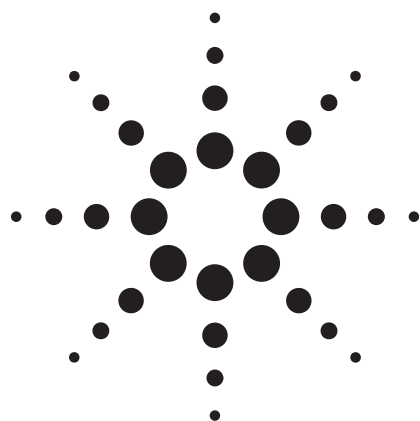


Quantitative Analysis of Perchlorate by Ion Chromatography MS/MS



Application

Environmental

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Abstract

Perchlorate in water is analyzed using a Metrohm Ion Chromatography system interfaced to an Agilent 6410 Triple Quadrupole (QQQ) Mass Spectrometer. Quantitation is based on the sum of two multiple reaction monitoring (MRM) transitions corresponding to both chlorine isotopes (^{35}Cl and ^{37}Cl) of perchlorate. Excellent linearity among calibration standards ranging from 0.5 to 25 ppb is

established using the Metrohm conductivity detector with a resulting coefficient of linearity of $R^2 > 0.999$. Linearity for the QQQ mass spectrometer is $R^2 > 0.998$ over the range of 0.01 to 10 ppb. Reproducibility among seven replicate injections of standards is also excellent for the QQQ, with seven replicates at the 0.1 ppb level resulting in a peak area relative standard deviation (RSD) of only 5.33%.

Confirming the presence of perchlorate by QQQ mass spectrometry involves measuring the peak area ion ratio of the two MRM transitions, corresponding to the ^{35}Cl and ^{37}Cl isotopes. The transitions are $101 > 85$ and $99 > 83$. The sum of the two is used for quantitation and the latter is used as a qualifier so that as long as all analyzed samples have qualifier to quantifier peak area ion ratios within $\pm 20\%$ of the value determined using one of the calibration standards, the presence of perchlorate is confirmed.

Perchlorate in the presence of the total dissolved solids (TDS) of chloride, carbonate, and sulfate in reagent water is also analyzed. For example, at the 3,000 ppm TDS concentration, reproducibility among seven replicate injections of perchlorate at 1 ppb is only 0.2%, when using the IC conductivity detector. Tandem IC conductivity and MSMS yields very similar results. The advantage of MSMS is to have confirmation and Metrohm Suppressor de-salts the matrix to yield better sensitivity for MSMS.

When using the QQQ mass spectrometer to analyze perchlorate in the presence of salt water, the reproducibility is very good. For example, at 1 ppb perchlorate in 1,000 ppm salt water, the peak area reproducibility among three injections is only 0.63% RSD.



Agilent Technologies

Introduction

Perchlorate is commonly used as an oxidant in solid fuel propellants for rockets and missiles. Recently, perchlorate contamination was found in many aquifers associated with the Colorado River (CA). Other sites were also identified, but by far the widest contamination problem is in California, Nevada, and Arizona. Perchlorate was also found at elevated levels in crops that use contaminated water for irrigation. Ion chromatograph (IC) with conductivity detection can be used to measure perchlorate levels in drinking and waste waters (as per EPA Method 314). The method is reliable to approximately 1 to 5 ppb in drinking water, but sensitivity decreases dramatically as the complexity of the matrix is increased (such as in surface and waste waters). Both false positive and false negative results may occur due to matrix effects and co-eluting substances detected by nonspecific conductivity detection. Lower detection limits (DLs) for perchlorate are needed as the EPA and state environmental agencies are looking to target levels in the 1 to 2 ppb range. Reliability of the measurement in heavy matrix samples is also important.

The use of a mass spectrometer as a detector for perchlorate at much lower DLs (50 to 100 ppt) has shown promise; however, reliability issues and problems related to suppression of the electrospray ionization (ESI) signals in typical matrices are well documented phenomena. The key to reducing suppression is to ensure that analyte and high concentrations of matrix are well separated and do not enter the ion source and interface at the same time.

In addition to ion suppression in the source, the m/z attributed to the perchlorate anion (99 and 101) have isobaric interferences that can be attributed to minor sulfate isotopes and from organic material that can be present and bleed from the column used for IC and the associated cation suppressor. The selection of separation column and suppressor are critical for reduction of sample bleed and for efficient separation of high levels of interfering ions, particularly sulfate.

