

# Measurement of perchlorate in water by use of an $^{18}\text{O}$ -enriched isotopic standard and ion chromatography with mass spectrometric detection<sup>☆</sup>

Elizabeth Hedrick\*, David Munch

*US Environmental Protection Agency, 26 West Martin Luther King Drive, Cincinnati, OH 45268, USA*

## Abstract

Currently, the most promising analytical methodology for low-level determination and confirmation of perchlorate ( $\text{ClO}_4^-$ ) in drinking water is ion chromatography followed by electrospray ionization mass spectrometric detection (IC–ESI–MS). However, there are still potentially limiting situations that must be considered when analyzing real world samples by IC–ESI–MS. They are: (1) co-elution of contaminants with fragment ions having the same  $m/z$  as  $\text{ClO}_4^-$ , (2) high background counts at the  $m/z$  of interest leading to a subsequent decrease in signal-to-noise, (3) gradual loss of sensitivity occurring over time as the sampling cone and/or ion optics of the mass spectrometer are fouled, and (4) suppression of gas phase ion formation (ionization suppression) that can occur if high concentrations of contaminants co-elute with  $\text{ClO}_4^-$ . An internal standard whose response, on the column and in the electrospray, is similar to that of  $\text{ClO}_4^-$  would give the highest degree of accuracy possible in situations 3 and 4 listed above. Commercially available  $\text{NaClO}_4$  that was enriched with oxygen-18 was evaluated for its potential as an internal standard. The level of oxygen-18 ( $^{18}\text{O}$ ) enrichment was verified, the stability of the enriched  $\text{ClO}_4^-$  in aqueous solutions was determined, and method performance parameters such as method detection limits, accuracy, precision and ruggedness using the enriched  $\text{ClO}_4^-$  as an internal standard were determined. Internal and external calibration yielded similar results with respect to calibration, detection limits, and short-term precision. However, the enriched isotopic internal standard showed superior results with respect to ruggedness and percent recovery of spikes in ground water and synthetic water samples.

© 2004 Elsevier B.V. All rights reserved.

*Keywords:* Water analysis; Isotopic internal standard; Perchlorate; Inorganic anions

## 1. Introduction

Perchlorate is a drinking water contaminant originating from the dissolution of the salts of ammonium, potassium, magnesium, or sodium in water. It is used primarily as an oxidant in solid propellant for rockets, missiles, pyrotechnics, as a component in air bag inflators, and in highway safety flares. From accidental releases and improper disposal practices of the past,  $\text{ClO}_4^-$  has become a contaminant in surface and ground waters where it is highly mobile and, due to its chemical stability, may persist for decades [1].

Based on US Environmental Protection Agency (EPA) Information Request Responses and occurrence monitoring, 95  $\text{ClO}_4^-$  releases in 25 states have been confirmed and 230 users or manufacturers in 40 states have been identified. The primary human health effect is inhibition of iodide uptake by the thyroid gland [2–4]. By disrupting thyroid hormone production,  $\text{ClO}_4^-$  interferes with metabolism and can affect brain development in fetuses and children, leading to mental impairment. The National Academy of Sciences has been given the charge to review the science used by the EPA to determine a reference dose level for  $\text{ClO}_4^-$ . Should the  $\text{ClO}_4^-$  concentration level of concern in drinking water be an order of magnitude below the original estimate of 4–18 ppb, and below the UCMR minimum reporting level of 4 ppb using EPA Method 314.0, a more sensitive and specific method than ion chromatography with conductivity detection will be needed. Although EPA Method 314.0 is a relatively low-level method having a method detection limit of 0.53 ppb, it is vulnerable to sensitivity loss caused by high

<sup>☆</sup> This paper has been reviewed in accordance with the EPA's peer and administrative review policies and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

\* Corresponding author. Tel.: +1-513-569-7296; fax: +1-513-569-7757.

