

# IC-MS Analysis of Perchlorate, Bromate, and Bromide in Drinking Water

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## Introduction

Ion chromatography (IC) is commonly used for the sensitive and selective analysis of ions and polar species in environmental sample matrices. Conductivity detectors are most common, but IC can also be amenable to UV/Vis, Amperometric, and mass spectrometric detection. Mass spectrometry pairs well with IC, as it offers lower detection limits, superior analyte identification, and better extraction from interfering sample matrix. An IC-MS method was developed for looking at trace levels of perchlorate, bromate, and bromide in drinking water, using a Metrohm ion chromatograph paired with an Agilent iQ MS. Agilent Open Lab CDS provided a single software solution for both instrument control and data analysis.

## Instrument



- 940 HP Anion Gradient IC
- 858 Sample processor
- Partial Loop Injection with Dosino Technology
- Agilent iQMS
- Agilent Open CDS version 2.6 or higher

## Analysis

Most commonly, perchlorate ions in various waters are analyzed by USEPA method 314.0 (suppressed conductivity). However, this method has difficulty analyzing trace levels of perchlorate with high Total Dissolved Solids (TDS) content. Hence, USEPA method 332.0 was developed to analyze perchlorate ion using a hyphenated technique like IC-MS (SQ) or IC-MSMS (QQQ). ICMS analysis is beneficial for lower detection levels even in the presence of high TDS (up to 3000 ppm) content. Mass spectrometry provides high selectivity and sensitivity.

Using ICMS for perchlorate offers a simplified analysis of inorganic disinfectant byproducts.

## Experimental Conditions

USEPA method 332.0 is developed for perchlorate analysis for various types of water (drinking, surface, ground and wastewater)

One of the requirement of this method is to analyze 1 part per billion (ppb) of perchlorate in presence of 3000 parts per million (ppm) of TDS. 3000ppm TDS = 1000ppm each of chloride, bicarbonate and sulfate)

### Metrohm Ion Chromatography

Column – Metrosep ASUPP7 – 250/4  
 Eluent – A) 12.8mM Na<sub>2</sub>CO<sub>3</sub> + 4mM NaHCO<sub>3</sub> + 30% Acetonitrile  
 B) UHP Water + 10% Acetonitrile

Binary High Pressure Gradient setup  
 Column Flow – 0.7 mls per minute  
 MSM Regenerant – 1 M Nitric Acid + 10% Acetonitrile  
 MSM Rinse – 10% Acetonitrile

### Agilent iQMS parameters

Nitrogen Gas Temperature – 325 degrees C  
 Nitrogen Gas Flow – 10 Liters per minute  
 Capillary Voltage – Negative 2500  
 Nebulizer Pressure – 45 psig  
 Negative SIM mode  
 SIM Ions (m/z): USEPA 332.0 - 99, 101, 107(IS),  
 Oxyhalides and Perchlorate: 67, 69, 83, 85, 99, 101, 107(IS), 79,81, 127, 129