Two USEPA methods (EPA Method 332.0 and SW-846 Method 6860) have been developed and published for this analyte using ion chromatography mass spectrometry (ICMS) and/or ICMSMS. The advantage of using tandem mass spectrometers is that interference from the hydrogen sulfate ion (HSO_4^- , m/z 99) can be completely eliminated

because in secondary fragmentation, the perchlorate transition is $99 > 83$ (loss of ^{16}O) but sulfate (HSO_4^-) ion is completely destroyed and does not even interfere. This helps to quantify the perchlorate ion with an excellent isotope ratio for chlorine ($^{35}\text{Cl}/^{37}\text{Cl}$) without any distortion. Data in this application is demonstrated. This application is also applicable to complex matrices like green leafy vegetables, fruits, plants (bio-accumulation of perchlorate), wines, and liquid medicines.

The chemical structure of perchlorate is shown in Figure 1. The compound is an excellent candidate for negative polarity electrospray ionization as it exists as an ion in solution.

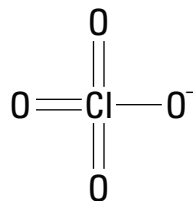


Figure 1. Chemical structure of perchlorate.

Experimental

Sample Preparation

The following samples are prepared for use in the analysis:

Perchlorate stock standard (1,000 ppm) is prepared from sodium perchlorate (Sigma p/n S-1513, MW 122.4, CAS 7601-89-0). The stock standard is spiked into reagent-grade water to make up both calibration levels and lowest concentration minimum reporting limits (LCMRL). The LCMRL samples are used as quality controls and a reproducibility evaluation is made from replicate injections at differing concentrations.

Total dissolved solid (TDS) samples, which contain 3,000 ppm each of chloride, carbonate, and sulfate, dissolved in reagent water, are made up using ACS-grade sodium chloride, sodium carbonate, and sodium sulfate purchased from Aldrich (Milwaukee, WI).

Isotopic (^{18}O) enriched sodium perchlorate is used as internal standard and spiked into all TDS samples, calibrators, and LCMRLs at 10 ppm. The internal standard solution is purchased commercially from SPEX (Metuchen, NJ).

IC/MS/MS Details

Metrohm IC components

Metrohm Model 818 Inert Dual Piston Pump
Metrohm Model 819 Conductivity Detector
Metrohm Model 820 Separation Center (with two injection valves)
Metrohm Model 830 Interface
Metrohm Model 833 MSM-II
Metrohm Model 853 Sequential Suppressor
Metrohm Model 838 Auto Sample Processor
Metrosep ASUPP7-250 column (4.0 mm id × 250 mm length)
Metrosep RP Guard disc

Ion Chromatography Conditions

Eluent 10 mM sodium carbonate (Na_2CO_3) + 35% acetonitrile
Column temperature 45 °C
Column flow rate 0.7 mL/min
Injection volume 100 μL
Conductivity detector Range and full scale = 100 $\mu\text{Siemens/sec}$

The mass spectrometry component is the **Agilent 6410 Triple Quadrupole Mass Spectrometer**.

Mass Spectrometry Conditions

Mode Negative ESI using the Agilent G1948B ionization source
Nebulizer 45 psig
Drying gas flow 12 L/min
Drying gas temp 350 °C
 V_{cap} 1750 V
Resolution (FWHM) Q1 (unit) = 0.7 amu; Q2 (unit) = 0.7 amu
Fragmentor 120 V
Collision energy 30 V
Dwell time 200 msec
MRM transitions:
Perchlorate (sum of both Cl^{35} and Cl^{37} isotopes) = m/z 99 > 83 + 101 > 85
Perchlorate internal standard (O^{18}) = m/z 107 > 89

Results and Discussion

Part 1: Calibration Levels and LCMRLs

The conductivity calibration curve using the signal generated from the Model 819 conductivity detector of the Metrohm IC system is shown in Figure 2. Conductivity is measured in units of micro-Siemens per sec ($\mu\text{S/sec}$). The calibration curve fit has a coefficient of linear regression $R^2 > 0.999$ over the calibration level range of 0.5 to 25 ppb.