E-mail address: [hedrick.elizabeth@epa.gov](mailto:hedrick.elizabeth@epa.gov) (E. Hedrick).

concentrations of common anions. There are also anionic compounds (benzene sulfonates) which elute at a retention time close to perchlorate that can lead to false positive identification. The loss of sensitivity in high ionic waters and the possibility of false positives using conductivity detection has been the impetus to develop better methods. Thus, ion chromatography with electrospray ionization mass spectrometric detection (IC–ESI–MS) and IC–ESI–MS–MS methods are currently being developed in a number of laboratories for the determination of  $\text{ClO}_4^-$  in drinking waters. Both MS approaches are sensitive and specific; however, both show an intolerance for high ionic matrices. Ionization suppression and cone fouling in the electrospray ion source are the most common problems facing IC–ESI–MS or IC–ESI–MS–MS. The goals of this method development effort have been to achieve a consistently sensitive, accurate and rugged method requiring the minimum amount of sample pretreatment. Toward that end, several simple techniques to reduce cone fouling and the need for sample pretreatment to remove the common anions sulfate, chloride and carbonate have been implemented. Ruggedness and accuracy have been improved by using an isotopically enriched  $\text{ClO}_4^-$  internal standard.

## 2. Experimental

Table 1 contains the IC–ESI–MS instrumental conditions used for most of this work. An auxiliary pump was used to deliver continuous liquid flow to the MS while the eluate from the column was diverted to waste until 2 min prior to the elution of  $\text{ClO}_4^-$  using a second six-port valve. It is during the first 7 min of a chromatographic run that the cations and most of the common anions found in drinking water matrices ( $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ , and  $\text{Cl}^-$ ) elute from the column. By diverting the eluate to waste, cone fouling is greatly

reduced. Since electrolytic conductivity suppression is being used, it is also during this time frame that the pH of the eluate becomes acidic ( $\text{pH} \approx 2$ ). The pH of the eluate out of the suppressor returns to pH 5 just prior to switching the eluate flow back to the MS. In an effort to improve ruggedness, 50% acetonitrile (ACN) was placed in the auxiliary pump instead of 100% DDI water to rinse the probe during the first 7 min of a chromatographic run when the column eluate is being diverted to waste. So as not to damage the conductivity suppressor with the 50% ACN, the second six-port valve had to be placed after the conductivity suppressor in this configuration. However, placing the second six-port valve before the conductivity suppressor and using DDI water in the auxiliary pump had advantages that will be discussed later.

The oxygen-18 ( $^{18}\text{O}$ )-enriched  $\text{NaClO}_4$  was obtained from Isotec (Miamisburg, OH, USA). The  $\text{NaClO}_4$  salt was synthesized by Isotec using water that was 95% enriched on oxygen-18 and was guaranteed to yield at least a 90%  $^{18}\text{O}$ -enriched  $\text{ClO}_4^-$  salt. This meant that there would be some  $^{16}\text{O}$ -containing  $\text{ClO}_4^-$ . To verify the minimum 90% enrichment, five solutions ranging from 10 to 100 ppb of the enriched  $\text{ClO}_4^-$  isotope were analyzed by IC–ESI–MS. The average area counts at  $m/z$  99 ( $^{35}\text{Cl}^{16}\text{O}_4^-$ ),  $m/z$  101 ( $^{35}\text{Cl}^{16}\text{O}_3^{18}\text{O}_1^-$ ,  $^{37}\text{Cl}^{16}\text{O}_4^-$ ),  $m/z$  103 ( $^{35}\text{Cl}^{16}\text{O}_2^{18}\text{O}_2^-$ ,  $^{37}\text{Cl}^{16}\text{O}_3^{18}\text{O}_1^-$ ),  $m/z$  105 ( $^{35}\text{Cl}^{16}\text{O}_1^{18}\text{O}_3^-$ ,  $^{37}\text{Cl}^{16}\text{O}_2^{18}\text{O}_2^-$ ) and  $m/z$  107 ( $^{35}\text{Cl}^{18}\text{O}_4^-$ ,  $^{37}\text{Cl}^{16}\text{O}_1^{18}\text{O}_3^-$ ), were measured. The actual ratios, when compared to the theoretical ratios, were found to verify greater than 90%  $^{18}\text{O}$  enrichment. Subsequently, the standard proved to be stable for long periods of time in DDI water, and in various aqueous solutions for short periods of time (i.e., no change in ratios), and there were no detectable peaks at  $m/z$  99 or 101 in the enriched standard (i.e., no contribution from the isotopic standard to the native species), so that the  $^{18}\text{O}$ -enriched  $\text{ClO}_4^-$  could be used as a simple internal standard mass by monitoring mass 107 ( $^{35}\text{Cl}^{18}\text{O}_4^-$ ,  $^{37}\text{Cl}^{16}\text{O}_1^{18}\text{O}_3^-$ ).