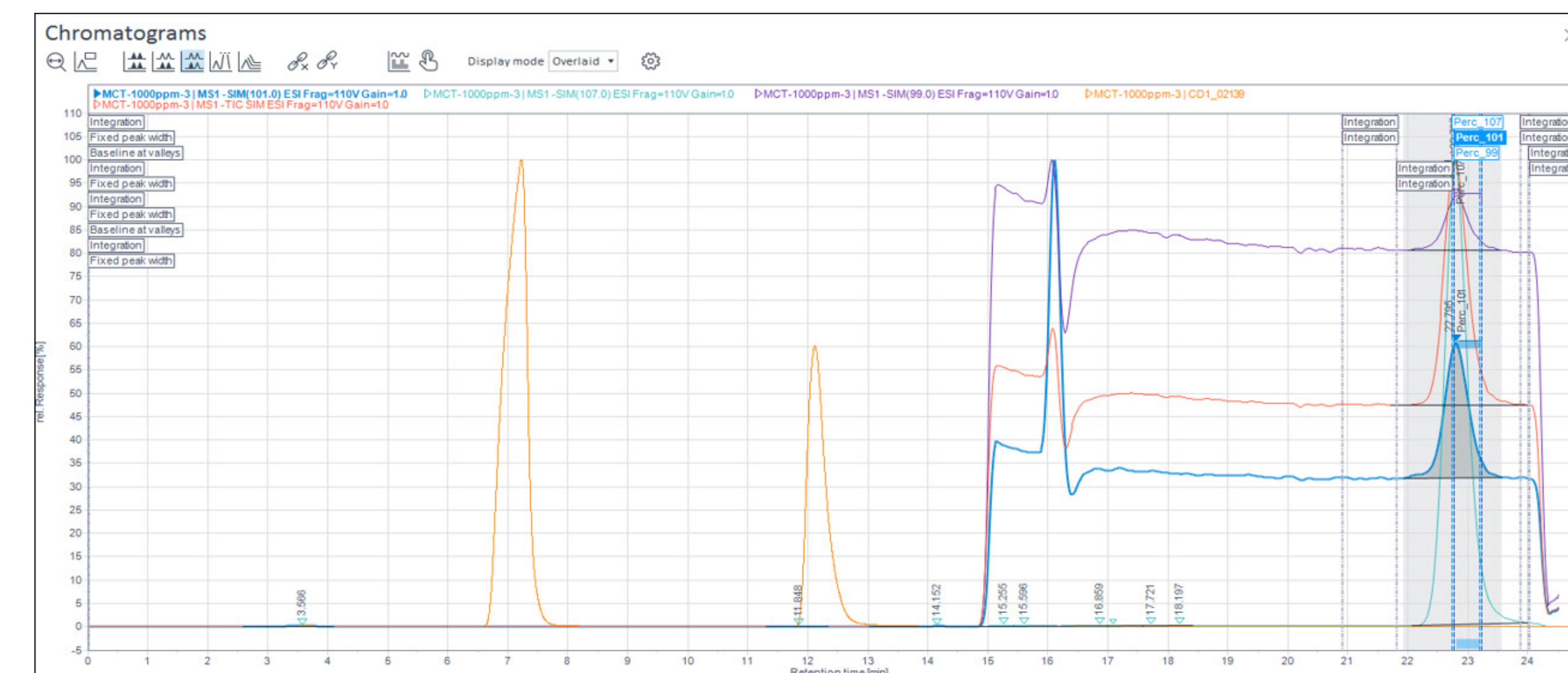


Figure 1 - 3000ppm Matrix (1000ppm each of Cl, CO<sub>3</sub>, SO<sub>4</sub>) + 1.0µg/L Perchlorate + 5µg/L ISTD

## MCT Study for Perchlorate

A Maximum Conductivity Threshold (MCT) study is required for all USEPA methods for perchlorate analysis. This study must demonstrate the resolution of interfering ions from perchlorate ion and prove the stability of retention times.

## Disinfectant Byproducts and Perchlorate Analysis

Sample ID	m/z 99	m/z 101
0.5 µg/L standard	0.475	0.448
0.5 µg/L standard	0.468	0.472
0.5 µg/L standard	0.459	0.506
0.5 µg/L standard	0.463	0.483
0.5 µg/L standard	0.473	0.483
0.5 µg/L standard	0.475	0.495
0.5 µg/L standard	0.486	0.495
Average	0.4713	0.4831
Std. Dev	0.01784	0.01899
Calculated MDL (µg/L)	0.056	0.060