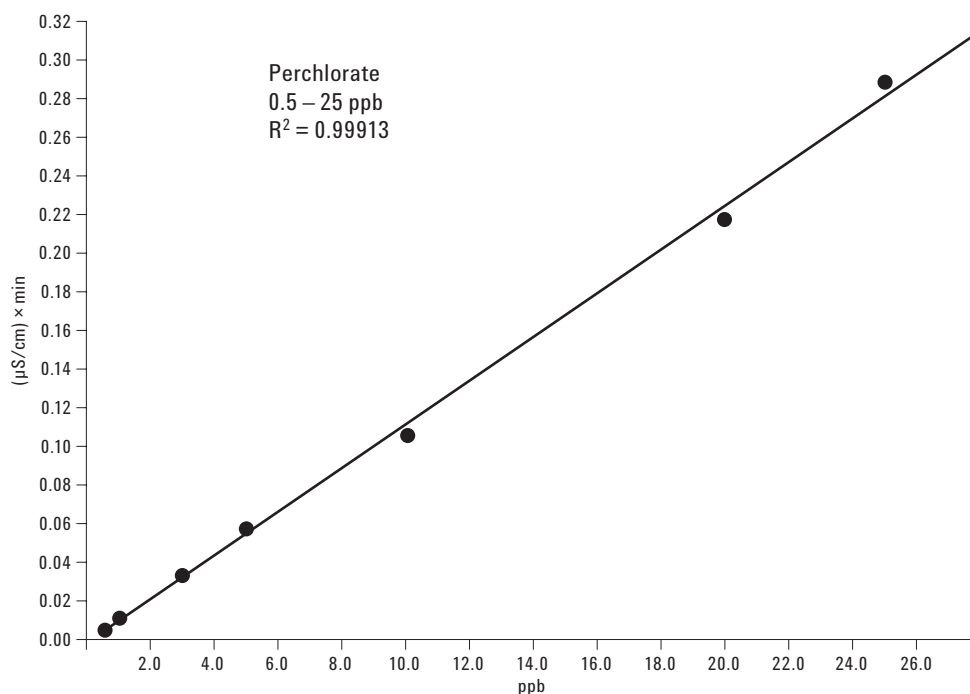


Figure 2. Conductivity calibration curve.

The calibration curve for the QQQ mass spectrometry analysis of this work is shown in Figure 3. The measured signal is the sum of two MRM transitions coming from both the ^{35}Cl ($99 > 83$) and ^{37}Cl ($101 > 85$) isotopic ion contributions. The lowest three levels are expanded to demonstrate excellent accuracy with respect to the curve as well as excellent

reproducibility of the lowest level LCMRL samples at 0.1 ppb. Reproducibility is further detailed in Table 1 as the percent relative standard deviation (% RSD) of the calculated concentrations for seven replicate injections. The reproducibility is also demonstrated in Figures 4a through 4c as overlaid chromatographic traces.

