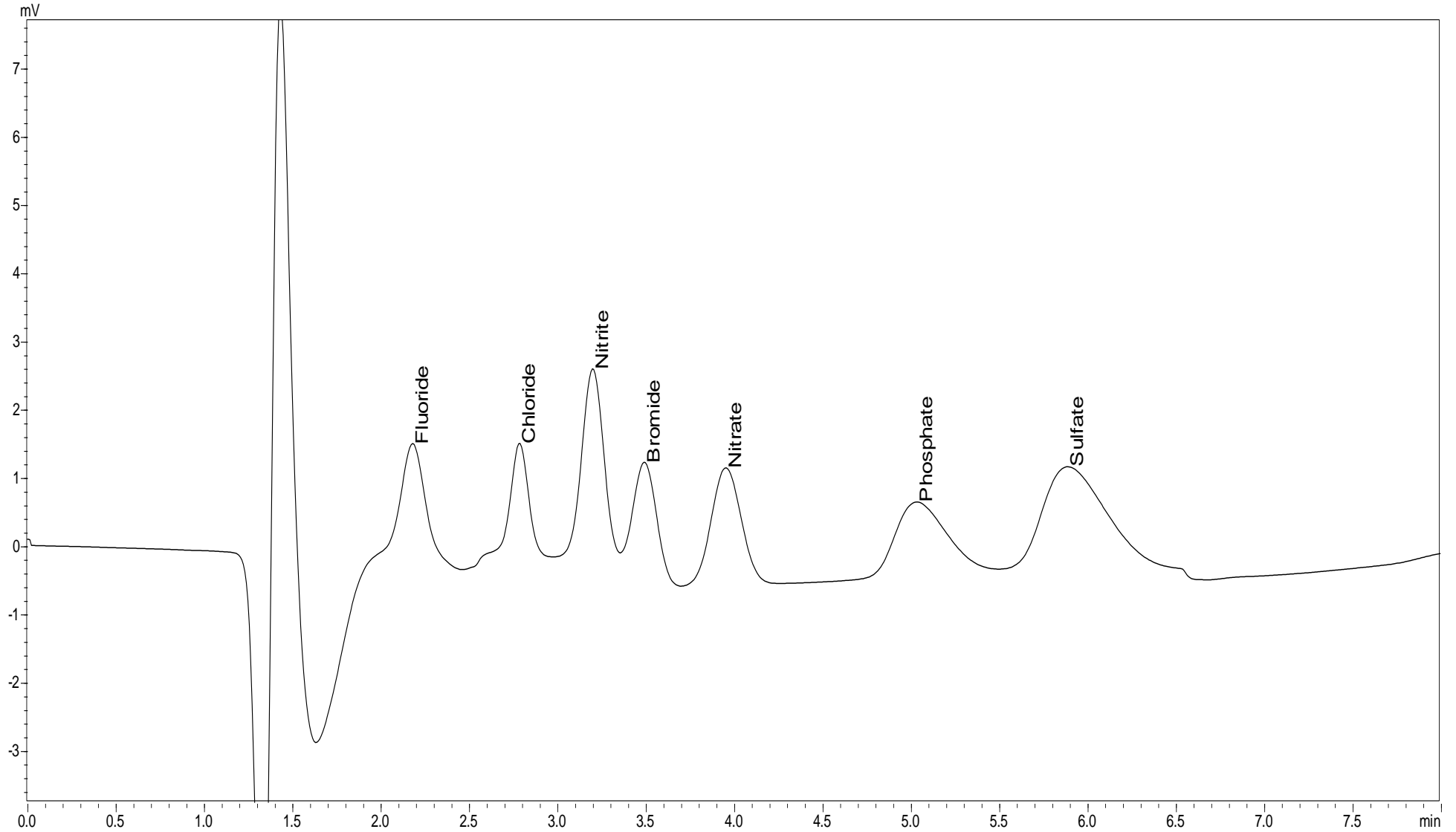
- **Mobile Phase Components:**
 - 18 mM Mannitol (3.279 g/L)
 - 6 mM Boric Acid (0.371 g/L)
 - 6 mM Trizma (0.727 g/L)

- **Column:**
 - Shodex I-524A, 4.6 x 100 mm, 12 μ m particle

- **Analytical Conditions**
 - 1 mL/min Isocratic for 2.5 minutes
 - 1.8 mL/min Isocratic until the last anion elutes
 - Detector A - UV @ 234 nm
 - Detector B – Unsuppressed Conductivity

