

USEPA method 314.0*[§] - Determination of Trace Level Perchlorate in Reagent Water, Ground Water, Surface Water, Water containing 3000ppm of Total Dissolved Solids (TDS) using Confirmation Column and Suppressed Conductivity Detection

Branch: Water, waste water, environmental protection

* Refer to page 51 of following document

ENVIRONMENTAL PROTECTION AGENCY
40 CFR Part 141

[Docket No. OW-2004-0001; FRL-]

RIN: 2040-AD93

*Unregulated Contaminant Monitoring
Regulation (UCMR) for Public Water Systems*

AGENCY: Environmental Protection Agency.

ACTION: Proposed Rule.

As per page 51, it is noted in first paragraph as

“Note: Since Method 314.0 was published in 1999 to support UCMR 1 monitoring at an MRL of 4.0 $\mu\text{g/L}$, new instrumentation has been made commercially available from Metrohm Peak that can, using this method, achieve the MRL of 0.57 $\mu\text{g/L}$ as called for by this proposed regulation, while meeting all of the quality control criteria of the method. Because enhanced Method 314.0 permits flexibility in the eluent, chromatographic column, and suppressor that are used, this new instrumentation would be permitted within the scope of the original method. Therefore, enhanced Method 314.0 is being proposed for use in this regulation”

Further details regarding these procedures are available through EPA's UCMR Web site (<http://www.epa.gov/safewater/ucmr/ucmr2/index.html>) in a document titled "UCMR 2 Laboratory Approval Requirements and Information Document" (USEPA, 2004k).

§ Reference herein to any specific commercial products or nonprofit organization, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government and shall not be used for advertising or product endorsement purposes.

Keywords

850 Professional IC / 858 Professional Sample Processor / Suppressed Conductivity / ASUPP7 - 250 / Perchlorate / USEPA / Method 314.0 / Confirmation Column

Summary

Trace level Perchlorate determination is performed by USEPA method 314.0

However, as Matrix ions specially Chloride, Carbonate and Sulfate are increased, it becomes difficult to measure Perchlorate at trace level by normal Ion Chromatography and conductivity detection.

This application note demonstrate trace level (0.5parts per billion) Perchlorate analysis in High Ionic Matrix (3000ppm TDS) where 3000ppm TDS = 1000ppm each of Chloride, Carbonate and Sulfate ions. Sodium Salt of these ions was used to prepare standards.

Also, this application demonstrates the analysis of Perchlorate using conformational column. However, using ICMS or ICMSMS technique, conformational column analysis is not required. This instrument set can be directly interfaced with Agilent single quad MSD or Agilent triple Quad MSD.

Sample

Sample:

1. Calibration standards in Reagent Water
2. Matrix containing 1000ppm each of Chloride, Carbonate, and Sulfate (Total TDS = 3000ppm)

Preparation of Sodium Perchlorate Stock Solution (1000 parts per million):

Accurately weigh 1.230g Sodium Perchlorate (CAS 7601-89-0) per 1Liter of UHP water

Make appropriate dilutions to prepare 10parts per million, 1parts per million and 100parts per billion working standards for Perchlorate

Preparation of Calibration Standards:

Using appropriate working standards, prepare Calibration Standards as listed below

Preparation of Stock Matrix Solution

(25000 parts per million each of Cl⁻¹, HCO₃⁻¹, SO₄⁻²):

Accurately weigh 10.2875g Sodium Chloride *Ultra pure*

(CAS 7647-14-5) into 250mls volumetric. Add 9.2419g Sodium Sulfate Anhydrous *Ultra pure* (CAS 7757-82-6) and add 8.6063g Sodium Bicarbonate *Ultra pure* (CAS 144-55-8). Add water and completely dissolve salts. Bring the volume to the mark. Use this stock solution to prepare simulated Matrix samples.

Reagents

Eluent: 10.0mM Sodium Carbonate + 45% Acetonitrile

Suppressor solutions:

100mM Nitric Acid + 10%Acetonitrile (Regenerant)

Ultra High Purity Water + 10% Acetonitrile (Rinse)

Sample Loop Size = 500uL (loops size can be up to 2000uL for this application)

Standards Perchlorate (ClO₄⁻¹) ug/L

level	1	2	3	4	5	6	7
ClO ₄ ⁻¹	0.50	1.00	3.02	5.02	10.04	20.15	26.75

Apparatus and Accessories

Metrohm 850 Professional IC – Anion System with In-Line Ultra filtration

Metrohm 858 Professional Sample Processor

Metrosep ASUPP7 – 250



Sample Preparation

Preparation of simulated Matrix sample fortified with Perchlorate:

