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Trace level perchlorate analysis by ion chromatography–mass spectrometry☆

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Abstract

Perchlorate is commonly used as an oxidant in solid fuel propellant for rockets and missiles. Recently perchlorate contamination was found in many aquifers associated with Colorado River and other sites. Perchlorate was also found at elevated level in crops that use contaminated water for irrigation. Ion chromatography with conductivity detection could be used to measure perchlorate levels in drinking and wastewaters as per United States Environmental Protection Agency method 314, but at lower levels and with complexity of the matrix there could be false positive and/or false negative. This study was done to demonstrate the detection of perchlorate with lower detection limit with high ionic matrix by ion chromatography–mass spectrometry.

Keywords: Perchlorate; IC; MS; IC–MS; ClO_4^-; Perchlorate by IC–MS; Trace perchlorate

1. Introduction

Perchlorate is an oxidant used primarily in solid fuel propellants for rockets, missiles and pyrotechnics. Perchlorate water has been found across the southwestern USA. Some sources have been traced to defense industry or to manufactures that supply the defense industry. Perchlorate is a known thyroid hormone inhibitor.

Ion chromatography (IC) with conductivity detection can be used to measure perchlorate levels in drinking and wastewaters (as per United States Environmental Protection Agency (EPA) Method 314 [1]). The method is reliable to approximately 1–5 μg/L in drinking water, but sensitivity decreases dramatically as the complexity of the matrix is increased (such as in surface and wastewaters). Both false positive and false negative results may occur due to matrix effects and coeluting substances detected by nonspecific conductivity detection. Lower detection limits (DLs) for perchlorate are needed, since the EPA and state environmental agencies are seeking to target levels in the 1–2 μg/L 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 (50–100 ng/L) has shown promise, but reliability issues and problems related to suppression of the electrospray ionization (ESI—the production of ions by evaporation of charged droplets obtained through spraying and electrical field) signals in typical matrices are well known. 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 perchlorate anion (99 and 101) have isobaric interferences that can be attributed to minor sulfate isotopes and organic material that can be present and bleed from the column used for IC and the associated cation suppressor. The

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proper selection of separation column and suppressor is critical to reduce sample bleed and to provide efficient separation of high levels of interfering ions, particularly sulfate.

1.1. Precautions unique to ion chromatography–mass spectrometry

The use of nonvolatile buffer systems is usually avoided when performing ESI or any atmospheric pressure ionization (API) technique. Some IC mobile phase reagents (such as strong inorganic acids) are not suited for direct introduction into API sources. The operator must be certain to avoid mobile phases that are not compatible with the stainless steel parts of the mass spectrometer. To avoid inorganic salt buildup, it is essential that a suppressor, unique to the IC technique, be employed. The suppressor removes cations from the eluent stream, after the separation column, and replaces them with a proton. In the API source, accumulation of salts from the mobile phase, and any dissolved solids in the sample, are eliminated. During system equilibration, prior to adding the suppressor to the flow path, it is important that the effluent from the IC be diverted by the integral valve of the mass selective detector and not directed to the ESI source. This eliminates the possibility of any sodium hydroxide or other mobile phase constituent from entering the source while the suppressor system is equilibrating or otherwise off-line. In the event that a contaminating solution is introduced to the source, the mass spectrometer (MS) system should be vented, and surfaces up to and including the glass capillary should be cleaned. This will recover the performance lost due to NaOH introduction in the MS system.

2. Instrumental and operating parameters

The analytical system consists of a MIC-2 advanced modular ion chromatograph (Metrohm-Peak) and an 1100 MSD SL Quad (Agilent Technologies). A standard electro-spray interface was used. The two systems were synchronized by use of contact closure between the chromatographic auto sampler and the mass spectrometer. A complete list of instrumental parameters is listed below.

Metrohm advanced ion chromatograph
- 100 μL loop injection
- Column: MetroSep ASUPP-5 (4 mm × 100 mm)
- Eluent: 30 mM NaOH + 30% methanol

Agilent 1100 LC/MSD ESI
- Negative mode “auto-tune”
- V_{cap} = 1400 V, drying gas = 9 L/min@320 °C
- Nebulizer pressure = 20 psig
- Fragmentor = 140 V

Flow rate: 0.8 mL/min with no splitting
(The above conditions are used for all the figures)

Instrumental parameters for the analysis of perchlorate by IC–MS were initially chosen to reduce or eliminate suppression due to co-elution of matrix and analyte ions, and to lessen the effective concentration of matrix in the electro-spray interface. Choosing operating conditions in this way increased reliability and stability of the system, but at the cost of potential sensitivity.