Natural isotope standards were prepared from 99% pure  $\text{NaClO}_4$  (Sigma–Aldrich, St. Louis, MO, USA) in distilled, deionized water. Five standards were prepared containing concentrations from 0.05 to 1.0 ppb of the natural  $\text{ClO}_4^-$  isotope and 1.0 ppb of the enriched  $^{18}\text{O}$   $\text{ClO}_4^-$ . Analyses were performed using the IC–ESI–MS conditions described in Table 1. A non-weighted, least squares linear regression was performed on the 99:107 area count ratio versus concentration (ppb) of the natural isotope. Slopes were between 1.02 and 1.07, y-intercepts were between  $-0.003$  and 0, and  $r^2$  values were  $>0.999$ .

Samples were collected in HDPE containers and were kept refrigerated at  $5^\circ\text{C}$  until analysis. Samples were mixed well before sample aliquots were withdrawn. The enriched  $^{18}\text{O}$   $\text{ClO}_4^-$  standard was added to each aliquot, or diluted aliquot, to yield a final concentration of 1.0 ppb enriched  $\text{ClO}_4^-$ . Prior to injection into the ion chromatograph, each sample was filtered through a  $10\ \mu\text{m}$  filter that was built into

Table 1  
IC–ESI–MS instrumental conditions

|   |   |
|---|---|
| Ion chromatograph                       | Dionex, Sunnyvale, CA, USA  |
| Mobile phase                            | 45 mM KOH   |
| Separator column                        | Dionex AS 16, 250 mm $\times$ 2 mm                                    |
| Flow rate (ml/min)                      | 0.3   |
| Conductivity suppressor and current     | ASRS-Ultra II, 45 mA  |
| Column temperature ( $^\circ\text{C}$ ) | 30  |
| Auxiliary pump flow rate (ml/min)       | 0.3   |
| Injection volume ( $\mu\text{l}$ )      | 200   |
| Mass spectrometer                       | MSQ with enhanced low mass option (ThermoFinnigan, San Jose, CA, USA) |
| Capillary voltage (kV)                  | $-3$  |
| Sampling cone voltage (V)               | $-70$   |
| Probe temperature ( $^\circ\text{C}$ )  | 400   |
| Nitrogen pressure (psi)                 | 80 (1 psi = 6894.76 Pa)   |
| Selected ion monitoring                 | Masses 99, 101, 107, 109  |
| Mass scan range                         | 0.3   |
| Dwell time per mass                     | 0.75  |

the autosampler. Analyses of samples without the added enriched isotope were performed to determine if there were any interferences at  $m/z$  107 or 109,  $^{35}\text{Cl}^{18}\text{O}_4^-$  and  $^{37}\text{Cl}^{18}\text{O}_4^-$ , respectively. The ratio of 99:107 in the enriched isotope spiked sample was used to determine the concentration of native  $^{35}\text{Cl}^{16}\text{O}_4^-$  from the calibration curve. The 99:101 ratio ( $^{35}\text{Cl}^{16}\text{O}_4^-/^{37}\text{Cl}^{16}\text{O}_4^-$ ) was used for confirmation of native perchlorate.

### 3. Results and discussion

Fig. 1 shows five chromatograms, in selected ion monitoring mode, for  $m/z$  99, 101, 103, 105 and 107 for a 40 ppb solution of the enriched  $^{18}\text{O}$  isotope standard. It is apparent that there is no detectable amount of  $^{35}\text{Cl}^{16}\text{O}_4^-$ ,  $^{37}\text{Cl}^{16}\text{O}_4^-$  or  $^{35}\text{Cl}^{16}\text{O}_3^{18}\text{O}_1^-$  in the standard.