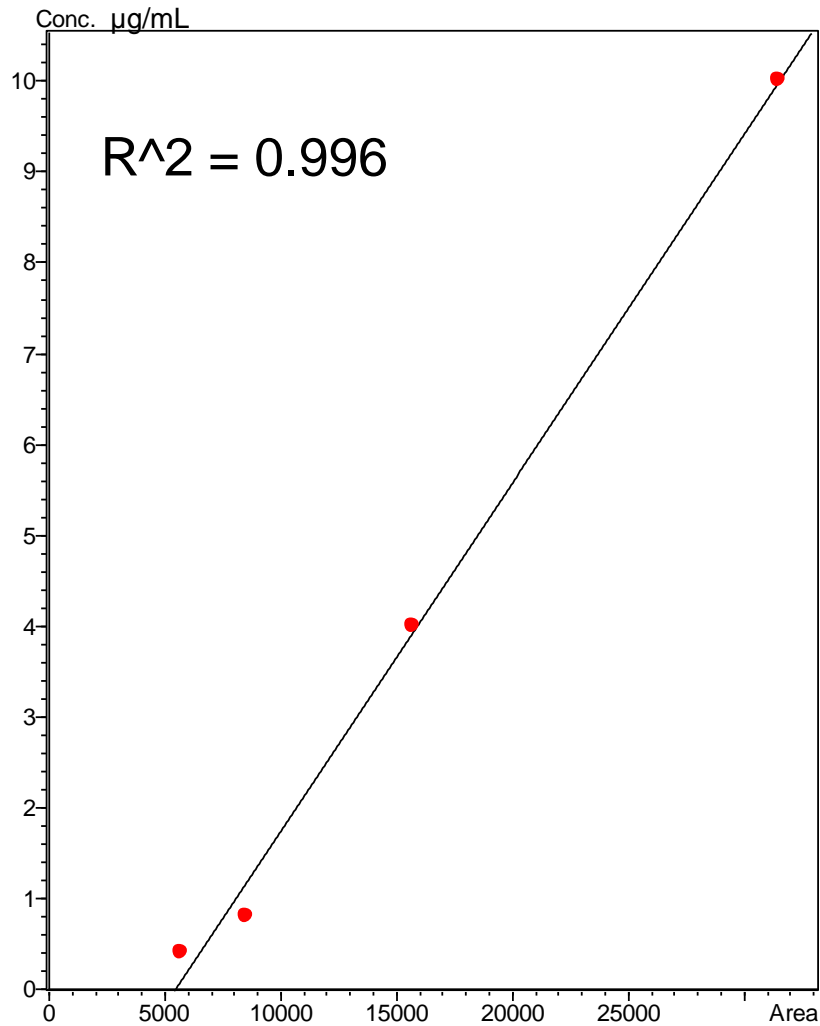
Chromatogram – Unsuppressed Conductivity