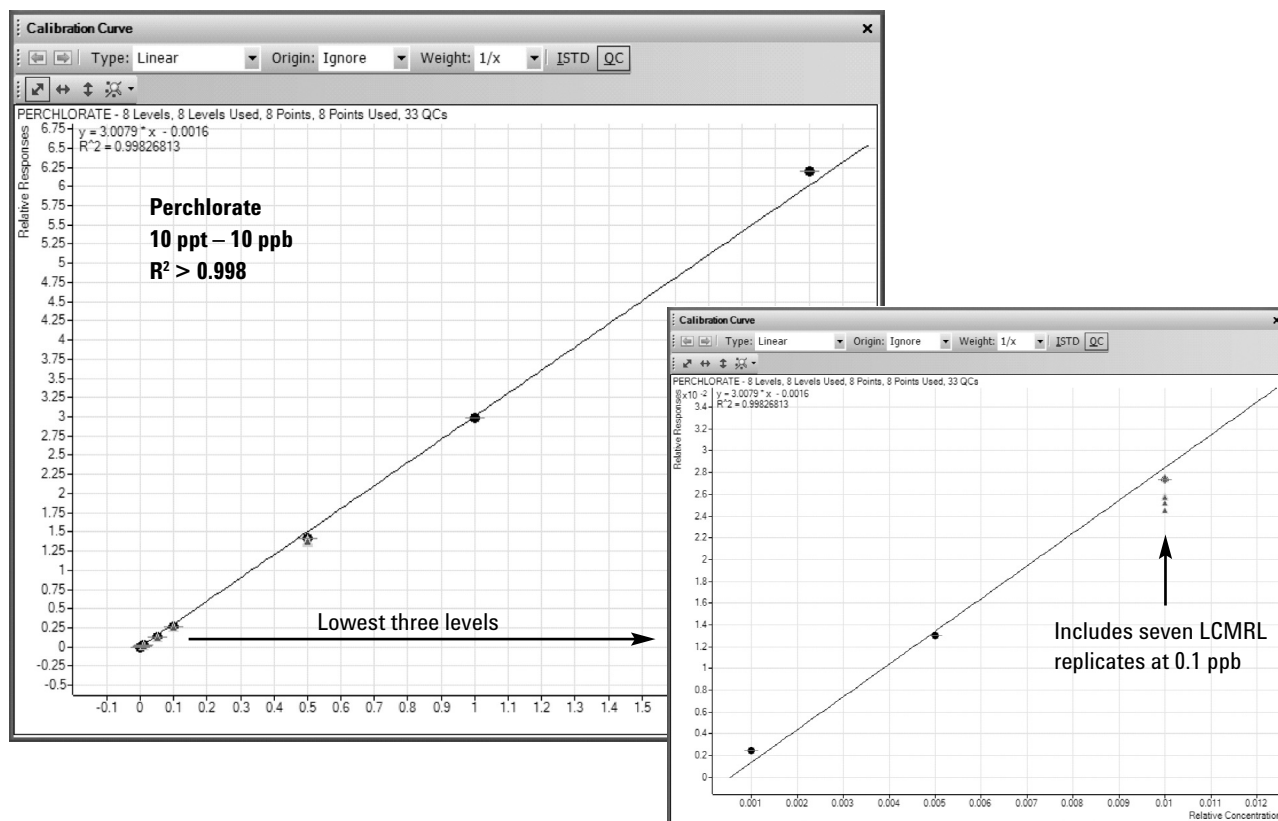


Figure 3. Good MS linearity for perchlorate over three orders of magnitude with excellent accuracy shown at lower end.

Table 1 Reproducibility of Calculated Concentrations for LCMRLs

LCMRL replicate	0.1 ppb Calc. conc.	0.5 ppb Calc. conc.	1 ppb Calc. conc.
1	0.1191	0.5546	1.0713
2	0.1089	0.5267	1.0863
3	0.1110	0.5149	1.0897
4	0.1140	0.5206	1.0809
5	0.1073	0.5417	1.1000
6	0.1087	0.5406	1.0888
7	0.1002	0.5534	1.0975
Standard dev	0.006	0.016	0.010
Average	0.110	0.536	1.088
% RSD	5.33	2.92	0.90

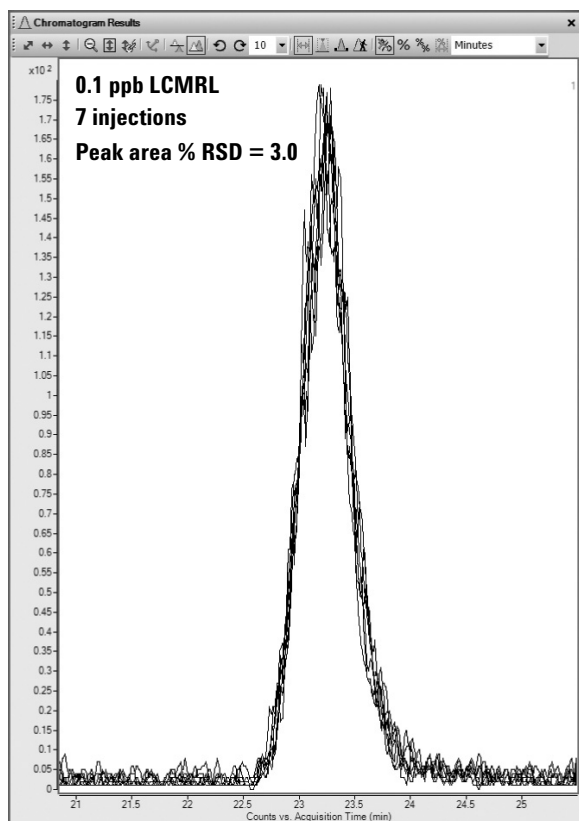


Figure 4a. MS chromatographic overlay of 0.1 ppb LCMRL.

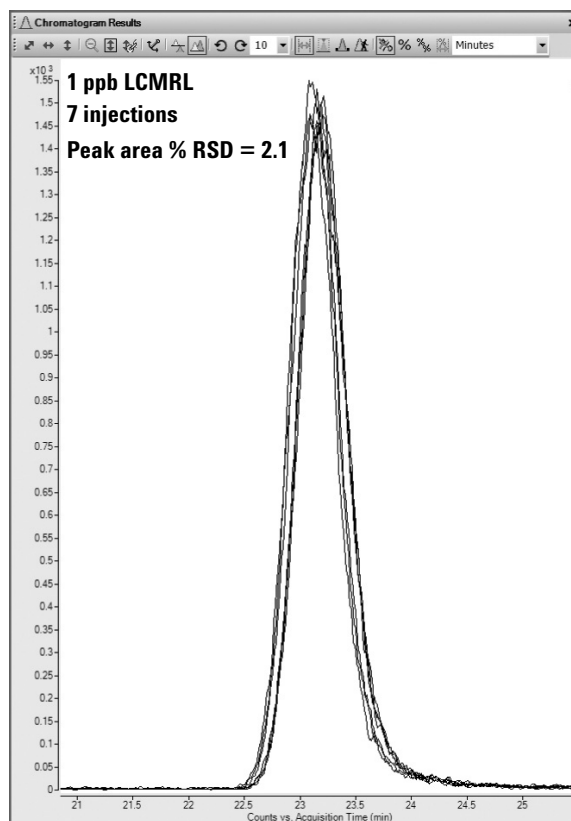


Figure 4c. MS chromatographic overlay of 1 ppb LCMRL.