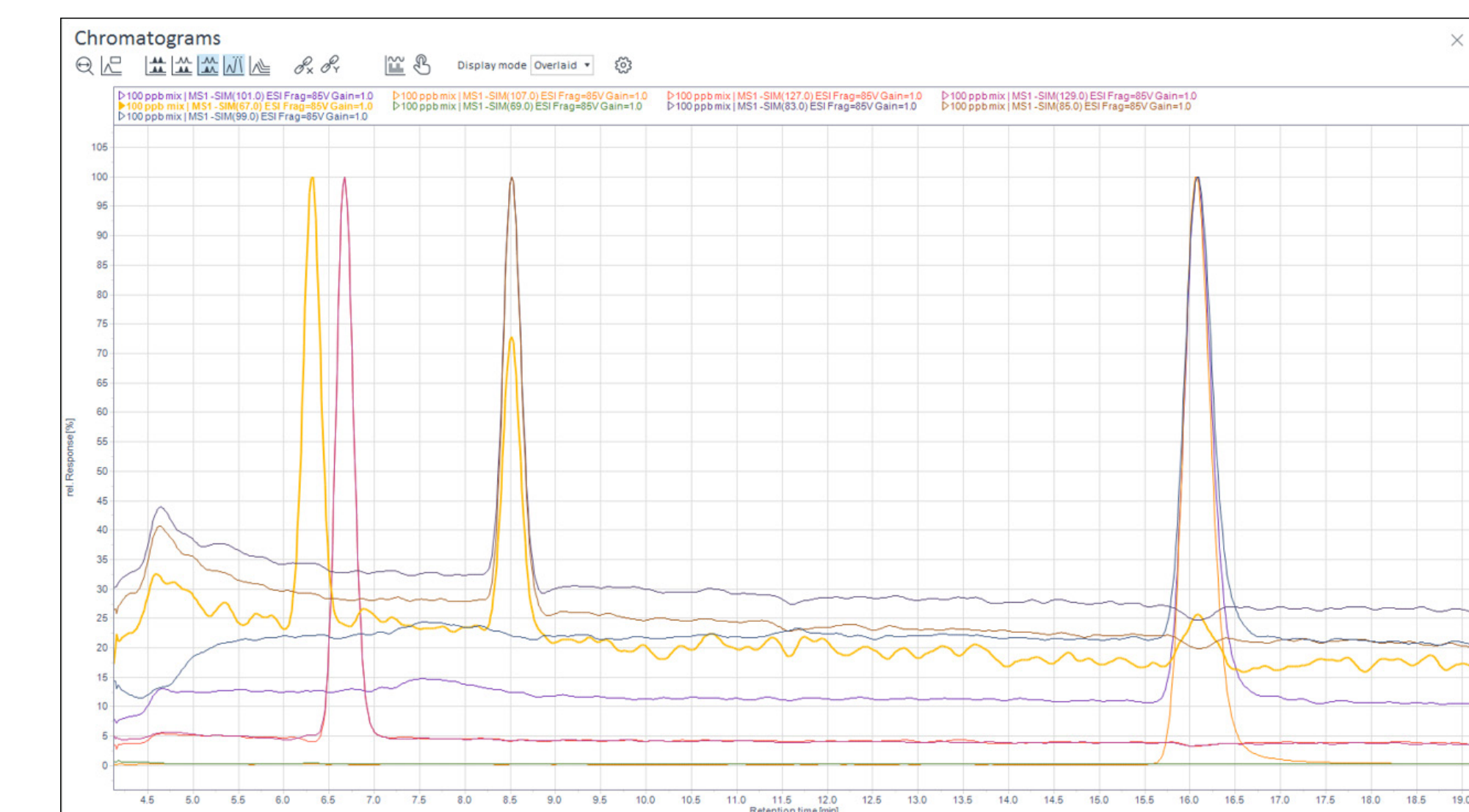


Figure 2. Disinfectant byproducts and Perchlorate Analysis at 5 parts per billion (ppb)

Binary high-pressure gradient IC optimizes the analysis within 20 minutes for Oxyhalides, especially Bromate and Perchlorate ions in drinking water.

## Conclusion

The Metrohm Ion Chromatograph hyphenated with an Agilent Single Quad (iQMS) Mass Spectrometer accurately and precisely determined perchlorate and other oxyhalide ions conforming to USEPA method 332.

The same instrument set up can be used for analyzing other oxyhalides like chlorate, chlorite and bromate ions in drinking water.