Datafile Name:Level-4_4.lcd
Sample Name:Level-4

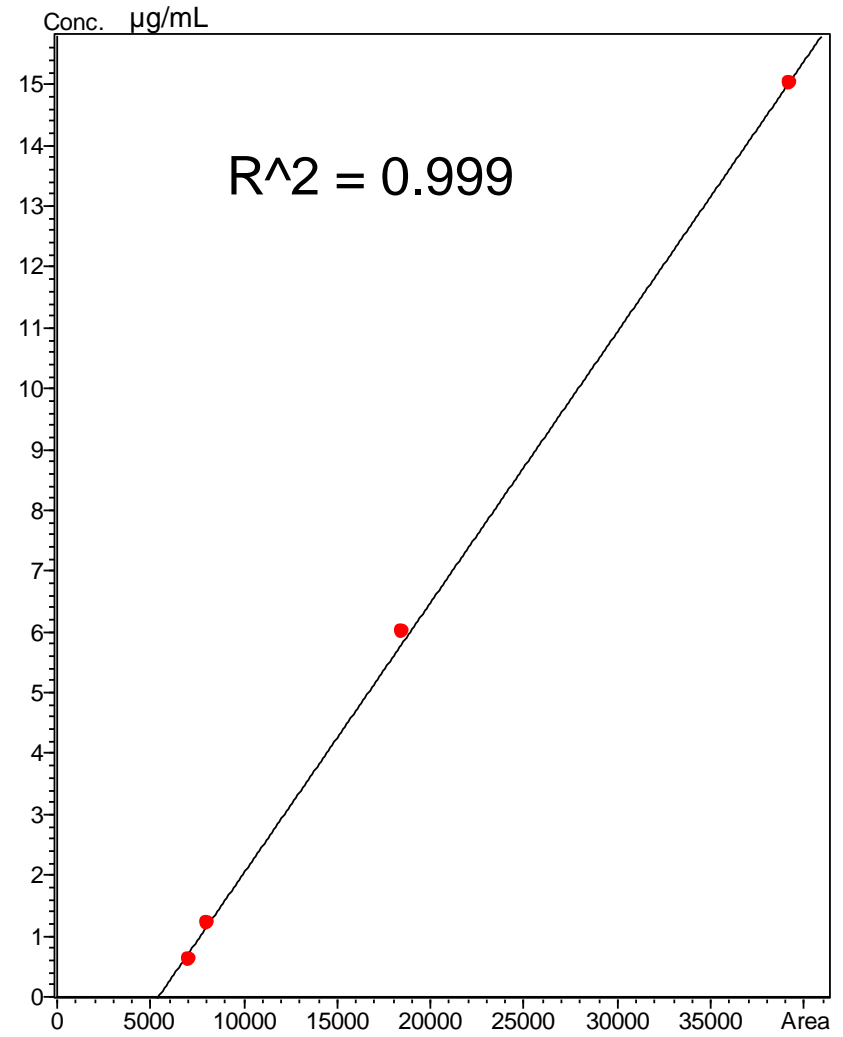


Calibration Curves – Unsuppressed Conductivity

Fluoride

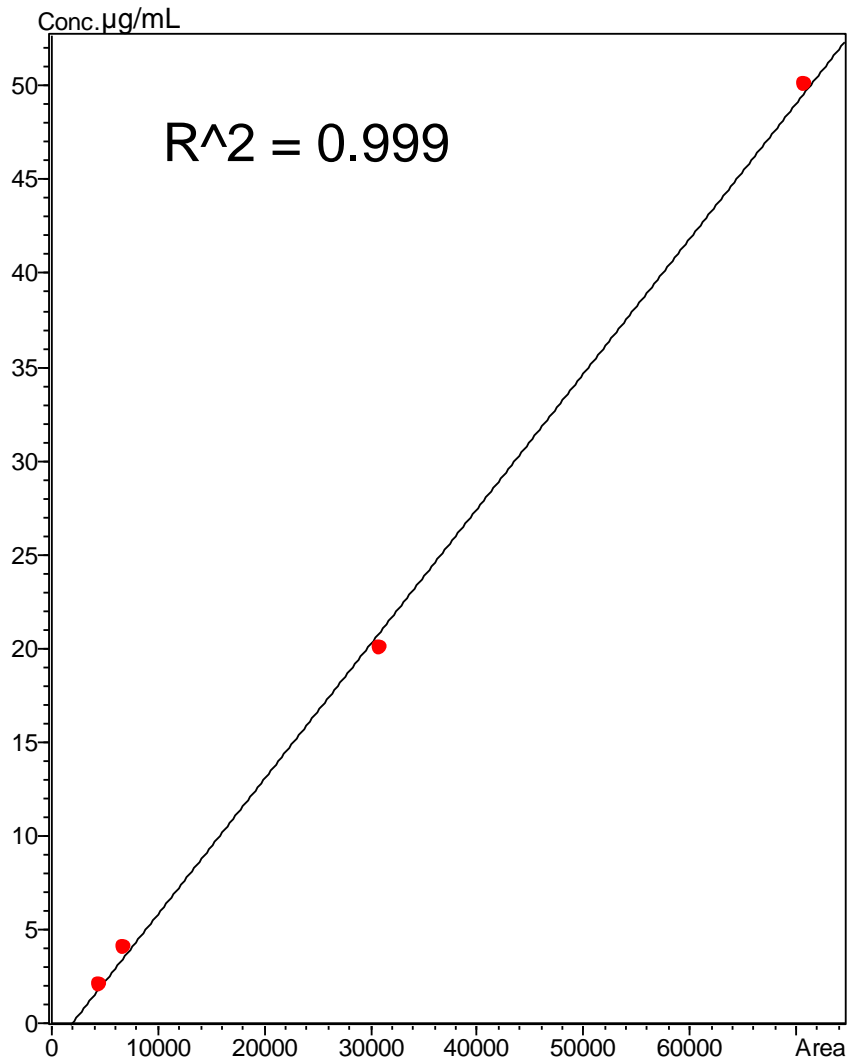


