

THE DETERMINATION OF PERCHLORATE IN WATER USING LC/MS/MS

Jim Krol, Waters Corporation, Milford, MA, USA

INTRODUCTION

Perchlorate is both a naturally occurring and man-made chemical. Naturally occurring perchlorate is a contaminant in fertilizers.

Man-made perchlorate is used in many applications, including tanning and leather finishing, rubber manufacture and paint and enamel production. Perchlorate is also used as an additive in lubricating oils, and is a primary ingredient of solid rocket propellant. Usage and improper disposal of the highly water soluble perchlorate migrates through the underground aquifers and surface water sources, contaminating soil, drinking water and irrigation water.

Thirty-five states have detected perchlorate in drinking water at higher levels than expected. The same water is used for crop irrigation. As a result, there is concern for the food safety of fruits, vegetables and grain, and their use as animal feed in the southwestern U.S.

Today, Maryland, Massachusetts and New Mexico have established a one part per billion (ppb) perchlorate action limit. California and Texas have established 4 ppb. Action limits are higher in Nevada and Arizona. In February 2005, the EPA established an official reference dose (RfD) of 0.0007 mg/kg per day of perchlorate. However, the creation of sub-ppb detection limits is desirable.

METHOD

US EPA method 314.1, "The Determination of Perchlorate in Drinking Water Using Ion Chromatography," 2004, is the current approved method for detecting perchlorate in drinking water. This ion chromatography method is capable of detecting sub-ppb ClO_4^- , but is limited by sample ionic strength, mainly chloride and sulfate concentrations, thus adversely limiting detection. Other common anions (thiosulfate, thiocyanate and iodide) elute in the same region. Analyte identification, an alternative, simpler method is required.

Chromatographic Conditions

System: Alliance® 2695 system with the Waters conductivity detector and Waters Micromass® Quattro micro™ mass spectrometer
Column: IC-Pak™ Anion HR, 4.6 x 75 mm, 6 μm (Waters part no. WAT026765)
Eluent: 25 mM NH_4HCO_3 , pH 10 with NH_4OH in 50% AcCN
Flow rate: 0.5 mL/min
Col temp: 30 °C
BackPress: <1000 psi
Back cond: ~1600 μS
Inj volume: 100 μL

Mass spectrometer tune conditions:

| | | | |
|--------------------|---------------------------|-------------------|------|
| Ionization | -ESP | LM 1 Resolution: | 15.0 |
| Capillary (V): | .58 | HM 1 Resolution: | 15.0 |
| Cone (V): | 40 | IonEnergy 1: | 0.6 |
| Extractor (V): | 3 | Entrance (V): | 1 |
| RF Lens (V): | 0.3 | Collision Energy: | 30 |
| Source Temp °C: | 125 | Exit: | 1 |
| Desolvation Temp: | 400 | LM 2 Resolution: | 14.0 |
| Cone Gas (L/hr): | 50 | HM 2 Resolution: | 14.0 |
| Desolvation Gas: | 500 | Ion Energy 2: | 1.0 |
| Gas Cell Pressure: | 2 x 10 ⁻² mbar | Multiplier: | 650 |

The key to this application is the resolution of <0.5 ppb perchlorate from mid-ppm levels of chloride and sulfate. Sulfate is the main interferent with method 314.1, and the ^{34}S isotope as $\text{H}^{34}\text{SO}_4^-$, at 4.2% abundance, has the same MS/MS transition as perchlorate. It is critical to remove SO_4 or provide baseline resolution from perchlorate.

By combining chromatographic selectivity and mass spectrometry selectivity and sensitivity, perchlorate can be determined in High Total Dissolved Solids (HTDS) water at the sub-ppb levels.

HTDS is a synthetic solution defined as 1000 mg/L each of bicarbonate, chloride and sulfate prepared in drinking water.

Using increased concentrations of organic solvent, acetonitrile (AcCN), in this case because of low back pressure, perchlorate can be chromatographically positioned after high chloride and before high sulfate. Use of ammonium bicarbonate eluent allows for the sub-ppb determination of perchlorate within 15 minutes without the need for sample prep. (See Figure 1.)