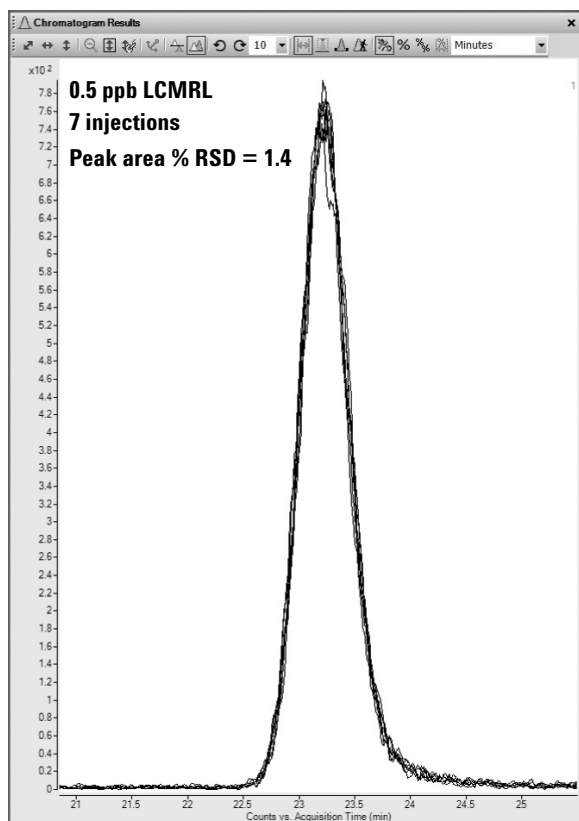


Figure 4b. MS chromatographic overlay of 0.5 ppb LCMRL.

For confirming the presence of the perchlorate ion the less intense ³⁷Cl MRM transition can be used as a qualifier ion. As long as all samples have ion ratios within $\pm 20\%$ of the expected value, the presence of perchlorate in that sample is confirmed. An example involving one of the 0.5 ppb LCMRL injections is shown in Figure 5.

Part 2: TDS Samples

These samples are made up of reagent water, spiked perchlorate analyte, and internal standards, as well as 3,000 ppm each of chloride, carbonate, and sulfate.

Figure 6 shows the Metrohm conductivity trace of perchlorate in the presence of the 3,000 ppm TDS and the need to have a relatively long elution time of approximately 21 minutes in order to chromatographically separate the perchlorate from the TDS matrix. The reproducibility of seven replicate injections is demonstrated in Figure 7, with corresponding peak area reproducibility shown in Table 2.