Chloride

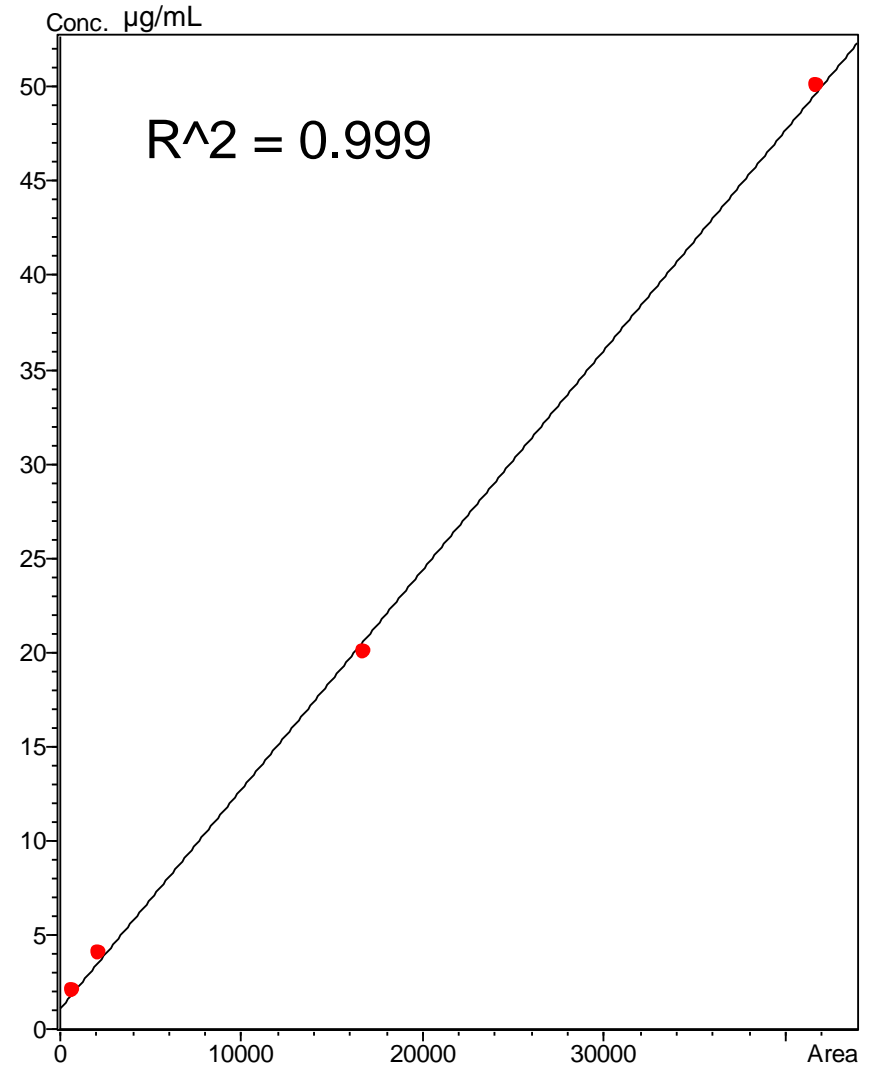


Calibration Curves – Unsuppressed Conductivity

Nitrite

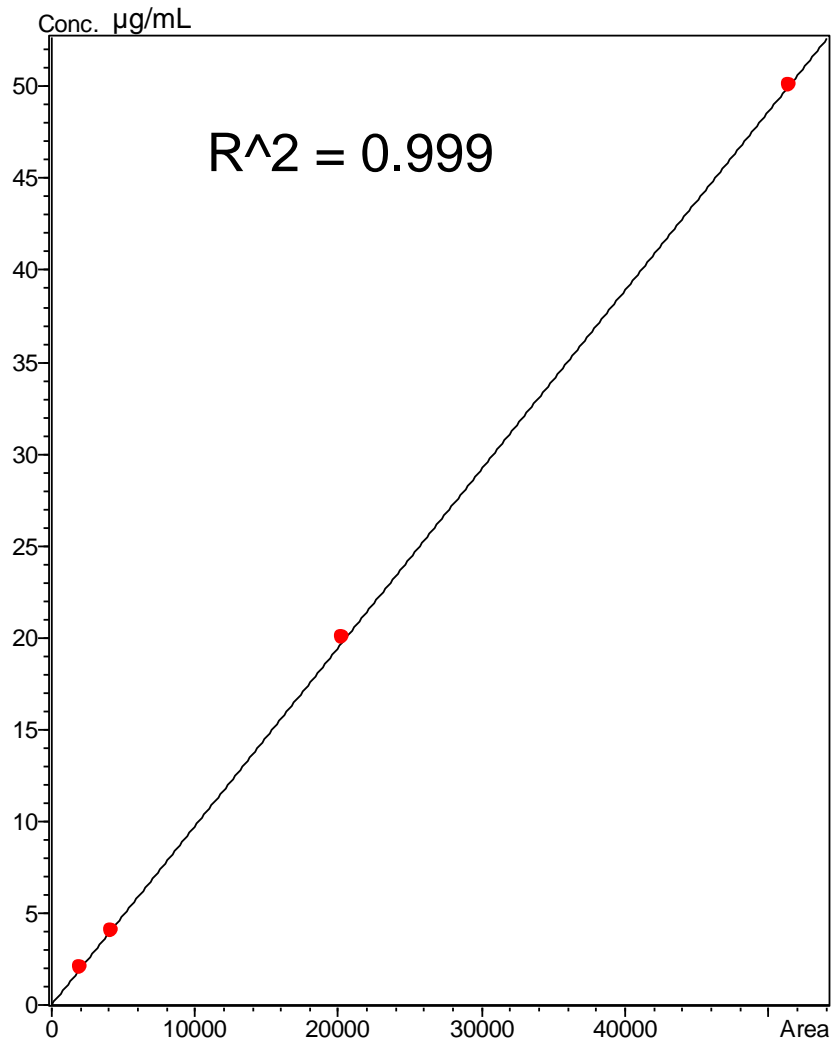


Bromide

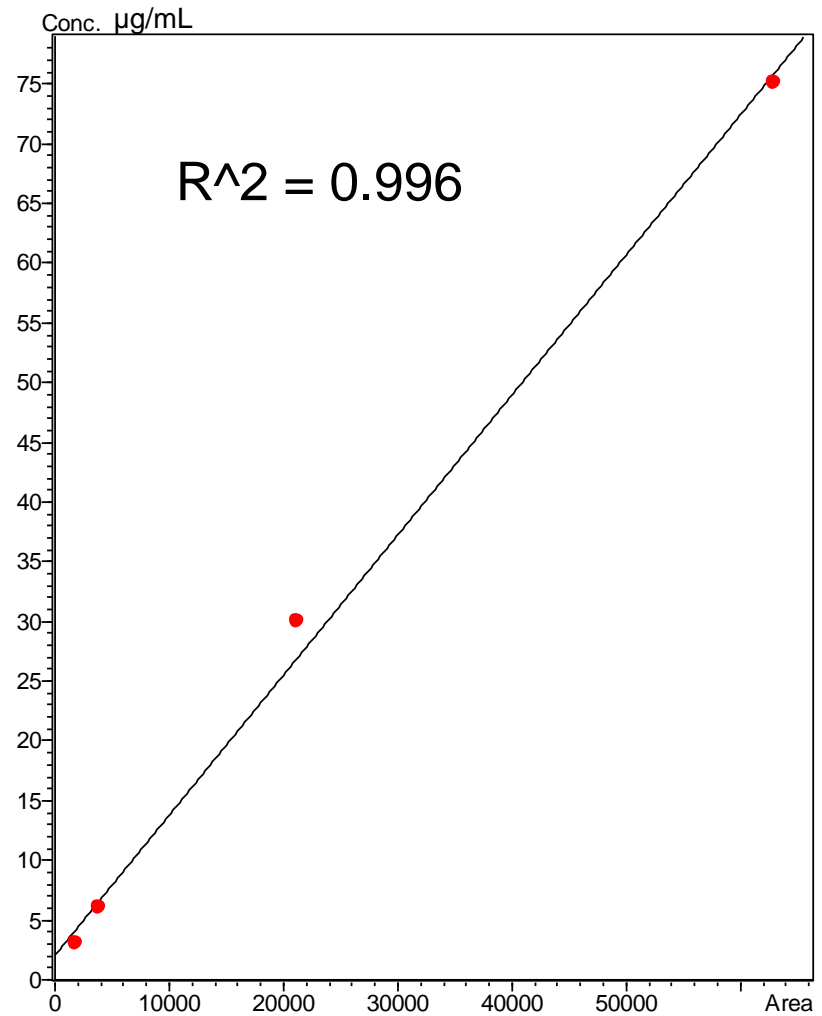