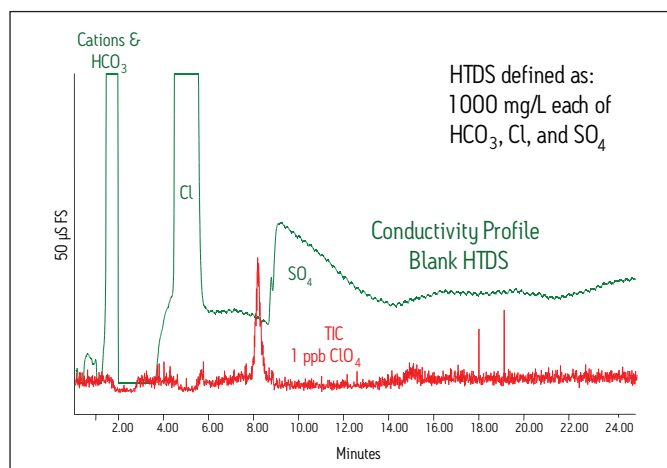


Figure 1. 1 ppb perchlorate in HTDS.

Ammonium bicarbonate is also a volatile buffer conducive for use with mass spectrometry. Any sodium (Na) or potassium (K) based eluent requires chemical suppression prior to MS. Chemical suppression converts KOH to H₂O. Chemical suppression is not needed for this application.

To quantitatively measure sub-ppb perchlorate requires a method detection limit of less than 0.5 ppb perchlorate, using either 3x signal to noise (S/N) or EPA protocols. Figure 2 shows a 0.5 ppb perchlorate standard prepared in reagent water, drinking water and HTDS solutions. Detection limit is approximately <0.1 ppb, defined as 3x S/N, and limit of quantification is 0.2 ppb, at 10 times S/N.

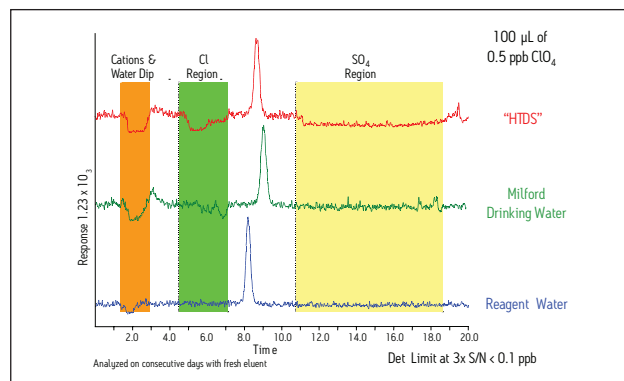


Figure 2. 0.5 ppb perchlorate detection in three different sample matrices by LC/MS/MS.

This LC/MS/MS method meets the requirements. Lower detection may be achieved by using a larger injection volume.

The use of multiple reaction monitoring (MRM) mass spectrometry to monitor the transition of perchlorate to chlorate, 99.1>82.7 (loss of 1 oxygen) is used for perchlorate quantification. Positive perchlorate confirmation is achieved using a second transition of 101.1>84.7 for the ³⁷Cl isotope and the ion ratio of the ³⁵Cl and ³⁷Cl isotopes. Although H³⁴SO₄⁻ sulfate may give a 99>83 response, it will not yield the required Cl isotope ratio (See Figure 3).

The linearity of this method was evaluated between 0.25 and 100 ppb perchlorate containing 10 ppb internal standard using a 100 µL injection. The calibration curve, using 1/x weighting, Figure 4 shows good linearity between 0.25 and 10 ppb. Similar data is observed with calibration standards prepared in HTDS solution and drinking water.

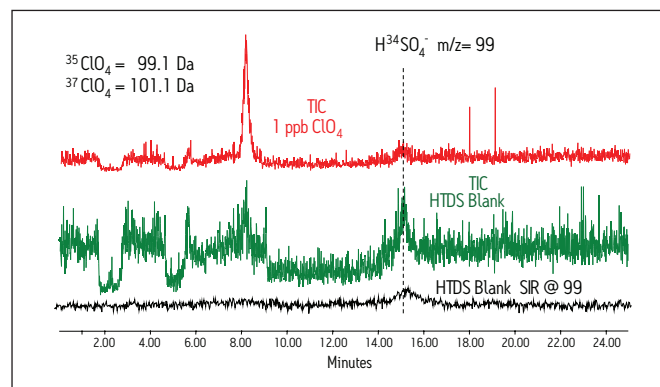


Figure 3. Sulfate interference.