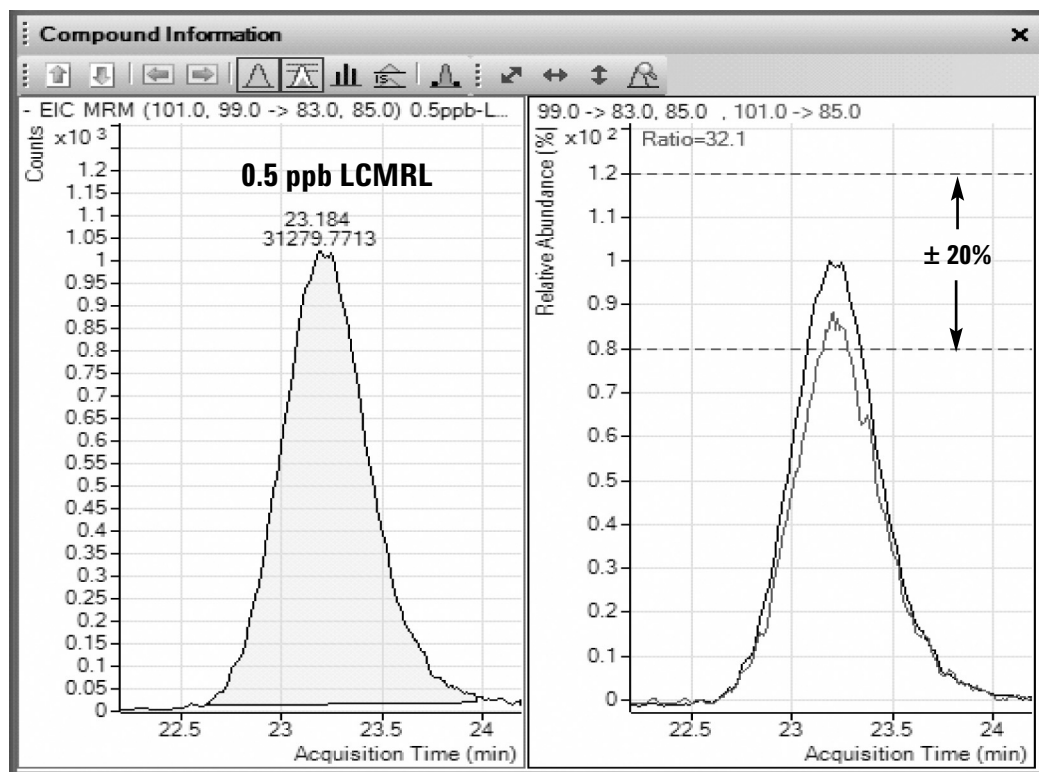


Figure 5. Confirmation of perchlorate using qualifier/quantifier peak area ion ratios.

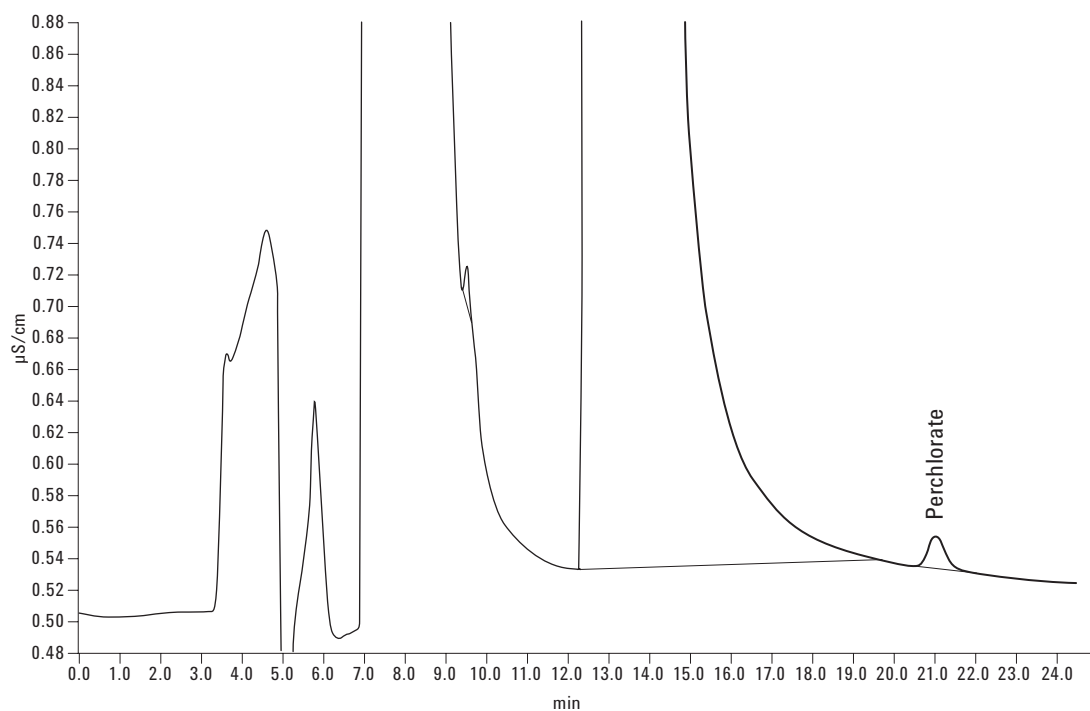


Figure 6. Chromatographic trace of 1 ppb perchlorate (RT = 21 min) in the presence of 3,000 ppm TDS. Plot of conductance ($\mu\text{S}/\text{sec}$) vs. time (min).