Calibration Curves – Unsuppressed Conductivity

Nitrate

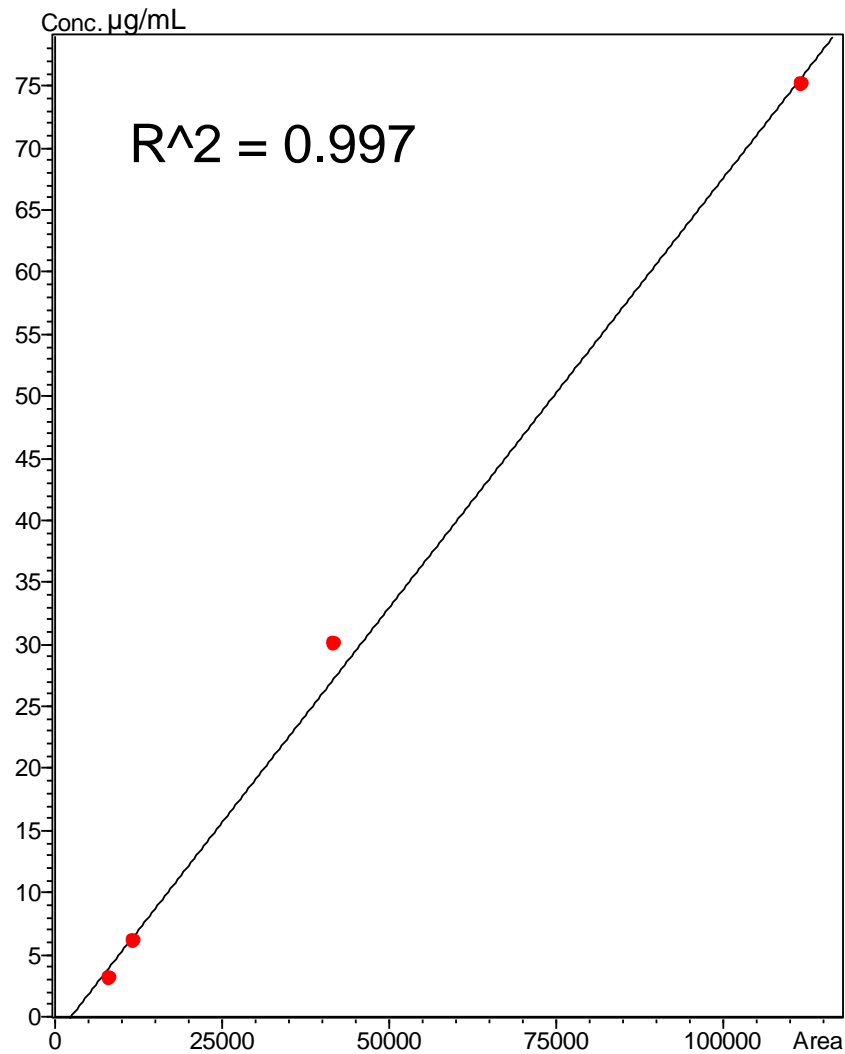


Phosphate



Calibration Curves – Unsuppressed Conductivity