1. Reagent Water fortified with 0.5ppb Perchlorate

Measure 0.5mls of 100ppb Perchlorate standard in 100mls of UHP water

2. Reagent Water fortified with 5.0ppb Perchlorate

Measure 5mls of 100ppb Perchlorate standard in 100mls of UHP water

3. Matrix (1000 ppm each of Cl⁻¹, HCO₃⁻¹, SO₄⁻² =3000ppm TDS) fortified with 0.5ppb Perchlorate

Measure 0.5mls of 100ppb Perchlorate standard and 4mls of Stock Matrix Standard in 100mls of UHP water

4. Matrix (1000 ppm each of Cl⁻¹, HCO₃⁻¹, SO₄⁻² =3000ppm TDS) fortified with 5.0ppb Perchlorate

Measure 5mls of 100ppb Perchlorate standard and 4mls of Stock Matrix Standard in 100mls of UHP water

Analysis

Samples were analyzed using 858 Ultra filtration auto sampler

Calculation

Calculation was performed using MagIC Net software. MagIC net software has integrated capability for statistical data analysis.

Parameters (Time Program for Professional IC)

Time program				
Main program				
Time	Device	Module	Command	Parameter
0.0	850 Professional IC 1	MSM	Step	
	858 Professional Sample Processor 1	Rack	Move	Sample position
	858 Professional Sample Processor 1	Tower	Lift	125 mm
0.0	850 Professional IC 1	Injector	Fill	
0.0	858 Professional Sample Processor 1	Peristaltic	On/Off	On, Rate=5
3.0	850 Professional IC 1	Injector	Inject	
3.0	Perchlorate-314_0		Start data acquisition	
3.0	858 Professional Sample Processor 1	Peristaltic	On/Off	Off
	858 Professional Sample Processor 1	Rack	Move	Rack position 149
	858 Professional Sample Processor 1	Tower	Lift	125 mm
0.0	858 Professional Sample Processor 1	Peristaltic	On/Off	On, Rate=5
2.0	858 Professional Sample Processor 1	Peristaltic	On/Off	Off
	858 Professional Sample Processor 1	Rack	Move	Rack position 150
	858 Professional Sample Processor 1	Tower	Lift	125 mm
0.0	858 Professional Sample Processor 1	Peristaltic	On/Off	On, Rate=5
2.0	858 Professional Sample Processor 1	Peristaltic	On/Off	Off
	858 Professional Sample Processor 1	Rack	Move	Rack position 151
	858 Professional Sample Processor 1	Tower	Lift	125 mm
0.0	858 Professional Sample Processor 1	Peristaltic	On/Off	On, Rate=5
2.0	858 Professional Sample Processor 1	Peristaltic	On/Off	Off

Results

Refer to Appendix for Precision Data

Comments

1. To ensure good precision for low level standards, all standards were prepared gravimetrically.
2. Instrument was subjected to run continuously for 33.4 hours without losing precision and accuracy for Perchlorate analysis.
3. Built-in sample degasser enhances baseline even though organic solvent is used.
4. Sequential suppressor from Metrohm removes Carbonate from sample matrix very effectively to enhance the baseline noise by 33%

Appendix

Calibration curves and chromatograms with peak tables

Date

February 11, 2008

Name

USA Applications Team / Metrohm Peak Inc.

§ Mr. Johnson Mathew – *Env. Scientist*, USEPA Region 6 Laboratory, Houston TX USA

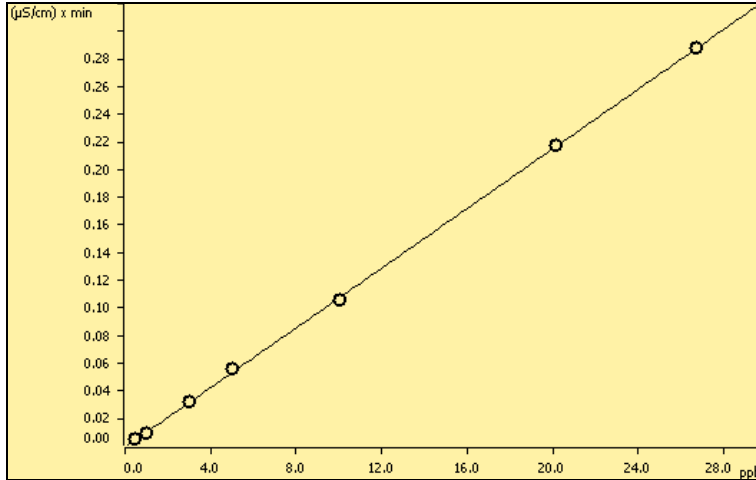
IC Application Work CODE
Title

Page 4/8 Appendix

CALIBRATION INFO

CALIBRATION OF COMPONENT Perchlorate

Method: Perchlorate USEPA 314.0.imet
RSD: 1.382 %
Correlation coefficient: 0.999932