A series of experiments were performed to determine if  $^{18}\text{O}$  to  $^{16}\text{O}$  exchange would occur in various aqueous solutions. In the first experiment, 50 ppb of the enriched isotope was prepared in three different 50 mM hydroxide matrices: NaOH, KOH and  $\text{NH}_4\text{OH}$ . The standard needed to prove stable for at least 10 min, which is the length of time it takes for perchlorate to elute from the separator column. To determine if there was any oxygen exchange in hydroxide solutions that could be seen over time, the solutions were analyzed every 30 min over a period of 5 h. The ratios of

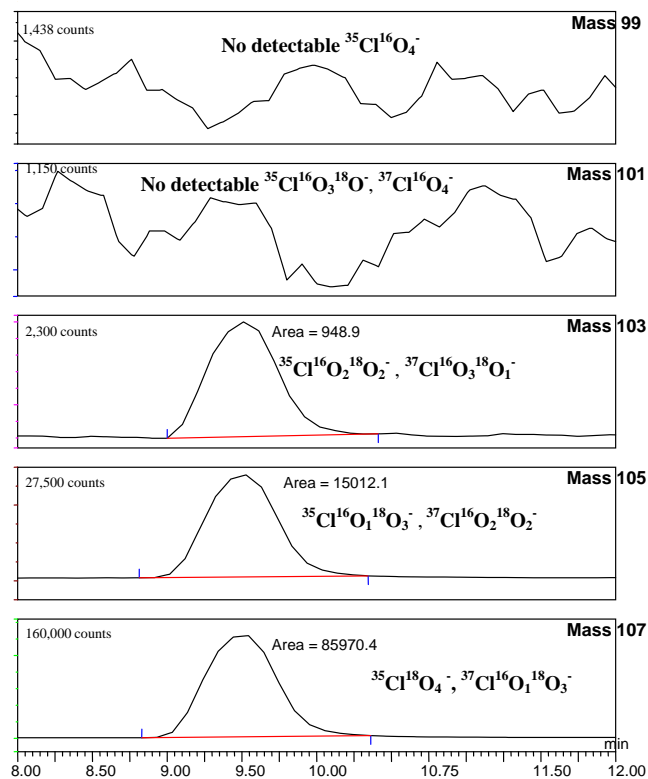


Fig. 1. Forty ppb enriched isotope in deionized water. For IC conditions, see Table 1.

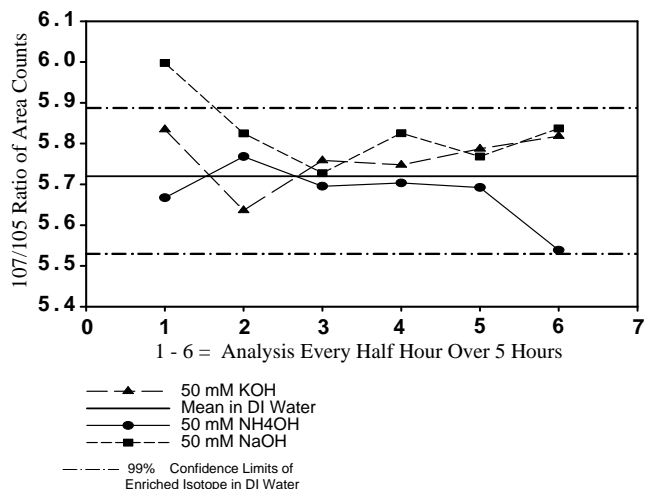


Fig. 2. Stability of 50 ppb enriched isotope in hydroxide matrices. For conditions, see Table 1.

area counts at  $m/z$  107:105 (Fig. 2) and 107:103 (not shown) were plotted and compared to the 99% confidence interval of the ratios obtained in DDI water on the first day of analysis of the enriched isotope. The data showed no time trends and the majority of the ratios were within the 99% confidence interval for the ratios in DDI water. Therefore, it was concluded that no detectable oxygen exchange occurred in any of the hydroxide matrices. In another experiment, 10 ppb of the enriched isotope standard was prepared in tap water, left at room temperature, and monitored over 16 days for oxygen exchange. Fig. 3 is a plot of the 107:105 and 107:103 ratios over time as compared to the mean in DDI water on the first day of analysis of the enriched isotope. There was no measurable oxygen exchange over 16 days in tap water at room temperature. No peaks at masses 99 or 101 were ever detected in either experiment. The enriched isotope in DDI water continues to be monitored on