Figure 5 shows the LOD and LOQ for perchlorate quantification. LOD = 0.02 ppb, LOQ = 0.05 ppb by EPA definition of method detection limit (MDL).

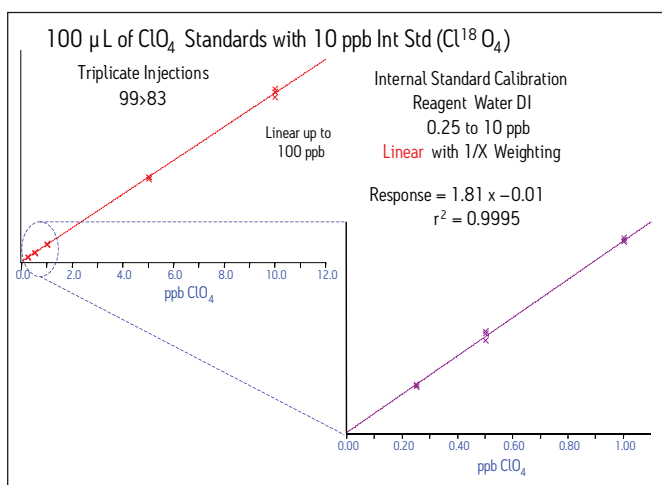


Figure 4. Perchlorate linearity.

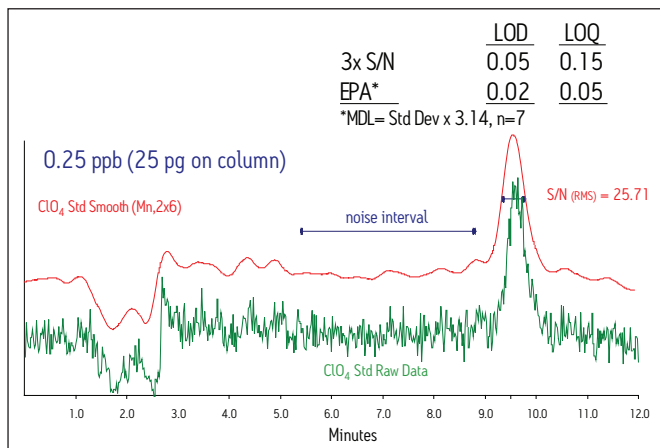


Figure 5. Perchlorate LOD and LOQ after chromatographic smoothing.

CONCLUSION

This work demonstrates the feasibility of using Waters IC-Pak Anion/HR chemistry with the Waters Alliance® HPLC system and the Quattro micro™ API mass spectrometer for the selective analysis of perchlorate in environmental waters.

Chromatographic selectivity of the polymethacrylate-based IC-Pak A/HR column using ammonium bicarbonate and AcCN, eliminates the interference from sulfate and the need for sample prep to remove chloride and sulfate.

LC/MS/MS is capable of detecting <100 ppt in a high totally dissolved solids water, such as 0.3% brackish water or soils leachate, within 15 minutes injection to injection.

The 50% AcCN eliminates any build-up neutral TOC effecting column performance, normally observed with all aqueous eluents.

This chromatographic method has not been fully validated and represents feasibility. It is the responsibility of the user of this method to provide an initial demonstration of performance on the expected matrices before quantitative work can begin. However, draft EPA method 331.0 (2005) has validated the MS/MS acquisition and processing for perchlorate in drinking and waste water using a similar column and eluent.

Waters

THE SCIENCE OF WHAT'S POSSIBLE.™

Waters, Micromass, and Alliance are registered trademarks of Waters Corporation. IC-Pak, Quattro micro, and The Science of What's Possible are trademarks of Waters Corporation. All other trademarks are the property of their respective owners.

©2005-2007 Waters Corporation. Printed in the U.S.A.
June 2007 720000941EN RB-AC

Waters Corporation
34 Maple Street
Milford, MA 01757 U.S.A.
T: 1 508 478 2000
F: 1 508 872 1990
www.waters.com