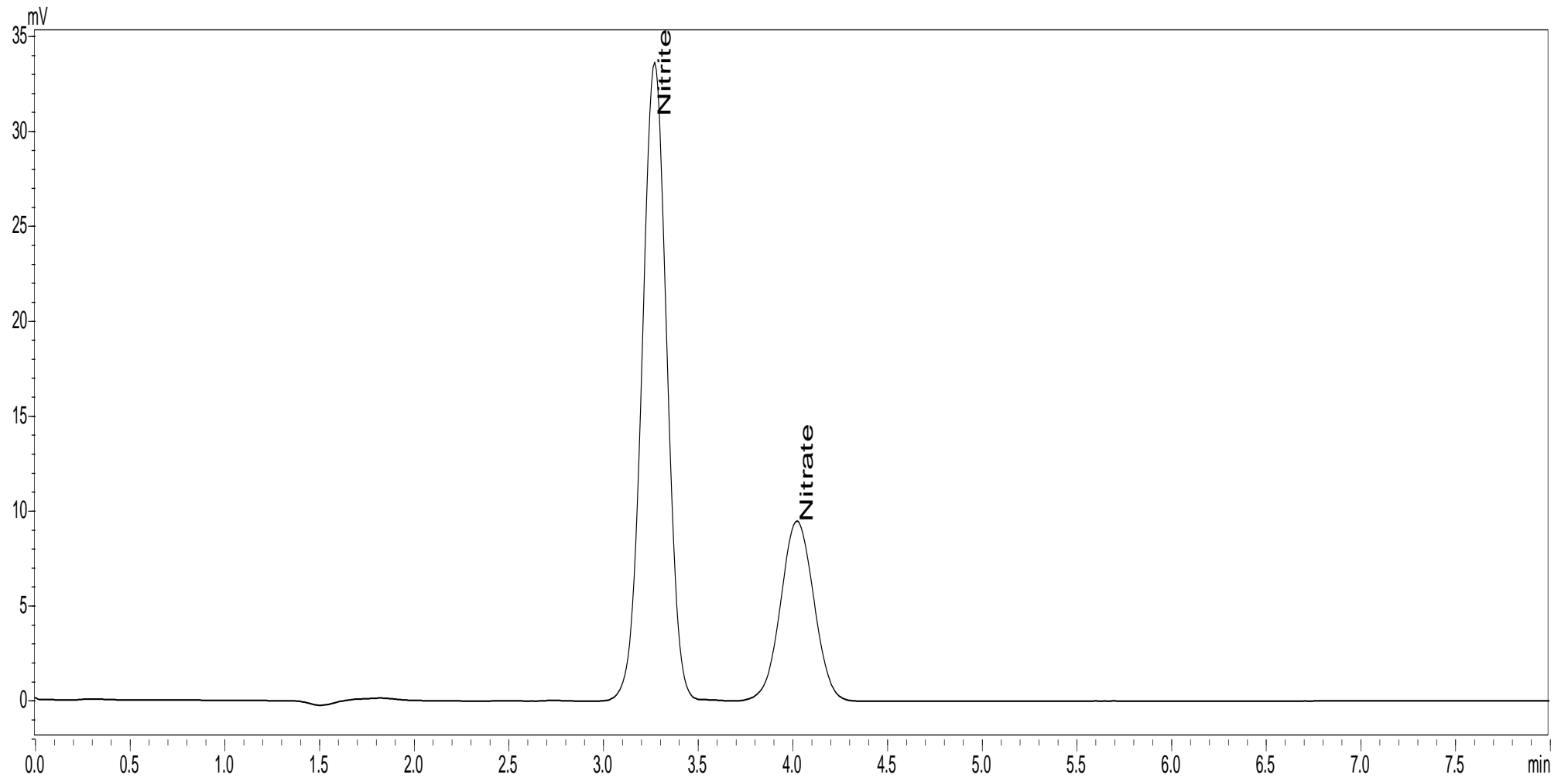
Sulfate



Chromatogram – UV

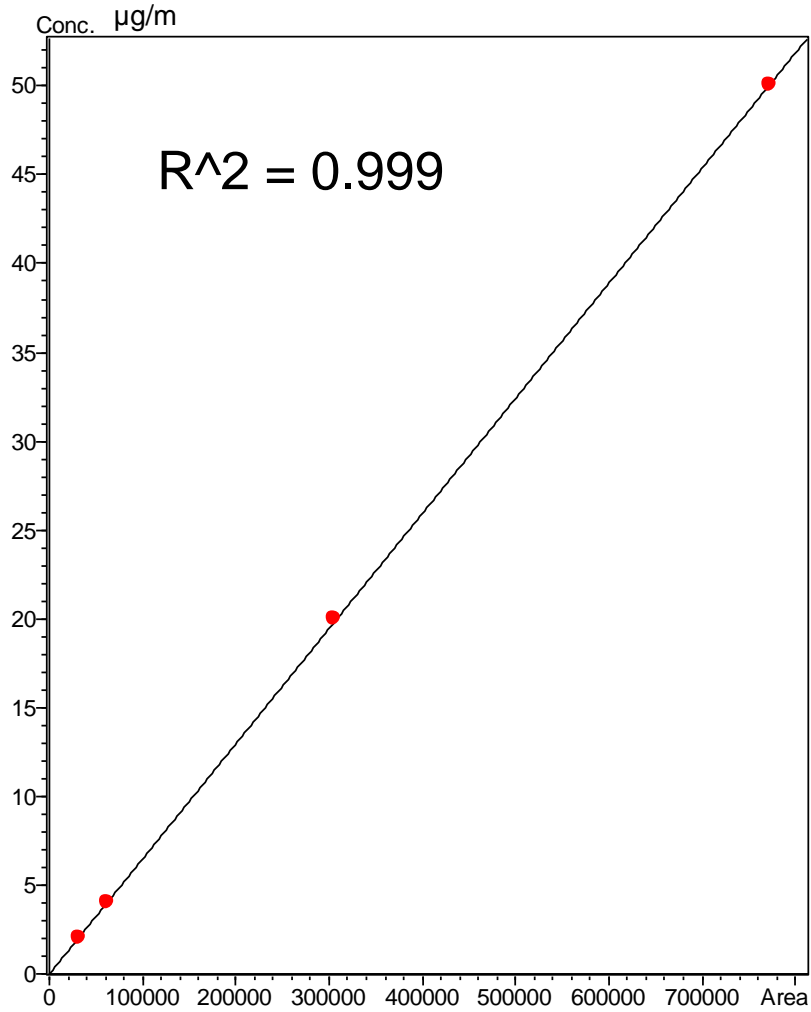
Datafile Name:Level-4_4.lcd

Sample Name:Level-4

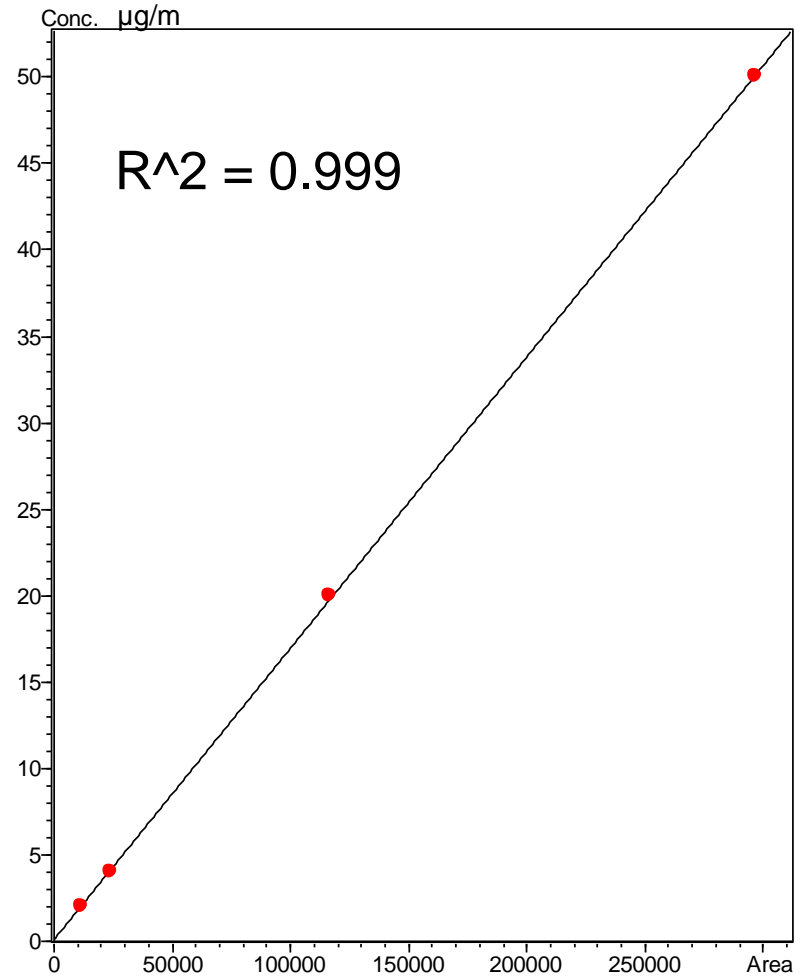