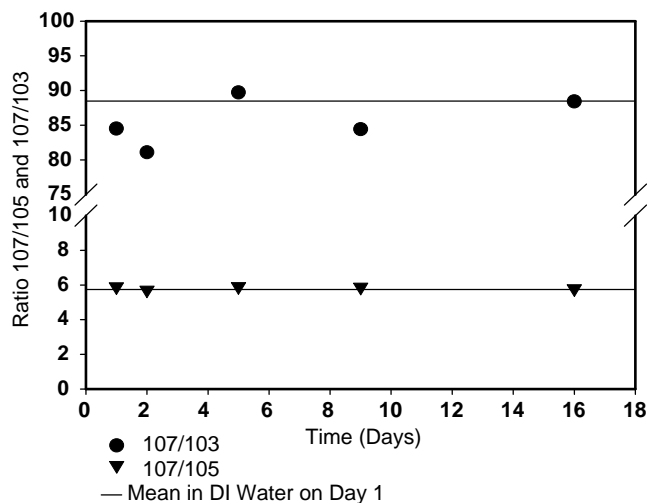


Fig. 3. Stability of enriched isotope in tap water. For IC conditions, see Table 1.

an on-going basis to determine the long-term stability of the enriched isotope in aqueous solution. After 1 month, no measurable oxygen exchange had been detected.

### 3.1. High background noise and cone fouling

One problem is background counts at  $m/z$  99 occurring in the presence of high concentrations of sulfate in the sample. As the  $\text{SO}_4^{2-}$  peak tails into the retention time of  $\text{ClO}_4^-$ , the S-34 isotope gives rise to the  $\text{HSO}_4^-$  ion,  $m/z$  99, as  $\text{K}^+$  is exchanged for  $\text{H}^+$  in the electrolytic conductivity suppressor. There are ion exchange resins in syringe cartridges that can be used to remove  $\text{SO}_4^{2-}$  from the sample; however, up to 1000 ppm of  $\text{SO}_4^{2-}$  can be tolerated if the column eluate is diverted from the suppressor, as well as the MS system, for the first 7 min of the chromatographic run. Fig. 4 shows two chromatograms of 0.1 ppb  $\text{ClO}_4^-$  in a solution of 1000 ppm each  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$ . In Fig. 4A, the eluate from the column was diverted from the suppressor, as well as the MS system, until 2 min prior to the elution of  $\text{ClO}_4^-$  while DDI water was pumped through the suppressor to the MS system using the auxiliary pump. In Fig. 4B, the eluate from the column was directed through the suppressor before being diverted to waste until 2 min prior to the elution of  $\text{ClO}_4^-$ , while 50% ACN was pumped to the MS system using the auxiliary pump. Note in Fig. 4B, when the eluate from the column is switched back to the MS system, that the background counts at  $m/z$  99 are twice the background counts in Fig. 4A at the same point in time (10 000 versus 5000). The background counts at  $m/z$  99 are due to  $\text{HSO}_4^-$  ion formed in the suppressor from the  $\text{SO}_4^{2-}$  eluting from the column. The fact that there appears to be twice as much when the eluate flow goes through the suppressor indicates

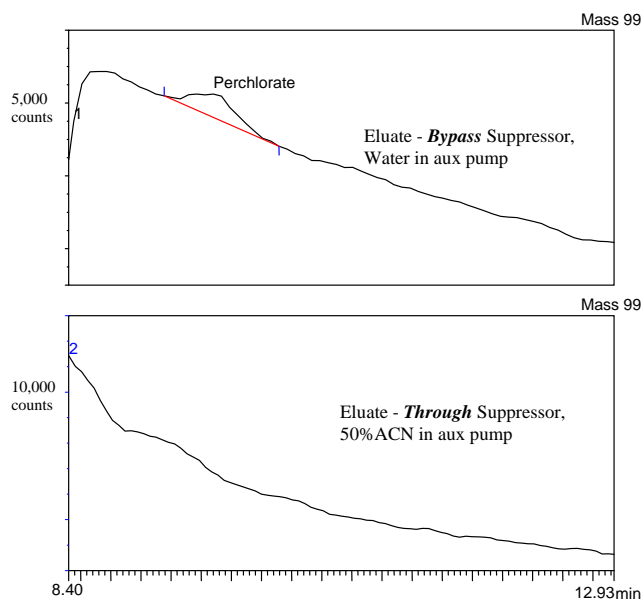


Fig. 4. (A) 0.1 ppb  $\text{ClO}_4^-$  in 1000 ppm chloride, sulfate and carbonate; (B) 0.1 ppb  $\text{ClO}_4^-$  in 1000 ppm chloride, sulfate and carbonate.

