

Simultaneous Detection of Haloacetic Acids using Ion Chromatography

Electrospray Ionization Tandem Mass Spectrometry

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Introduction & Objective

Context and Background:

- Haloacetic acids (HAAs) are a group of disinfection byproducts that has caused concern due to its potential harmful effects from long term exposure.
- HAAs are especially concerning when the drinking water source is linked with water reuse, which typically involves multiple forms of disinfection.
- Typical forms of detection are time consuming and allow for possible analyte loss.
- HAAs are moderately strong acids in drinking water (pH >6) and disassociate to haloacetate ions, making them suitable for ion chromatography.

Objective:

- Detection of HAAs in drinking water through ion chromatography, negative-ion electrospray ionization tandem mass spectrometry through direct injection and without the need for extraction and concentration.

Mass Spectrometer Acquisition Conditions

Mass Spectrometer: Agilent 6490 MS/MS

Source Parameters:

- Gas Temperature: 120°C
- Gas Flow: 13 l/min
- Nebulizer: 45 psi
- Sheath Gas Temperature: 390°C
- Sheath Gas Flow: 12 l/min
- Capillary: 3000V
- Nozzle Voltage: 1500V
- Chamber Current: 0.24 μA

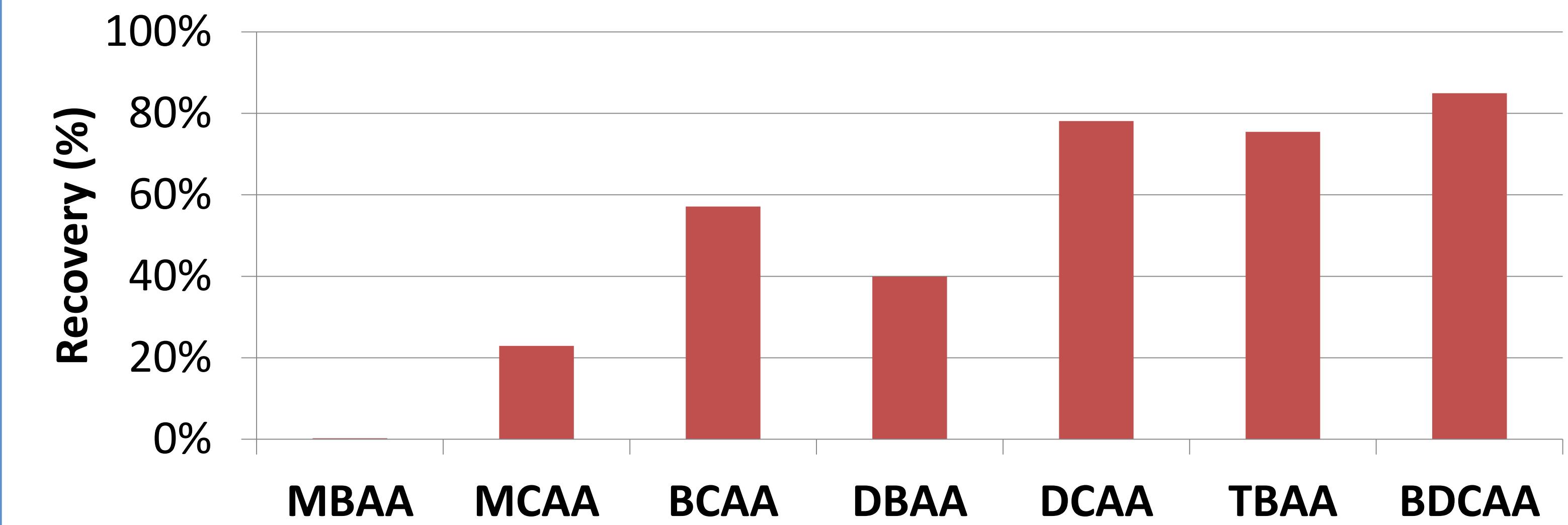
iFunnel Parameters:

- High Pressure RF: 160 V
- Low Pressure RF: 40

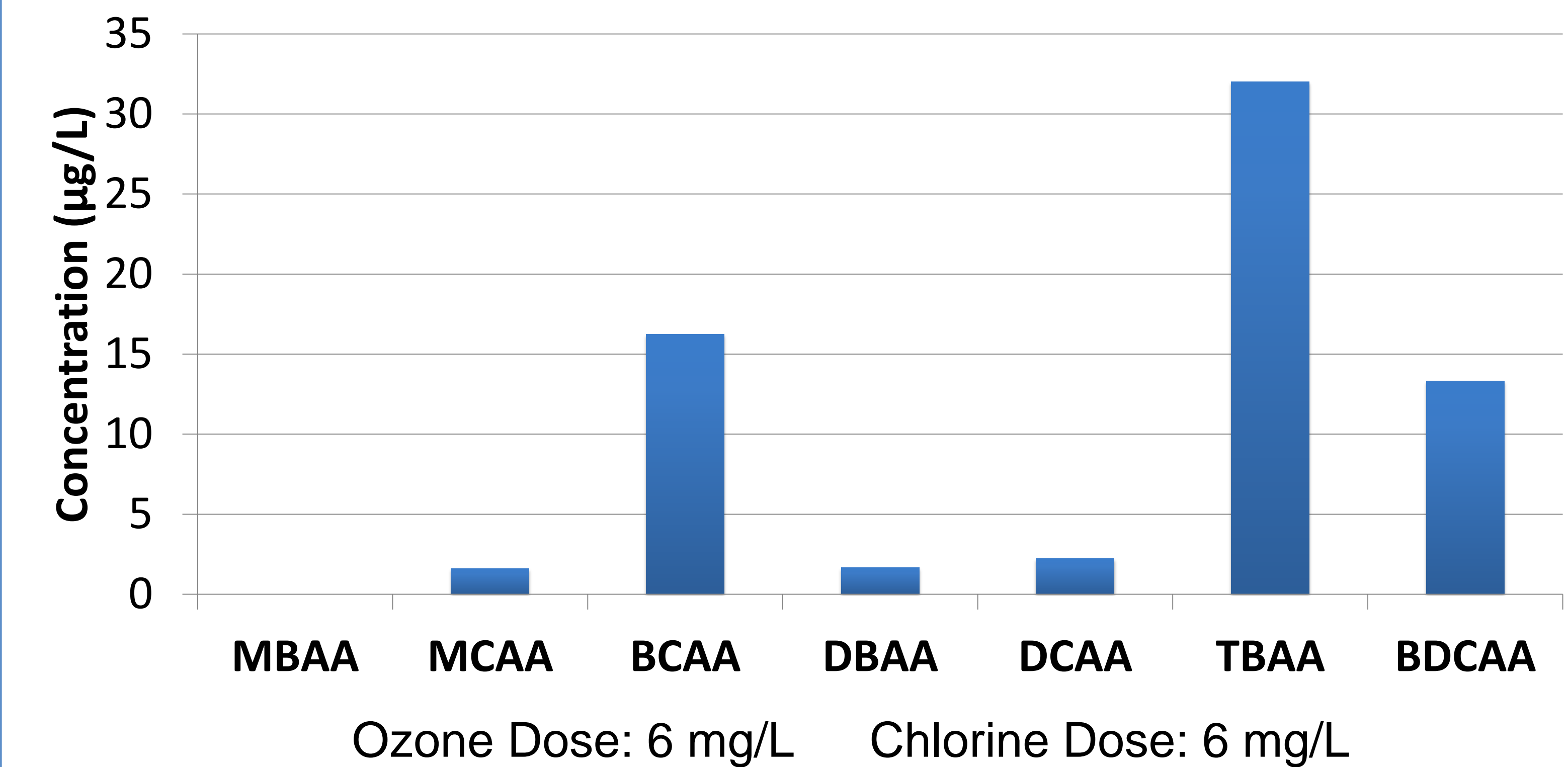
| Compound Name | Precursor Ion | Product Ion | Collision Energy |
|----------------------------------|---------------|-------------|------------------|
| Monobromoacetic Acid (MBAA) | 137 | 83 | 6 |
| Monochloroacetic Acid (MCAA) | 93 | 35 | 6 |
| Bromochloroacetic Acid (BCAA) | 173 | 128.9 | 8 |
| Dibromoacetic Acid (DBAA) | 216.8 | 173 | 8 |
| Dichloroacetic Acid (DCAA) | 127 | 83 | 6 |
| Tribromoacetic Acid (TBAA) | 250.9 | 78.9 | 20 |
| Bromodichloroacetic Acid (BDCAA) | 163 | 81 | 8 |