Calibration Curves - UV

Nitrite



Nitrate



Method Detection Limits per 40CFR Part 136 Appendix B

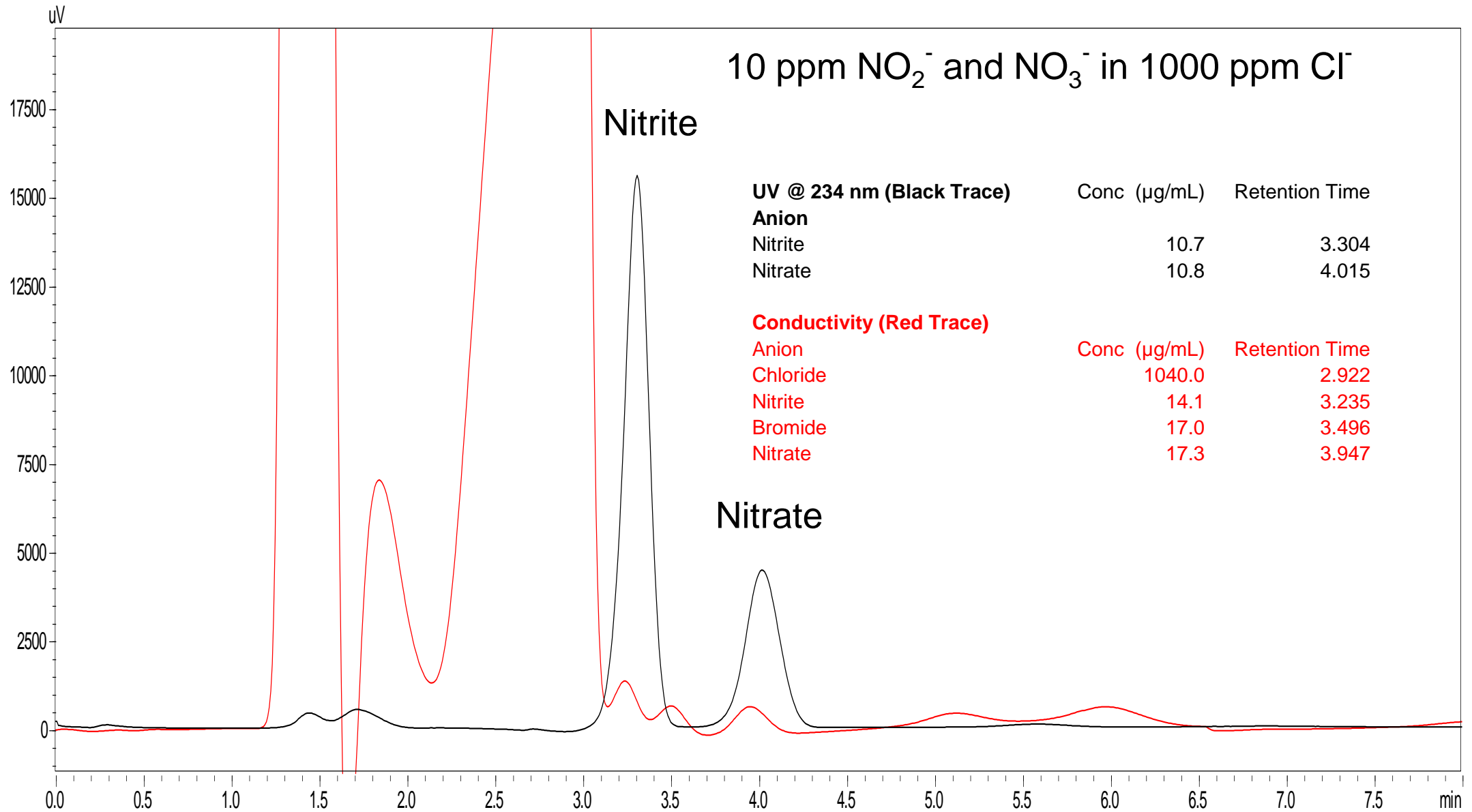
Unsuppressed Conductivity 9 Consecutive Replicates