that there is significant tailing of the  $\text{HSO}_4^-$  from the suppressor and not just tailing of  $\text{SO}_4^{2-}$  from the column. The background was so high under the conditions in Fig. 4B that the 0.1 ppb of  $\text{ClO}_4^-$  was not detectable. In previous work, it was demonstrated that placement of the second six-port valve before the suppressor helped prevent cone fouling and allowed up to 6 h of continuous analyses of high ionic matrices before cone cleaning and re-calibration was required [5].

### 3.2. Ionization suppression

Ionization suppression can occur when co-eluting contaminants, not necessarily having the same  $m/z$  as  $\text{ClO}_4^-$ , inhibit the gas phase ion formation of  $\text{ClO}_4^-$ . This is a problem endemic to electrospray ionization sample introduction. The only real solution is to perform the method of standard additions on every sample, or to have an internal standard that behaves on the column and in the electrospray just as native  $\text{ClO}_4^-$ .

### 3.3. Precision and accuracy

Short-term precision, as measured by the reproducibility of area counts on replicate (three) injections of 1 ppb  $\text{ClO}_4^-$ , was <10% relative standard deviation for the natural and enriched  $\text{ClO}_4^-$  isotopes ( $m/z$  99, 101, 107 and 109). Accuracy, as determined by the analysis of a commercially available  $\text{ClO}_4^-$  quality control sample (Environmental Resource Associates, Arvada, CO, USA), was comparable whether using external calibration or internal standardization using the enriched isotope ( $\pm 5\%$  of the certified value).

### 3.4. Ground water samples

The problem of co-elution of contaminants with  $\text{ClO}_4^-$  is rare but has been observed in some highly contaminated waters. In one particular ground water sample from a Superfund site, a peak was detected by conductivity within the retention time window of  $\text{ClO}_4^-$  and was tentatively quantified as 1400 ppb of  $\text{ClO}_4^-$ . Later, the sample was re-analyzed using IC-ESI-MS with the second six-port valve after the suppressor. Under these conditions, no native  $\text{ClO}_4^-$  was detected and a 1 ppb natural isotope  $\text{ClO}_4^-$  spike into the sample was 80% recovered. However, using IC-ESI-MS and the enriched isotope internal standardization method, a 1 ppb natural isotope  $\text{ClO}_4^-$  spike was 99% recovered.

Table 2 contains the results from the analyses of three local ground water samples. Native concentrations and spike recoveries of 1 ppb of the natural isotope  $\text{ClO}_4^-$  were both determined using the enriched isotope as an internal standard. Spike recoveries were between 93 and 107%.

### 3.5. Method detection limits

Table 3 contains method detection limits in DDI water and three synthetic high ionic matrices. Often referred to as

Table 2  
Analysis of raw ground waters using  $^{18}\text{O}$ -enriched isotope as an internal standard

| Ground water identity | Native $\text{ClO}_4^-$ (ppb) | Recovery of 1.0 ppb (%) |
|-----------------------|-------------------------------|-------------------------|
| FF3-1                 | 0.11                          | 101                     |
| FF3-2 (diluted 1:20)  | 20.45                         | 93                      |
| FF3-4                 | 0.50                          | 107                     |

Conditions: as described in Table 1. Diluted samples were spiked as necessary.

the EPA method detection limit (MDL), the MDL is defined as the minimum concentration of analyte in a specified matrix that can be identified, measured and reported with 99% confidence that the true analyte concentration is greater than zero [6]. MDLs were determined in four matrices: (1) DDI water, (2) 200, (3) 500, and (4) 1000 ppm of the common anions (chloride, sulfate and carbonate) in the following manner. Seven separate aliquots of the matrix of interest were spiked at a concentration that yielded a response at least three to five times the background noise. The aliquots were analyzed according to the method and conditions outlined in Table 1. The concentrations were calculated from the calibration curve and the average and standard deviation of the seven aliquot concentrations was determined. The MDL was then calculated according to the equation:

$$\text{MDL (ppb)} = t(n - 1, 1 - \alpha)S$$

where  $t$  is the Student's  $t$ -value, 3.143 for 6 degrees of freedom and  $\alpha = 0.01$ ; and  $S$  is the standard deviation of the seven measurements.