To decrease matrix suppression, a 4 mm i.d. column was selected over a 2 mm i.d. column. The larger diameter column reduced the effective concentration of matrix in the system by dilution effects. The larger i.d. column also allowed a 100-μL injection, as used for this work, and a larger injection volume can easily be accommodated. Capacity of the column is also far greater than smaller i.d. columns, resulting in improved peak shape of any matrix or high-concentration materials and reduced tailing into the analyte peak. All of these factors ensure that the majority of the matrix is well separated from the analyte for the reduction or elimination of suppression effects.

In addition to the ion exchange column used for the separation, a suppression column was utilized to eliminate sodium and calcium in the sample matrix. While not a direct problem with the detection of analyte, these involatile cations accumulate in the interface from mobile phase and interfere with the long-term stability of the system when high total dissolved solids (TDS) samples are analyzed. Complete removal of the metal cations also decreases the risk of suppression by ensuring that only protonated anions enter the mass spectrometer interface.

The 1100 MSD ESI interface is designed for relatively high flows while maintaining high sensitivity, reaching DLs of less than 100 ng/L. Many ESI interfaces are extremely flow sensitive and do not perform well at flows typical for 4 mm i.d. columns. The 1100 MSD ESI interface performs best at low flows but does not exhibit the same drastic decrease in sensitivity at higher flow as observed with other interfaces.

3. Results and discussion

The IC–MS trace of a 500 ng/L (Environmental Resource Associates, USA, certified perchlorate proficiency testing standards were used as reference standards) perchlorate standard is shown in Fig. 1. It demonstrates very good

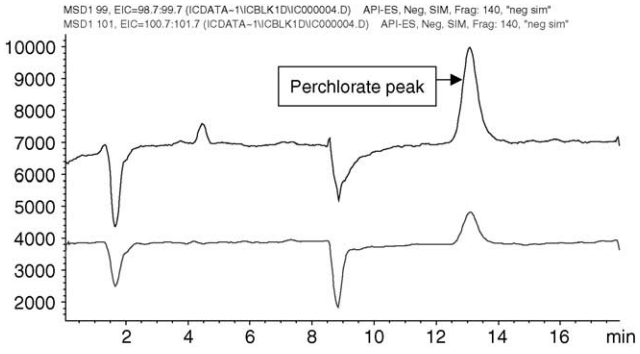

Fig. 1. The IC–MS trace of a 500 ng/L perchlorate standard.

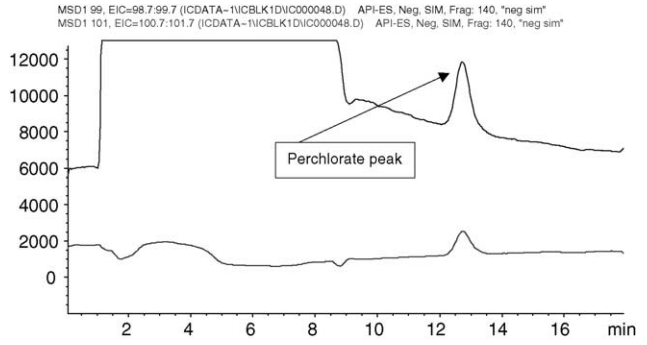

Fig. 2. *m*/*z* 99 and 101 traces for 1 μg/L perchlorate in a 1000-ppm matrix of sulfate, chloride, and carbonate.

signal-to-noise for perchlorate (*m*/*z* 99), eluting at a retention time (RT) of about 13 min. The Metrohm IC uses a combination of three suppressors that can be changed during a run to ensure that any one suppressor does not become saturated with cations. While one suppressor is in operation, another is reconditioning, while still another is rinsing with ultrapure water. The abrupt signal changes observed at 1.5 and 9 min are due to ultrapure water entering the flow path from the rinsed suppressor during automated operations of the suppression column system.

The sequential changing and reconditioning of the suppressors during analysis is extremely important in the analysis of high matrix samples. Fig. 2 shows *m*/*z* 99 and 101 traces for 1 μg/L perchlorate in a 1000 mg/L matrix of sulfate, chloride, and carbonate.

Early in the chromatogram, the effect of the matrix can be clearly seen as both interference at the monitored mass as well as suppression of the signal in general. The suppressor change at 9 min ensures that a clean suppressor is in place for the perchlorate ion. This results in a very clean signal for perchlorate at about 13 min.

Figs. 3 and 4 show the calibration data for both *m*/*z* 99 and 101 for perchlorate from 0.1 to 5 μg/L. Calibration at both masses is linear over the measured range.