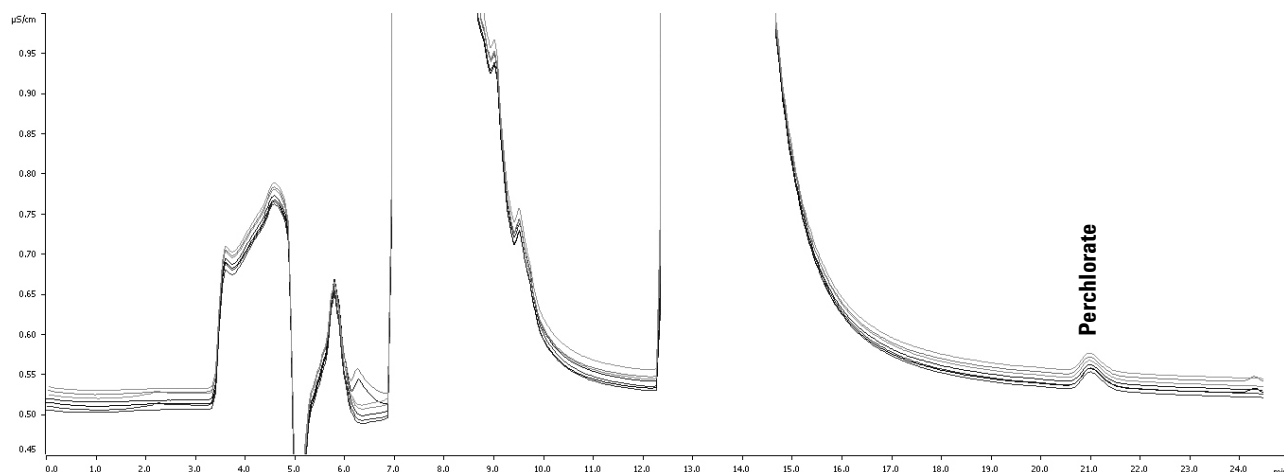


Figure 7. Overlay of seven 1-ppb perchlorate replicate injections in 3,000 ppm TDS.

Table 2. Reproducibility of Seven Replicate Injections at 1 ppb Perchlorate in 3,000 ppm TDS (Calculated concentrations based on conductivity calibration of Figure 2.)

Sample id	Perchlorate ug/L
MDL-1	1.220
MDL-2	1.221
MDL-3	1.223
MDL-4	1.221
MDL-5	1.216
MDL-6	1.220
MDL-7	1.219
Average	1.220
Standard dev	0.002
% RSD	0.177
True value	1.200
% Recovery	101.67

In Figure 8, three of the injections for perchlorate in the 3,000 ppm TDS are shown. The peak area reproducibility is not very good and is obviously affected by the presence of the chloride, carbonate, and sulfate, dissolved in reagent water. The peak area RSD is about 41%, even though the minimum peak-to-peak signal-to-noise ratio (p-p S/N) is 25:1.

And yet, when using the QQQ mass spectrometer to analyze perchlorate in the presence of salt water, the reproducibility is very good. For example, at 1 ppb perchlorate in 1,000 ppm salt water the peak area reproducibility among three injections is only 0.63% RSD, as shown in Figure 9.

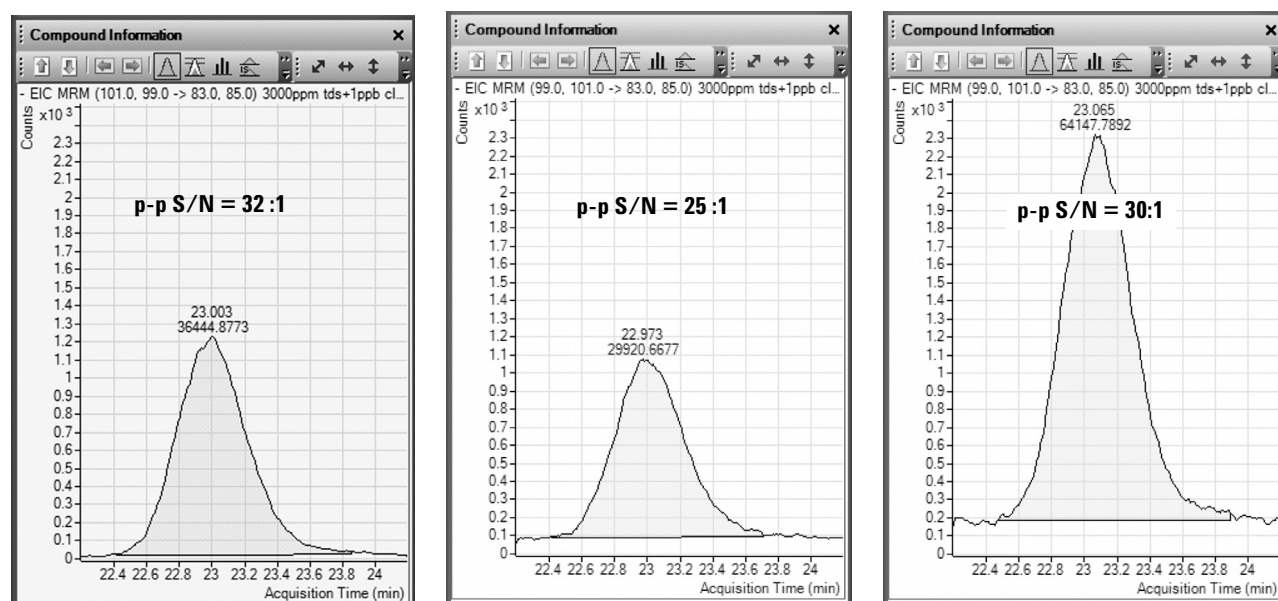


Figure 8. Peak area reproducibility for three injections of 1 ppb perchlorate in 3,000 ppm TDS is 41% RSD.