	Sample type	Index	Conc.	Volume	Area	Ident	Date ▲	Used
▶ 1	Standard 1	1	0.500	500.0	0.005	Calibration-1	2007-11-28 19:33:06 UTC-6	<input checked="" type="checkbox"/>
2	Standard 2	1	1.000	500.0	0.009	Calibration-2	2007-11-28 20:00:58 UTC-6	<input checked="" type="checkbox"/>
3	Standard 3	1	3.020	500.0	0.032	Calibration-3	2007-11-28 20:28:50 UTC-6	<input checked="" type="checkbox"/>
4	Standard 4	1	5.020	500.0	0.056	Calibration-4	2007-11-28 20:56:43 UTC-6	<input checked="" type="checkbox"/>
5	Standard 5	1	10.040	500.0	0.106	Calibration-5	2007-11-28 21:24:36 UTC-6	<input checked="" type="checkbox"/>
6	Standard 6	1	20.150	500.0	0.217	Calibration-6	2007-11-28 21:52:29 UTC-6	<input checked="" type="checkbox"/>
7	Standard 7	1	26.750	500.0	0.288	Calibration-7	2007-11-28 22:20:22 UTC-6	<input checked="" type="checkbox"/>

Chromatograms with peak tables

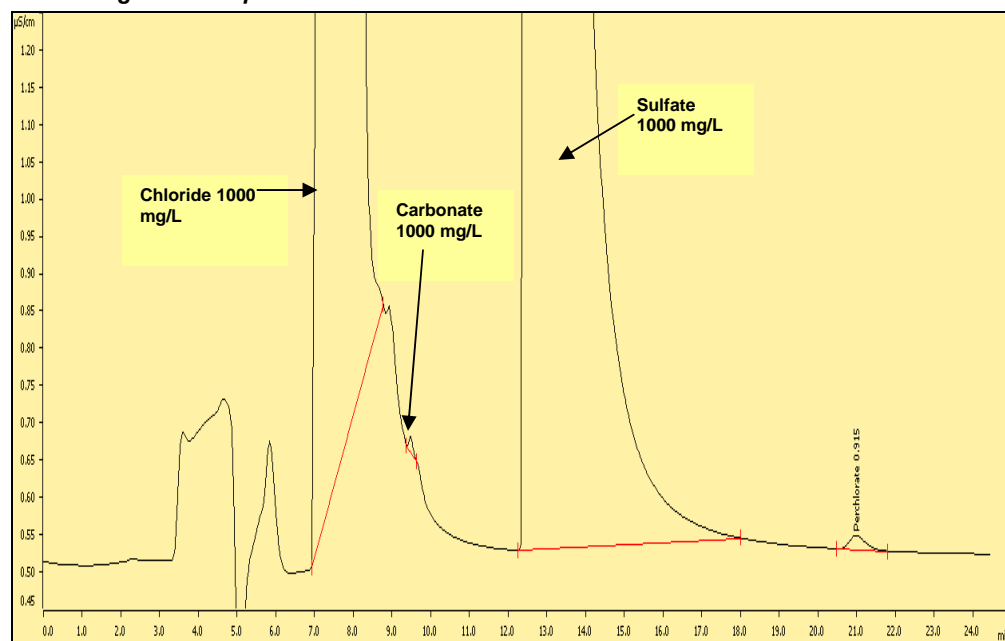


Figure 1 Reagent Water Fortified with 1.0ppb Perchlorate + 1000ppm each of Chloride, Carbonate, Sulfate