The DDI water was spiked with 0.05 ppb of the natural isotope  $\text{ClO}_4^-$  and 1.0 ppb of the enriched isotope. The synthetic high ionic waters were spiked with 0.1 ppb of the natural isotope  $\text{ClO}_4^-$  and 1.0 ppb of the enriched isotope. The MDLs, using mass 99 corresponding to the natural isotope

Table 3  
Method detection limits using enriched isotope as an internal standard

| Matrix                | Selected ion monitoring mass | Spike level (ppb) | Average recovery (%) | R.S.D. (%)   | MDL (ppb)    |
|-----------------------|------------------------------|-------------------|----------------------|--------------|--------------|
| DDI water             | 99                           | 0.05              | 102                  | 9.7          | 0.02         |
|                       | 101                          | 0.05              | 94                   | 22           | 0.03         |
| 200 ppm <sup>a</sup>  | 99                           | 0.1               | 97                   | 15.4         | 0.05         |
|                       | 101                          | 0.1               | 92                   | 10.1         | 0.03         |
| 500 ppm <sup>a</sup>  | 99                           | 0.1               | 90                   | 17.5         | 0.05         |
|                       | 101                          | 0.1               | 97                   | 18.6         | 0.06         |
| 1000 ppm <sup>a</sup> | 99                           | 0.1               | <sup>b</sup>         | <sup>b</sup> | <sup>b</sup> |
|                       | 101                          | 0.1               | 108                  | 15.5         | 0.05         |

Conditions: as described in Table 1. Second six-port valve was placed after the suppressor; paired  $t$ -tests of mass 99 and 101 recoveries revealed no significant difference at  $\alpha = 0.01$  for any of the matrices.

<sup>a</sup> Concentration each of chloride, carbonate and sulfate.

<sup>b</sup> High background at  $m/z$  99, caused by  $\text{HSO}_4^-$ , resulted in no  $\text{ClO}_4^-$  detected in this matrix at mass 99.

$^{35}\text{Cl}^{16}\text{O}_4^-$  or mass 101, corresponding to  $^{37}\text{Cl}^{16}\text{O}_4^-$ , appeared to become more similar as the ionic strength of the synthetic water matrix increased. The higher MDLs at mass 99 are believed to be due to the problem of background at  $m/z$  99 due to  $\text{HSO}_4^-$  tailing from suppressor. There was no significant difference between the spike recoveries using mass 99 or 101 at  $\alpha = 0.01$ . If the  $\text{HSO}_4^-$  suppresses the gas phase ion formation of  $\text{ClO}_4^-$ , the enriched isotope standard appears to behave similarly as is evidenced by the good percent recoveries of the 0.1 ppb natural isotope spike in these samples. At 1000 ppm of the common anions, it was impossible to detect the  $\text{ClO}_4^-$  peak on the high  $\text{HSO}_4^-$  background. Therefore, no MDL is reported for mass 99 at 1000 ppm common anion concentration. Table 4 contains MDLs using external calibration. The IC system was configured with the second six-port valve before the suppressor for these analyses. This made it possible to determine 0.1 ppb in the 1000 ppm common anion matrix. There was no significant difference in the calculated spike recoveries between mass 99 or 101 at  $\alpha = 0.01$ .

### 3.6. Ruggedness

With the second six-port valve placed after the suppressor, the instrument was calibrated from 0.05 to 1.0 ppb  $\text{ClO}_4^-$  prior to sample analyses. Ruggedness was evaluated by determining the percent recovery of a check standard analyzed after every tenth high ionic matrix sample (200–1000 ppm common anions) over the course of 15 h of continuous operation. Fig. 5 compares the percent recovery of the check standards using either external or internal standardization with the enriched isotope. Using external calibration, percent recovery dropped to 85% over the course of 15 h of continuous operation. However, 98–107% recovery was maintained over the 15 h of operation using the enriched isotope as an internal standard.