The *m*/*z* 99 single ion chromatograms for a set of matrix spikes each containing a 1 μg/L perchlorate are shown in Fig. 5. A small RT change is noted for perchlorate between a perfectly clean standard and the matrix additions. This minor shift is normal for IC due to initial overloading of the separation column. It does not interfere with the identification or determination of perchlorate. If desired, the RT shift between standards and matrix-laden samples can be avoided by using standards prepared with a limited amount of matrix.

Table 1 shows the results from replicate injections of perchlorate spikes at 0.49 and 0.78 μg/L in deionized water. Recoveries for analysis using both ions are excellent, as expected in a clean matrix. Precision is also quite good for both ions at these levels.

The results of a much more difficult test of the system, the analysis of 1 μg/L spikes in three different levels of matrix prepared according to EPA Method 314, are listed in Table 2.

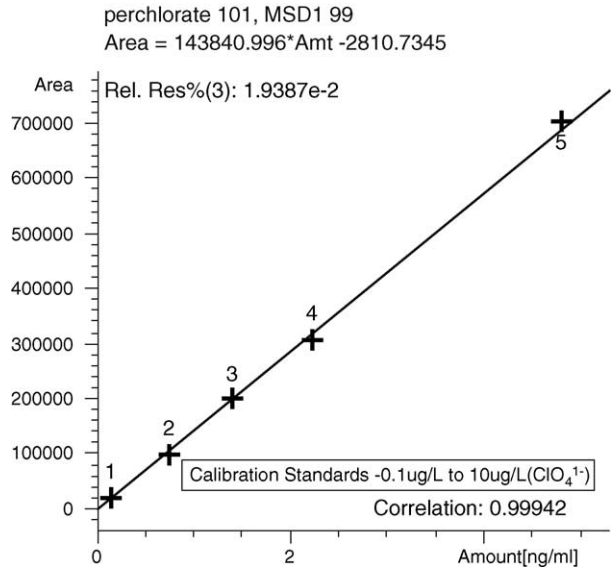

Fig. 3. Calibration data for both *m*/*z* 99 for perchlorate from 0.1 to 5 μg/L.

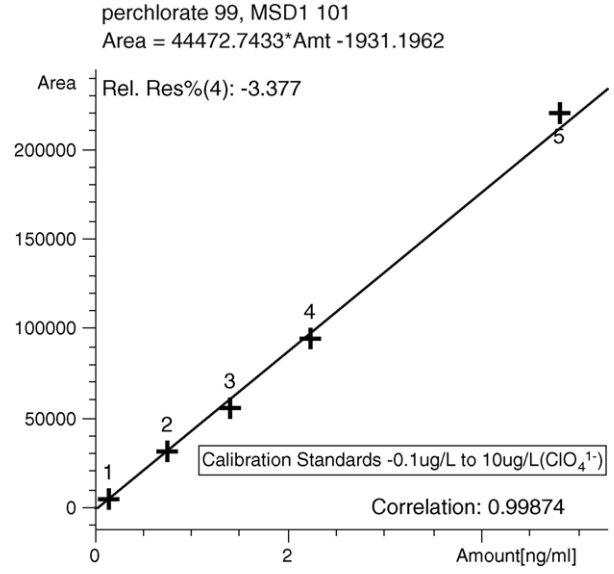

Fig. 4. Calibration data for both *m*/*z* 101 for perchlorate from 0.1 to 5 μg/L.

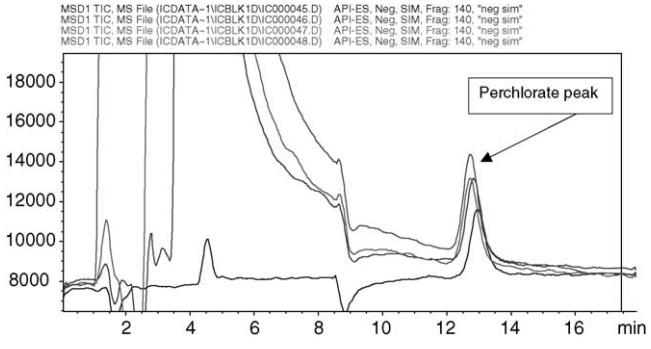

Fig. 5. The *m*/*z* 99 single ion chromatograms for a set of matrix spikes each containing a 1 μg/L perchlorate.