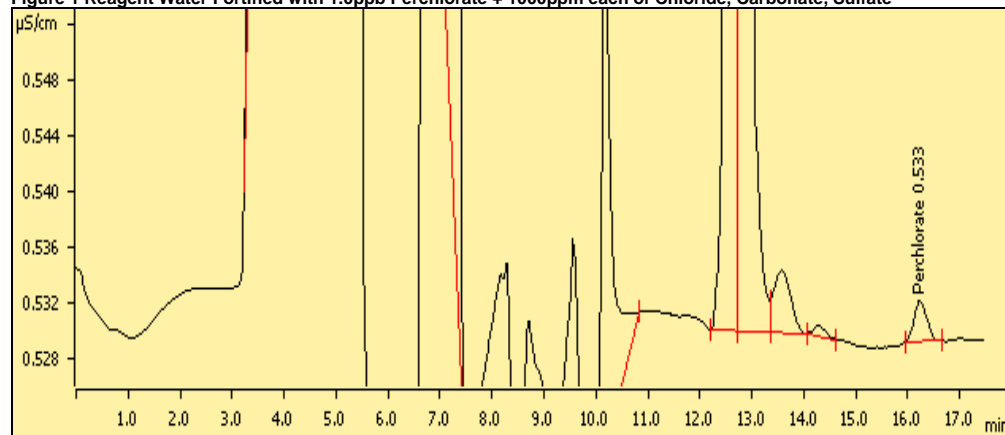


Figure 2 Reagent Water Fortified with 0.5ppb Perchlorate

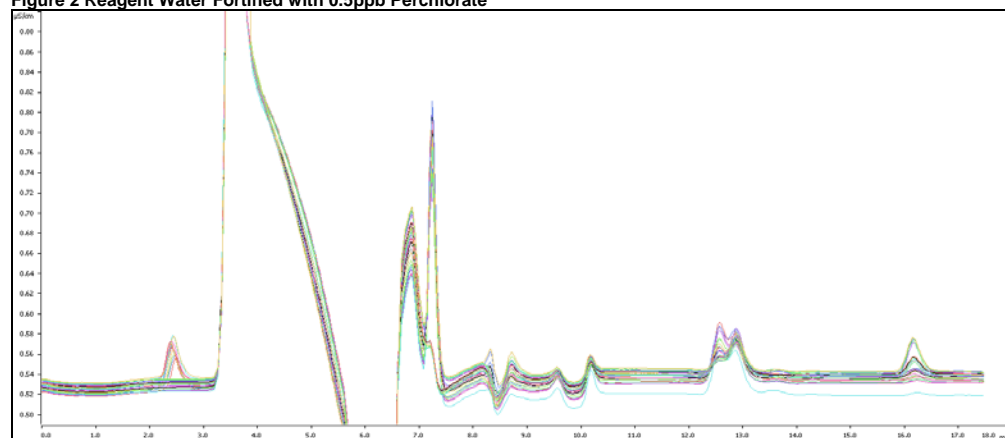


Figure 3 Stack of 7 replicates of each LCMRL standards

Precision Data

Number	Ident	Sample type	.	.	Perchlorate
1	Blank DI water	Sample	
2	Blank DI water	Sample	
3	Blank DI water	Sample	
4	Calibration std-1	Standard 1	0.589 ppb
5	Calibration std-2	Standard 2	1.054 ppb
6	Calibration std-3	Standard 3	2.586 ppb
7	Calibration std-4	Standard 4	4.853 ppb
8	Calibration std-5	Standard 5	9.793 ppb
9	Calibration std-6	Standard 6	20.125 ppb
10	Blank DI water	Sample	
11	CCV	Sample	4.920 ppb
12	LCMRL-1-1	Sample	0.566 ppb
13	LCMRL-1-2	Sample	0.539 ppb
14	LCMRL-1-3	Sample	0.543 ppb
15	LCMRL-1-4	Sample	0.575 ppb
16	LCMRL-1-5	Sample	0.533 ppb
17	LCMRL-1-6	Sample	0.557 ppb
18	LCMRL-1-7	Sample	0.564 ppb
19	Blank DI water	Sample	
20	CCV	Sample	4.957 ppb
21	LCMRL-2-1	Sample	1.055 ppb
22	LCMRL-2-2	Sample	1.067 ppb
23	LCMRL-2-3	Sample	1.071 ppb
24	LCMRL-2-4	Sample	1.046 ppb
25	LCMRL-2-5	Sample	1.050 ppb
26	LCMRL-2-6	Sample	1.053 ppb
27	LCMRL-2-7	Sample	1.063 ppb
28	Blank DI water	Sample	

29	CCV	Sample	4.994 ppb
30	LCMRL-3-1	Sample	2.541 ppb
31	LCMRL-3-2	Sample	2.559 ppb
32	LCMRL-3-3	Sample	2.538 ppb
33	LCMRL-3-4	Sample	2.590 ppb
34	LCMRL-3-5	Sample	2.537 ppb
35	LCMRL-3-6	Sample	2.532 ppb
36	LCMRL-3-7	Sample	2.504 ppb
37	Blank DI water	Sample	
38	CCV	Sample	5.030 ppb
39	LCMRL-4-1	Sample	5.164 ppb
40	LCMRL-4-2	Sample	5.046 ppb
41	LCMRL-4-3	Sample	5.025 ppb
42	LCMRL-4-4	Sample	5.004 ppb
43	LCMRL-4-5	Sample	5.071 ppb
44	LCMRL-4-6	Sample	4.988 ppb
45	LCMRL-4-7	Sample	5.106 ppb
46	Blank DI water	Sample	

USEPA – LCMRL Calculation * (Evaluated by US EPA Office of Drinking water and ground water – Cincinnati, OH)
LCMRL for Perchlorate on ASUPP7 - 250 column = 0.25 parts per billion. USEPA 314.0 enhanced method
Perchlorate Minimum Reporting Limit (MRL) = 0.57 parts per million

Further information for LCMRL, visit - <http://www.epa.gov/safewater/methods/sourcalt.html>