UV Detection 7 Consecutive Replicates

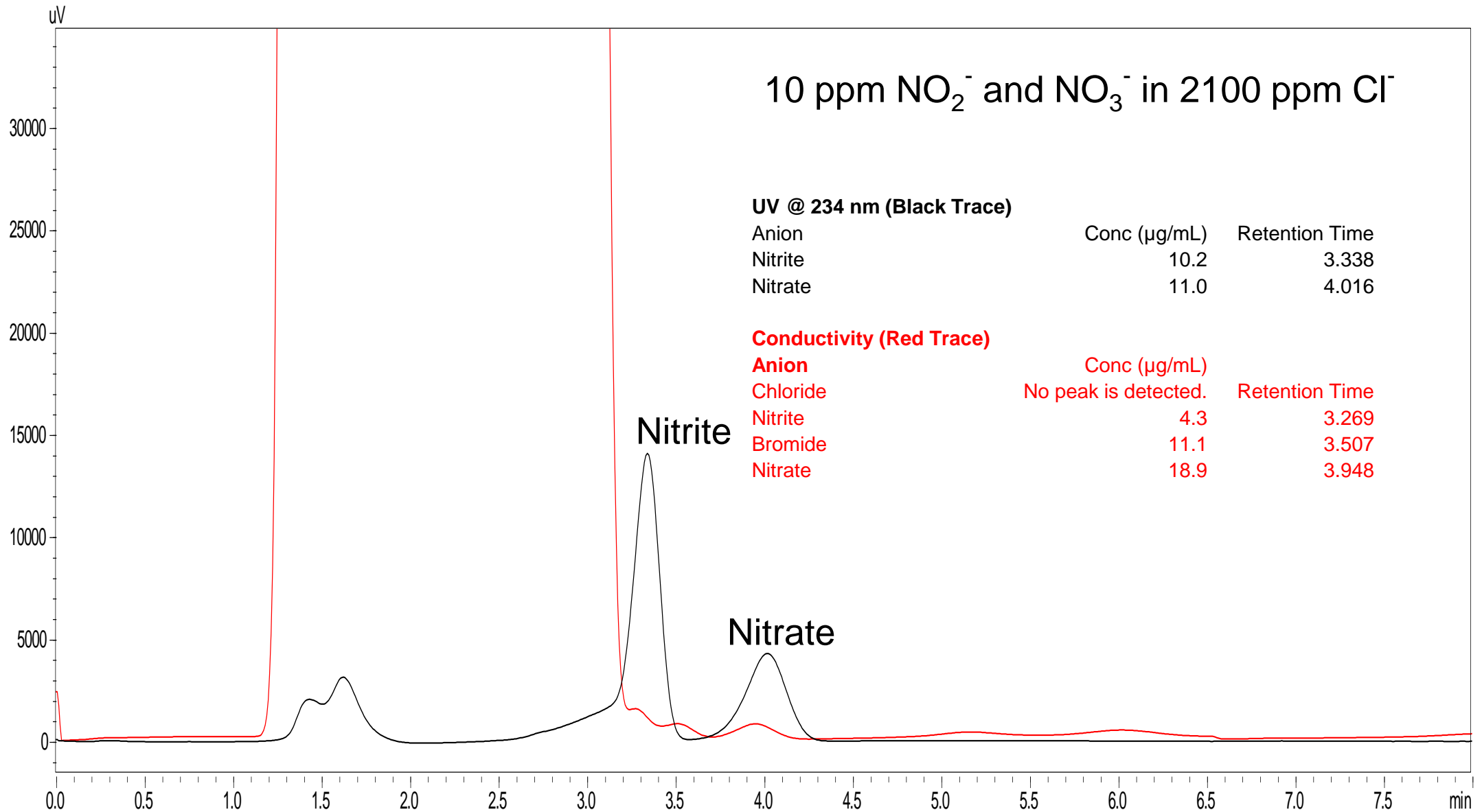
Anion	Spike Level (µg/mL)	MDL (µg/mL)
Fluoride	0.20	0.031
Chloride	0.30	0.15
Nitrite	1.0	0.24
Bromide	1.0	0.16
Nitrate	1.0	0.14
Phosphate	1.5	1.3
Sulfate	1.5	0.33

Anion	Spike Level (µg/mL)	MDL µg/mL
Nitrite	0.020	0.0045
Nitrate	0.020	0.0040

Overlay UV/Conductivity in 1000 ppm Chloride



Overlay UV/Conductivity in 2100 ppm Chloride



Future Work

- Improve fluoride chromatography
 - Eliminate the “water dip”
- More modern column
- Less baseline drift

References

Standard Methods for the Examination of Water and Wastewater
Part 4000 INORGANIC NONMETALLIC CONSTITUENTS
18th Edition, 1992

CFR-2011-title40-vol23-part136-appB
APPENDIX B TO PART 136—DEFINITION AND PROCEDURE FOR THE DETERMINATION OF THE METHOD
DETECTION LIMIT—REVISION .11

“Alternative Sulfate Analysis Methodology for Ethanol Production Plants”
Shimadzu Scientific Instruments, Inc.
J. Mott *et al.*