Table 1
Replicate injection of perchlorate spikes at 0.49 and 0.78 ppb in deionized water (ppb = μg/L)

Sample ID	True concentration (ppb)	$m/z = 99$		$m/z = 101$	
		ppb	%Recovery	ppb	%Recovery
0.48 ppb replicates					
0.5 ppb	0.480	0.487	101.46	0.519	108.13
0.5 ppb	0.480	0.477	99.38	0.471	98.13
0.5 ppb	0.480	0.460	95.83	0.490	102.08
0.5 ppb	0.480	0.477	99.38	0.492	102.50
0.5 ppb	0.480	0.520	108.33	0.505	105.21
0.5 ppb	0.480	0.494	102.92	0.509	106.04
Average	0.480	0.486	101.22	0.498	103.68
SD		0.020	0.042	0.017	0.035
RSD (%)		4.18	4.18	3.41	3.41
0.78 ppb replicates					
10 ppb	0.780	0.756	96.92	0.768	98.46
10 ppb	0.780	0.810	103.85	0.830	106.41
10 ppb	0.780	0.776	99.49	0.772	98.97
10 ppb	0.780	0.799	102.44	0.754	96.67
10 ppb	0.780	0.788	101.03	0.768	98.46
10 ppb	0.780	0.792	101.54	0.807	103.46
Average	0.80	0.787	100.88	0.783	100.41
SD		0.019	0.024	0.029	0.037
RSD (%)		2.40	2.40	3.70	3.70

The samples were run sequentially with a blank and calibration verification run after each set of nine samples. Recoveries of analyte at the μg/L level are very good for all matrices, with an average recovery of better than 95% for both monitored ions in all matrices. The recovery data in matrix demonstrate that the system is not affected by the presence of potential interferents in the system at very high concentrations. Table 3 shows the recovery data for perchlorate in other matrices. These matrices demonstrate favorable recovery where perchlorate is present. More importantly, perchlorate was not found in samples known not to have perchlorate or in samples containing high levels of interferents acknowledged to

Table 2
Results of varying matrix fortified (ppm = mg/L) with perchlorate (ppb = μg/L)

Sample ID	True concentration (ppb)	$m/z = 99$		$m/z = 101$	
		ppb	%Recovery	ppb	%Recovery
200 ppm each of $ClCO_3$ and SO_4	0.780	0.799	102.44	0.784	100.51
500 ppm each of $ClCO_3$ and SO_4	1.000	0.804	80.40	0.808	80.80
1000 ppm each of $ClCO_3$ and SO_4	1.000	0.930	93.00	0.940	94.00
200 ppm each of $ClCO_3$ and SO_4	0.780	0.700	89.74	0.770	98.72
500 ppm each of $ClCO_3$ and SO_4	1.000	0.870	87.00	0.860	86.00
1000 ppm each of $ClCO_3$ and SO_4	1.000	0.973	97.30	0.986	98.60
200 ppm each of $ClCO_3$ and SO_4	0.780	0.810	103.85	0.796	102.05
500 ppm each of $ClCO_3$ and SO_4	1.000	0.851	85.10	0.846	84.60
1000 ppm each of $ClCO_3$ and SO_4	1.000	0.990	99.00	0.977	97.70
Blank	0.000	0.000		0.000	
CC 10 ppb	0.780	0.747	95.77	0.742	95.13
200 ppm each of $ClCO_3$ and SO_4	0.780	0.799	102.44	0.777	99.62
500 ppm each of $ClCO_3$ and SO_4	1.000	0.920	92.00	0.921	92.10
1000 ppm each of $ClCO_3$ and SO_4	1.000	1.000	100.00	1.040	104.00
200 ppm each of $ClCO_3$ and SO_4	0.780	0.860	110.26	0.830	106.41
500 ppm each of $ClCO_3$ and SO_4	1.000	0.930	93.00	0.913	91.30
1000 ppm each of $ClCO_3$ and SO_4	1.000	1.090	109.00	1.050	105.00
200 ppm each of $ClCO_3$ and SO_4	0.780	0.800	102.56	0.850	108.97
500 ppm each of $ClCO_3$ and SO_4	1.000	0.890	89.00	0.904	90.40
1000 ppm each of $ClCO_3$ and SO_4	1.000	1.040	104.00	1.070	107.00
Average			96.67		97.10
SD			0.082		0.080
RSD (%)			8.48		8.22

Table 3
Recovery data for perchlorate in other matrices (ppb = μg/L)

