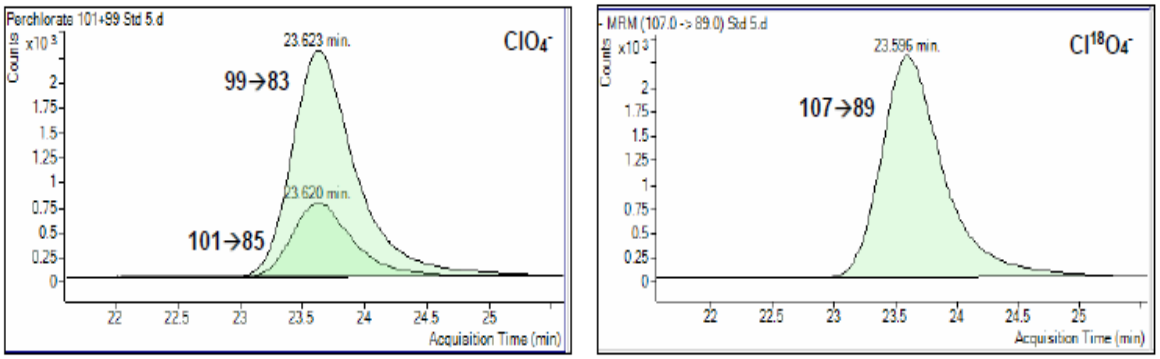
IC Application Note M–14

Trace perchlorate in drinking water

Determination as per US EPA 332.0 applying IC-MS/MS



Extracted MRM Ion Chromatograms of perchlorate (left) and the internal standard ($Cl^{18}O_4^-$, right)

Perchlorate contamination in drinking water may have different sources. Besides natural deposits, anthropogenic sources like fertilizers and rocket fuel residue add to hazardous water contamination. Perchlorate interferes with iodine uptake into the thyroid gland. Newborns and children are particularly vunerable, affected as thyroid hormones are essential for growth. Besides ion chromatography (IC) followed conductivity detection, IC hyphenated with an MS detector can be used to measure perchlorate down to sub-µg/L levels. In this application IC is hyphenated with a triple-quadrupole MS (IC-MS/MS) for perchlorate determination in order to meet the requirements of EPA 332.0. This IC-MS/MS setup avoids the possible interference of sulfate.

Results

ID	Tap water	Pond water	Creek water
Perchlorate 1	0.2393	0.0936	0.1008
Perchlorate 2	0.2254	0.0964	0.1011
Perchlorate 3	0.2202	0.0963	0.1010
Mean [µg/L]	0.228	0.095	0.101
Std. Dev. [µg/L]	0.010	0.002	0.000
RSD [%]	4.33	1.67	0.15

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Sample

Fortified matrix sample, water samples

Sample preparation

None

Columns

Metrosep A Supp 7 – 250/4.0	6.1006.630
Metrosep A Supp 5 Guard/4.0	6.1006.500

IC Solutions

Eluent	10 mmol/L sodium carbonate 10 % (v/v) acetonitrile
Regenerant Dosino	1 mol/L nitric acid 10 % (v/v) acetonitrile
Rinsing	10 % (v/v) acetonitrile

Parameters IC

Flow rate	0.7 mL/min
Injection volume (MiPT)	100 µL
P_{max}	150 MPa
Column temperature	45 °C
Recording time	28 min

Parameters MS/MS

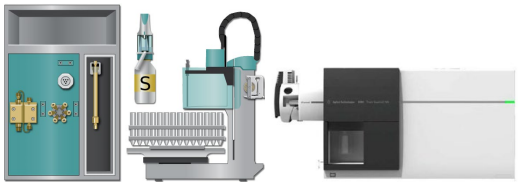
Nebulizer	45 psig
Drying gas flow	12 L/min
Drying gas temperature	350 °C
Capillary voltage	3500 V
MS polarity	Negative
Resolution	Unit (0.7 amu)
Dwell time	200 ms
Fragmentor	120 V
Collision energy	30 V
MRM $Cl^{18}O_4$ transition	107→89
MRM ClO_4 transitions	101→85 + 99→83

Analysis

MS/MS detection (triple quad)

Instrumentation

940 Professional IC Vario ONE/SeS	2.940.1400
Agilent 6470A Triple Quadrupole Mass Spectrometer w/Jet Stream ESI Source	
858 Professional Sample Processor	2.858.0020
800 Dosino	2.800.0010
Remote Box MSB	6.2148.010
MSM-HC Rotor	6.2842.000
IC equipment: Dosino Regeneration	6.5330190
MagIC Net Professional	6.6059.322
Agilent Mass Hunter Software	Ver. B.08.00



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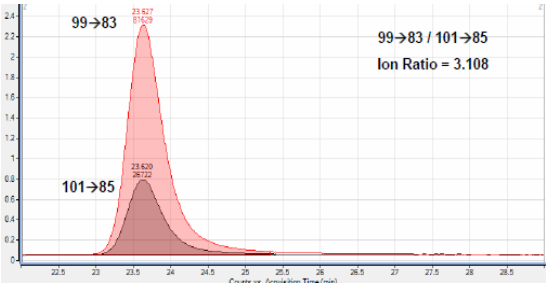
Results:

Perchlorate ion ratio

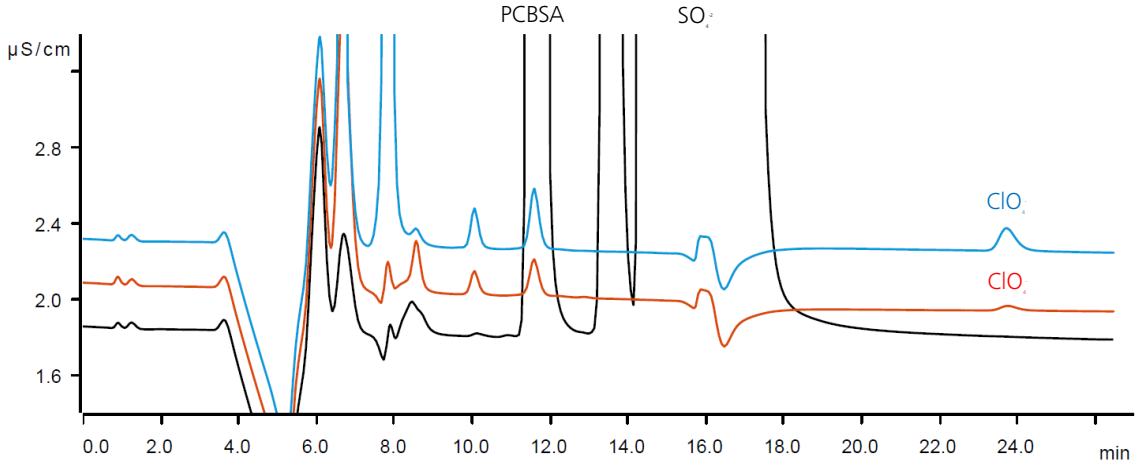


Cal Std level (1 … 11	Ion ratio 99→83 / 101→85
Average ratio	3.138
Std. Dev	0.022
% RSD	0.71

7 replicates	LCMRL 0.1 µg/L Ion ratio	LCMRL 0.25 µg/L Ion ratio
Average Ratio	3.211	3.211
% RSD	4.14	2.46
% Deviation from Cal STD Average	2.34%	2.46%
QC Deviation Limit	20%	20%
QC Ratio Result	Pass	Pass

PCBSA interference check:

Para-Chloro Benzene Sulfonic Acid (PCBSA) is an ingredient of a well-known industrial surfactant formula. On some anion column types PCBSA behaves similarly to perchlorate. The figure below demonstrates chromatographic separation of PCBSA from perchlorate using conductivity detection.



Black: 100 mg/L PCBSA + 1g/L sulfate; red: 1 µg/L perchlorate; blue: 5 µg/L perchlorate

LCMRL Sample Data:

Seven replicates of several LCMRL standards are analyzed to determine reproducibility. Using the standard deviation from the 0.1 µg/L (ppb) LCMRL and a student's t value for six degrees of freedom and a 99% confidence limit (3.143), the estimated detection limit was determined to be 0.041 µg/L (ppb) perchlorate (Detection limit = standard deviation x student's t).

Replicate	0.11 µg/L	0.24 µg/L	0.47 µg/L	0.73 µg/L
1	0.1590	0.2837	0.4524	0.7817
2	0.1605	0.2786	0.4615	0.7718
3	0.1775	0.2786	0.4855	0.8719
4	0.1392	0.2774	0.4825	0.8652
5	0.1415	0.2746	0.4823	0.7328
6	0.1468	0.2730	0.4879	0.7240
7	0.1495	0.2996	0.4887	0.9006
Average (µg/L)	**0.153**	**0.281**	**0.477**	**0.807**
Std. Dev.	0.013	0.009	0.014	0.072
% RSD	8.68	3.19	3.00	8.87
LCMRL	**0.041**			

Perchlorate detection in salt matrices:

Recovery of spiked samples with high ion matrix (including chloride, carbonate, and sulfate).

Replicate	150 mg/L TDS [µg/L ClO_4^-]	450 mg/L TDS [µg/L ClO_4^-]	900 mg/L TDS [µg/L ClO_4^-]	2100 mg/L TDS [µg/L ClO_4^-]	3000 mg/L TDS [µg/L ClO_4^-]
1	0.8949	0.8953	0.9691	1.0283	0.9662
2	0.8983	0.9098	0.9660	1.0423	0.8758
3	0.9622	0.9030	1.0429	0.9840	0.9745
4	0.9615	0.9073	0.9880	0.9824	0.9675
5	0.9546	0.8934	0.9936	0.9865	0.9534
6	0.9722	0.9128	1.0137	1.0061	0.9892
7	1.0692	0.8977	0.9721	1.0469	0.9844
Average (µg/L)	**0.959**	**0.903**	**0.992**	**1.011**	**0.973**
Std. Dev.	0.058	0.008	0.28	0.028	0.012
% RSD	6.04	0.0.83	2.81	2.78	1.23
Spike actual (1µg/L)	0.9515	0.9001	0.9549	0.9850	0.9569
Recovery	**99.22**	**99.71**	**96.24**	**97.44**	**98.35**

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