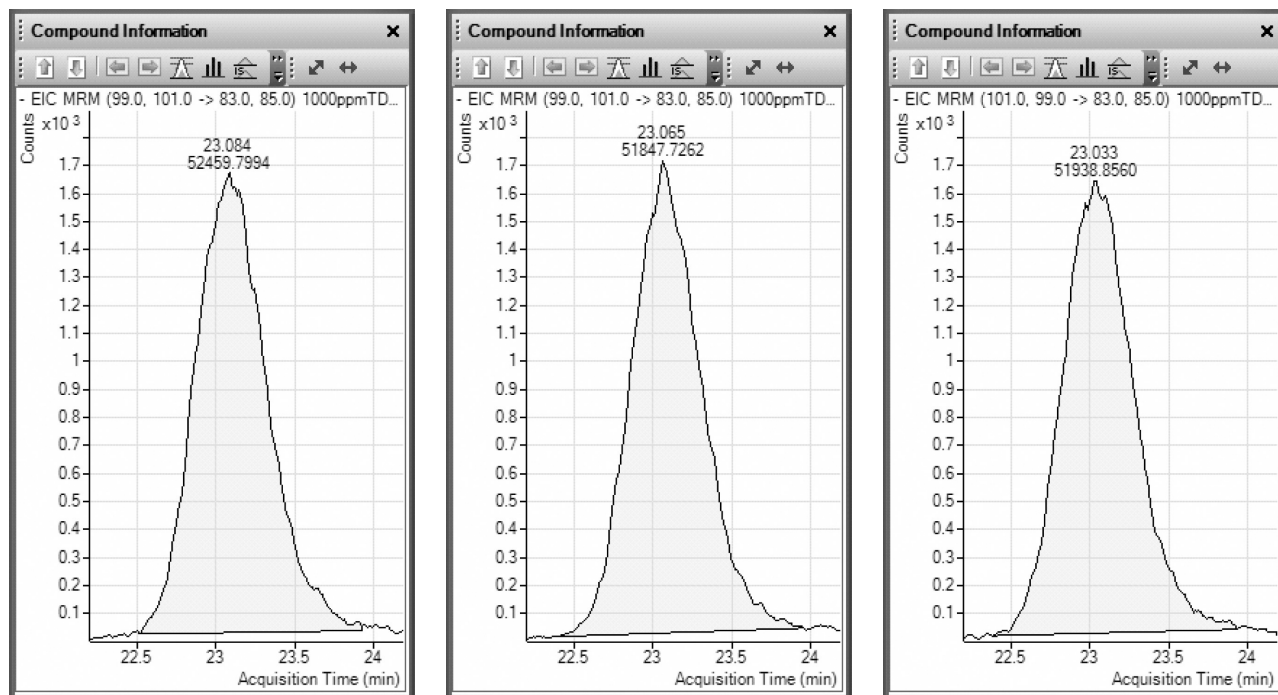


Figure 9. Peak area reproducibility for three injections of 1 ppb perchlorate in 1,000 ppm salt water is 0.63% RSD.

Conclusions

The analysis of perchlorate in water using a Metrohm Ion Chromatography system interfaced to an Agilent 6410 QQQ Mass Spectrometer is carried out on several calibration standards in reagent water and at various concentrations in the presence of TDS consisting of chloride, carbonate, and sulfate and also in the presence of reagent water. A linearity coefficient of $R^2 > 0.999$ is established for perchlorate standards ranging in concentration from 0.5 to 25 ppb. Linearity for the QQQ mass spectrometer is $R^2 > 0.998$ over the range of 0.01 to 10 ppb. Reproducibility among seven replicate injections of standards is also excellent for the QQQ, with seven replicates at the 0.1 ppb level resulting in a peak area RSD of only 5.33%.

The confirmation of perchlorate by QQQ mass spectrometry is also done by using qualifier ion ratios.

Perchlorate at the 3,000 ppm TDS concentration shows excellent reproducibility among seven replicate injections of 1 ppb perchlorate with an RSD of only 0.2% when using the IC conductivity detector. However, in negative ion electrospray ionization mode, the QQQ mass spectrometer shows a 41% RSD at the same level, even though all peaks have a peak-to-peak signal-to-noise ratio of at least 25:1.

When using the QQQ mass spectrometer to analyze perchlorate in the presence of salt water, the reproducibility is very good. For example, at 1 ppb perchlorate in 1,000 ppm salt water, the peak area reproducibility among three injections is only 0.63% RSD.

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