Table 4  
Method detection limits by external calibration

| Matrix                | Selected ion monitoring mass | Spike level (ppb) | Average recovery (%) | R.S.D. (%) | MDL (ppb) |
|-----------------------|------------------------------|-------------------|----------------------|------------|-----------|
| DDI water             | 99                           | 0.05              | 95                   | 21         | 0.03      |
|                       | 101                          | 0.05              | 113                  | 31         | 0.07      |
| 200 ppm <sup>a</sup>  | 99                           | 0.1               | 101                  | 10.4       | 0.03      |
|                       | 101                          | 0.1               | 106                  | 31.7       | 0.11      |
| 500 ppm <sup>a</sup>  | 99                           | 0.1               | 87                   | 18.6       | 0.05      |
|                       | 101                          | 0.1               | 113                  | 25.4       | 0.09      |
| 1000 ppm <sup>a</sup> | 99                           | 0.1               | 95                   | 28.2       | 0.08      |
|                       | 101                          | 0.1               | 82                   | 26.1       | 0.07      |

Conditions: as described in Table 1. Second six-port valve was placed before the suppressor; paired  $t$ -tests of mass 99 and 101 recoveries revealed no significant difference at  $\alpha = 0.01$  for any of the matrices.

<sup>a</sup> Concentration each of chloride, carbonate and sulfate.



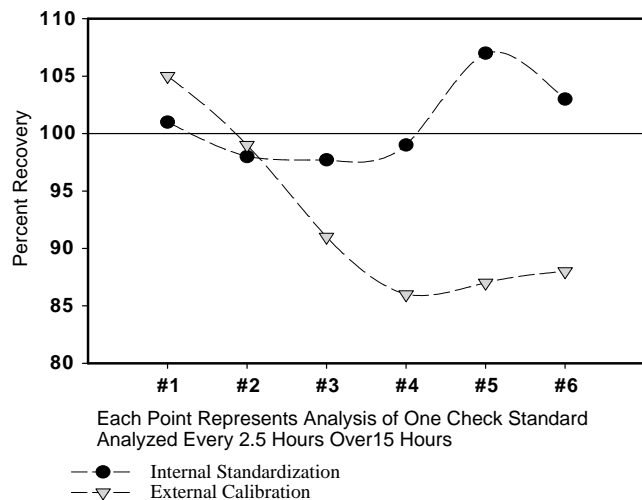


Fig. 5. Ruggedness recovery of check standards over time. For conditions, see Table 1. Second six-port valve after suppressor 15 h and 55 high ionic samples.

#### 4. Conclusions

IC-ESI-MS was evaluated for the low-level determination of  $\text{ClO}_4^-$  in ground waters and in synthetic high ionic waters using an  $^{18}\text{O}$ -enriched  $\text{ClO}_4^-$  compound as an internal standard. Results with respect to short-term precision, accuracy and low-level calibration were comparable to external calibration. However, results were superior with respect to

ruggedness of the method over long hours of operation. A higher degree of accuracy was obtained in percent recovery of spikes from ground waters and synthetic high ionic waters using the enriched isotope as an internal standard.

#### Acknowledgements

The authors thank Thomas Behymer of the EPA for calculating the theoretical ratios of the different  $\text{ClO}_4^-$  isotope compounds in the enriched isotope standard and for providing critical review of the manuscript. The authors also would like to thank Rosanne Slingsby, Chris Pohl, Kannan Srinivasan and Doug Later (Dionex Corporation) for their valuable technical assistance during this methods development effort.

#### References

- [1] C. Hogue, Chem. Eng. News Aug 18 (2003).
- [2] R. Brechner, et al., JOEM 42 (2000) 777.
- [3] J.E. Lawrence, S.H. Lamm, S. Pino, K. Rechman, L.E. Braverman, Thyroid 10 (2000) 659.
- [4] P.N. Smith, et al., Ecotoxicology 10 (2001) 305.
- [5] E. Hedrick, R. Slingsby, D. Munch, D. Hautman, in: Proceedings of the 51st ASMS Conference on Mass Spectrometry and Allied Topics, Montreal, Quebec, 2003.
- [6] J.A. Glaser, D.L. Forest, G.D. McKee, S.A. Quave, W.L. Budde, Environ. Sci. Technol. 15 (1981) 1426.