Sample ID	Perchlorate data					Notes
	Actual 1 ppb	*m/z* 99, ppb	*m/z* 101, ppb	*m/z* 99, %recovery	*m/z* 101, %recover	
Sample submitted by Metrohm-Peak customer						
Sample-1	0.50	0.44	0.51	88.00	102.0	0.5 ppb in distilled water
Sample-2	1.00	0.91	1.01	91.00	100.7	1.0 ppb in distilled water
Sample-3	1.00	0.95	1.00	95.16	99.7	1.0 ppb in tap water
Sample-4	0.42	0.41	0.43	97.33	102.1	Ground water *w*/0.42 ppb
Sample-5	???	0.00	0.00			Unknown value, but sample is loaded with sulfonate surfactants
Sample-6	0.35	0.30	0.33	86.93	95.0	Ground water *w*/0.35 ppb
Sample-6A	1.35	1.18	1.36	87.41	100.6	Sx-6 + 1 ppb spike
Sample-7	0.00	0.00	0.00	100.00	100.0	Ground water *w*/no perchlorate
Sample-8	0.00	0.00	0.00			Lettuce extract
Sample-9	7.92	7.35	7.41	92.86	93.6	Lettuce extract spike

complicate perchlorate determination when using conductivity detection.

Sample 5 in Table 3 is a wastewater sample that has an unknown perchlorate concentration (but less than 10 ng/L) and contains very high levels of sulfonate detergents. These are known to coelute with perchlorate and give high false positive analysis (hundreds of μg/L) when a conductivity detector is employed. The single quadrupole mass spectrometer in selected ion monitoring mode exhibits no signal to the detergents (of different mass than 99 or 101) and eliminates false values for samples that do not contain perchlorate.

Samples 6 and 6A in Table 3 are ground waters known to contain perchlorate and a 1 μg/L spike of the same sample. Samples 8 and 9, lettuce extract, illustrate the applicability of the method for the analysis of vegetables. Levels in vegetables were found to be significantly higher than irrigation source waters.

The chromatograms of the lettuce analysis and the lack of interferents around perchlorate are shown in Fig. 6. The dip in the blank and spike lettuce samples is due to large amounts of another eluting material entering the electrospray source, suppressing the ionization of the background signal.

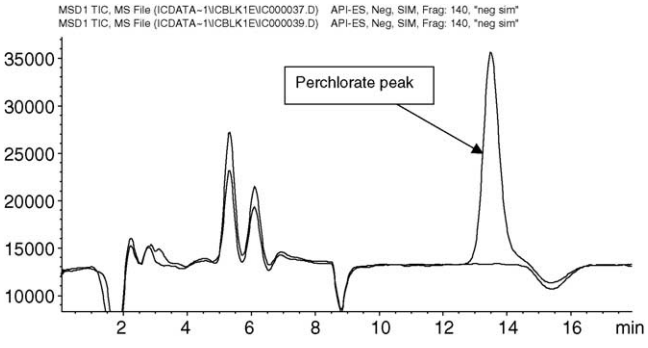

Fig. 6. The chromatograms of the lettuce analysis and the lack of interferents around perchlorate.

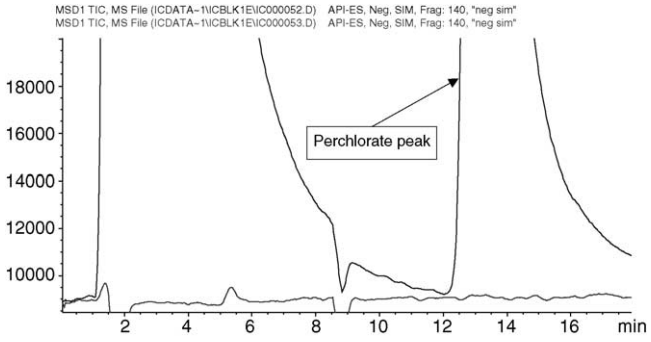

Fig. 7. Hardly any carryover of the system.

Conventional conductivity detection is useless for this sample since the area around perchlorate elution is overwhelmed by large amounts of coeluting material.

Fig. 7 is an example of the very low carryover of the system. A 500 μg/L standard of perchlorate in high matrix was analyzed. A sequential blank after the analysis of the high standard shows no interference from either the standard or the matrix previously injected.

4. Conclusion

By using a set of instrument conditions chosen to reduce background interference and increase reliability, an isocratic IC system and a single quadrupole 1100 MSD system can be used very effectively for the analysis. The analysis of perchlorate with such a system was shown to be feasible, robust, and accurate at sub-μg/L levels. The method demonstrates the efficacy of an IC coupled to a quadrupole mass spectrometer in general. By using relatively simple method parameters and durable instrumentation, many of the difficulties previously seen with perchlorate analysis in complex matrices by IC–MS can be overcome.

Latest work is being performed according to proposed EPA method 332, which uses ^{18}O enriched sodium perchlorate ($NaCl^{18}O_4$) as an Internal Standard and will be reported on in future articles.

Acknowledgments

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