Waste Water Sample Results

True Recovery (%) of HAAs in Waste Water



HAAs in Ozonated and Chlorinated Waste Water



Ion Chromatographic Conditions

Ion Chromatography System:
Metrohm 850 Professional IC Anion

Injection Volume: 150 μL

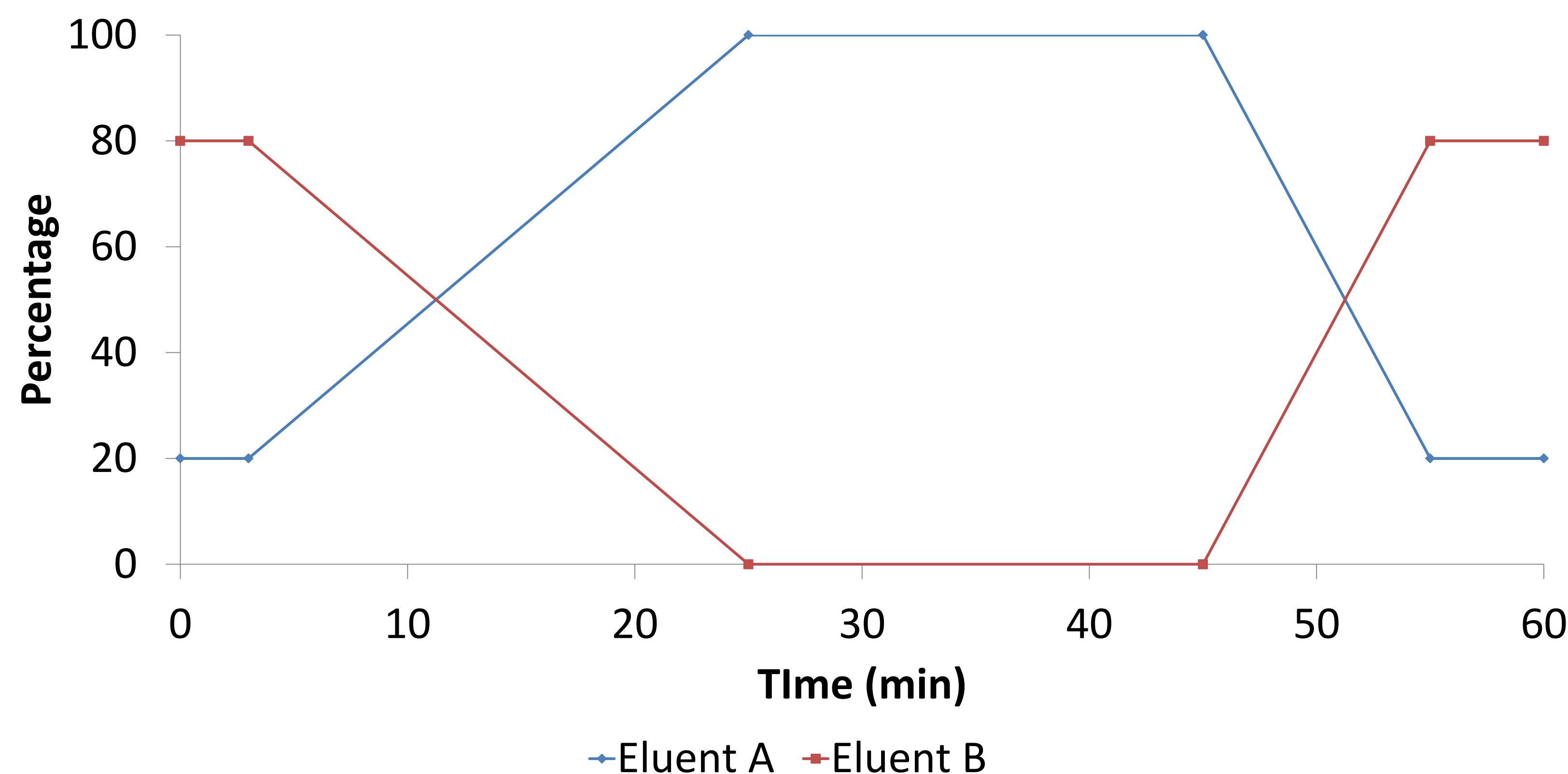
Column: Metrosep A Supp 7
250mm x 4mm

Eluent Flow Rate: 0.4ml/min

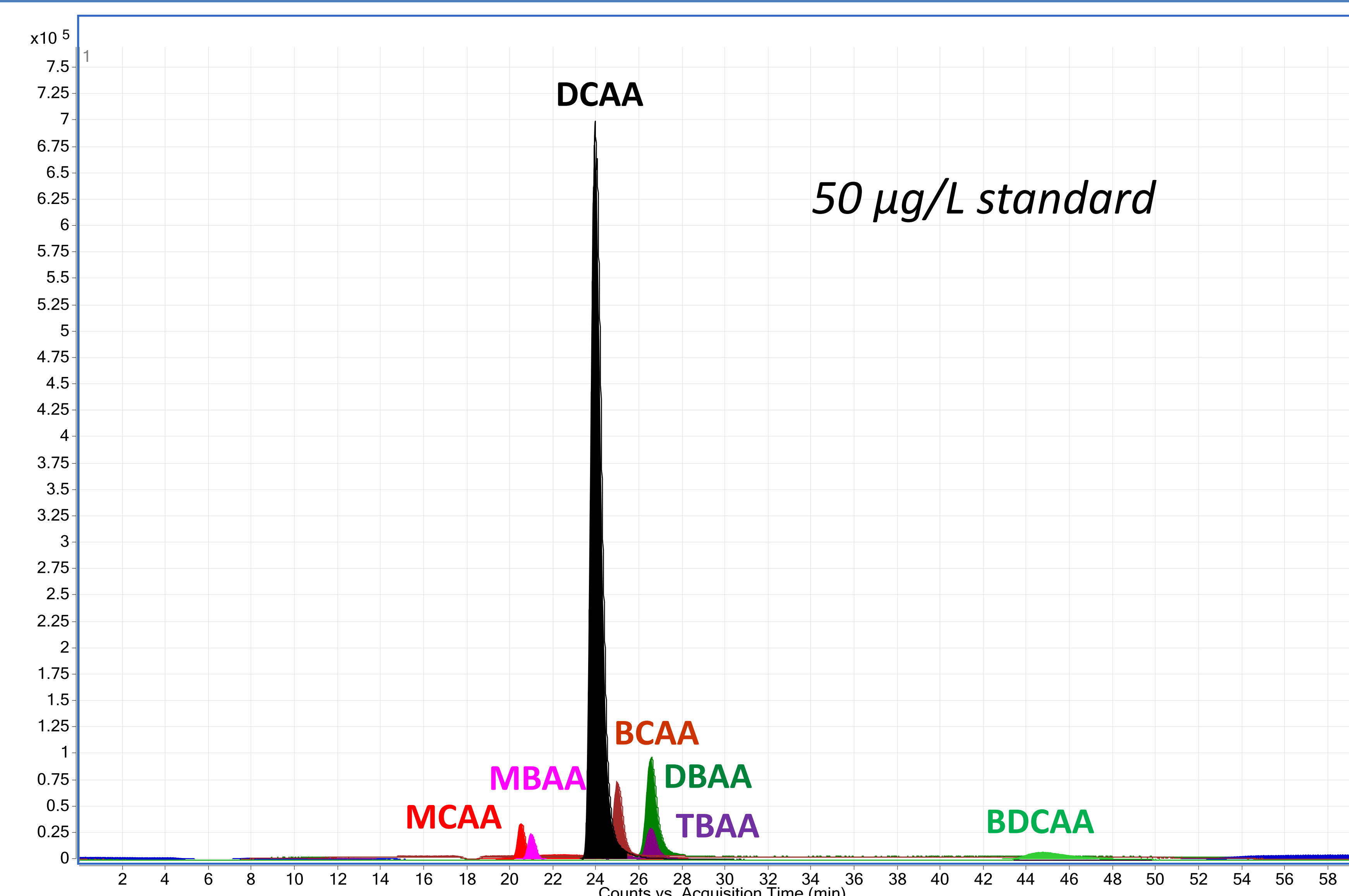
Eluents: A: 100mM NaOH
B: 5% Acetonitrile

Column Temperature: 20°C

Eluent Gradient



Chromatogram Results



Conclusion

- Successful detection of seven HAAs. Future method development must be made to account for missing HAAs.
- Use of isotopically labeled standards is suggested due to low recoveries in wastewater.
- Direct injection allows for easier determination by eliminating necessary derivatization and extraction typically needed in other HAAs detection methods.

Acknowledgment

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