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Determination of trace perchlorate in water: a simplified method for the identification of potential interferences

Maike A. Seiler[1,3], Detlef Jensen[2], Udo Neist[1], Ursula K. Deister[3] and Franz Schmitz[1,4*]

Abstract

Background: Perchlorate contamination of water and food poses potential health risks to humans due to the possible interference of perchlorate with the iodide uptake into the thyroid gland. Perchlorate has been found in food and drinking, surface, or swimming pool waters in many countries, including the United States, Canada, France, Germany, and Switzerland, with ion chromatography (IC) being the preferred analytical method. The standardization of a robust ion chromatographic method is therefore of the high interest for public health and safety. This article summarizes the experiments and results obtained from analyzing untreated samples, considering the sample's electrical conductance as guidance for direct sample injection as described in EPA 314.0.

Results: The suitability of ion chromatography with suppressed conductivity detection was tested for water samples in order to check the influence of matrix effects on the perchlorate signal of untreated samples. A sample injection volume of 750 µL was applied to the selected 2 mm IC column. The IC determination of perchlorate at low µg/L levels is challenged by the presence of high loads of matrix ions (e.g., chloride, nitrate, carbonate, and sulfate at 100 mg/L and above). Perchlorate recovery is impaired with the increasing matrix ion concentrations, and its chromatographic peak is asymmetric particularly at low perchlorate concentrations. The identification of the individual maximum concentration of interfering anions like chloride, nitrate, and sulfate that influence perchlorate recovery helps to reduce the number of sample preparation steps or an obligatory measurement of the electrical conductivity of the sample. Within the scope of this study, samples containing less than 125 mg/L of either anion did not need sample preparation.

Conclusion: The identification of the maximum concentration of interfering anions like chloride, nitrate, and sulfate influencing perchlorate recovery provides a simplified alternative to the EPA 314.0 method. This approach reduces unnecessary sample preparation steps while allowing a reliable prognosis of possible interferences and maintaining result quality. This study was performed to support the development of a respective international standard, which is being established by the International Organization for Standardization (ISO). The results of the study are also intended to be used as guidance for interested laboratories to optimize the analytical workflow for trace perchlorate determination.

Keywords: Perchlorate, Disinfection byproducts, Ion chromatography, Method validation, Chromatographic interferences

Background

This work is a continuation of our previously reported IC experiments for the determination of trace perchlorate, where manual sample preparation techniques were used to minimize matrix interferences [1]. We achieved a reporting limit (RL) of 1.5 µg/L perchlorate and an expanded measurement uncertainty calculated according to ISO 11352 [2] of 13.2%.

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*Correspondence: franz.schmitz@lhl.hessen.de
[4] Hessian State Laboratory, Glarusstr. 6, 65203 Wiesbaden, Germany
Full list of author information is available at the end of the article

Dissolved matrix ions, such as chloride or sulfate, interfere with the perchlorate determination at low µg/L levels. In reality, the perchlorate to total dissolved anions (TDA) concentration ratio can exceed 1:1,000,000 (Table 4). In chromatograms of such samples, perchlorate will likely elute as an asymmetric peak on the flank of a large tailing matrix ion signal. EPA 314.0 [3] specifies that sample treatment can be effective to eliminate certain matrix interferences. In an earlier study [1], we reported that SPE cartridges can be successfully applied. Other approaches employed to deal with matrix interferences required either additional hardware (e.g., heart-cutting technique), complex mathematical calculations [4], or the application of baseline subtraction [5]. Schär et al. [4] described higher recoveries applying a "Two-Dimensional-Calibration-Method." This method requires the use of a minimum of 20 calibration solutions with varying target analyte and interference concentrations and adopts a second-order calibration function. Bauer et al. [5] proposed recalculating chromatographic raw data applying the "Baseline Subtraction Method." This method involves baseline calculation using higher-order polynomials (e.g., 2nd to 6th order). The calculated theoretical baseline is then subtracted from the chromatographic raw data. Currently, commercially available chromatography software does not provide respective algorithms for either of the approaches. Consequently, the data would need to be exported and manually manipulated in a spreadsheet program, bearing the risk of not being in accordance with the requirements of data safety and data integrity [6].

We tested the EPA 314.0 approach to evaluate the analytical results of poorly separated perchlorate peaks by applying direct injection of untreated samples. According to the EPA approach, the user must measure the electrical conductivity of several synthetic samples with identical perchlorate concentration but varying matrix ion contents, including a zero-matrix solution, prior to ion chromatographic determination.

The linear correlation of the derived "peak-area to peak-height ratio" ($PD_{(A/H)}$) for the perchlorate peak, if plotted as the value on the abscissa against the corresponding conductivity on the ordinate, allows for the evaluation of a possible matrix influence on the chromatographic separation. With increasing sample conductivity, the $PD_{(A/H)}$ will increase. According to EPA 314.0, the "matrix conductivity threshold" (MCT) is the matrix conductance where the $PD_{(A/H)}$ exceeds 20%. The MCT is intended to help predict the chromatographic performance when routinely analyzing high conductivity samples. Our results revealed that the "$PD_{(A/H)}$ 20% rule" leads to false negative perchlorate concentrations, possibly leading to an unnecessary health risk for the consumers of such waters. This manuscript focuses on perchlorate analyses based on direct sample injection using common analytical IC equipment without sample preparation—with the exception of dilution and filtration—or heart-cutting techniques. The aim was to not only simplify the analytical workflow described in EPA 314.0 but also to enable analytical scientists to easily evaluate possible matrix interference due to the most common major anionic components being present in the evaluated sample matrices. The results of the validation experiments contribute to the ISO method development work [7].

Experimental

Reagents

The water used fulfilled the requirements of ISO 3696, Grade 1 [8], and had a specific resistance of 18.2 MΩ cm (Milli-Q Reference A+, Merck Millipore, Darmstadt, Germany). The anion stock standard solutions (1 g/L) for chloride, sulfate (Merck KGaA, Darmstadt, Germany), and perchlorate (CPAchem, Stara Zagora, Bulgaria and SCP Science, Courtaboeuf, France) were of p.a. quality. For the preparation of standard and test solutions, the sodium salts of chloride, sulfate, nitrate, and hydrogen carbonate were used in p.a. quality (Merck KGaA, Darmstadt, Germany). The perchlorate solution from CPAchem was used for the method validation and calibration experiments, while the perchlorate solution from SCP Science served as an independent source for quality-control measurements [1].

Materials for sample preparation

Disposable 10-mL-syringe Inject Solo on polypropene/polyethene basis (Braun Melsungen AG, Melsungen, Germany) and disposable non-sterile cellulose acetate syringe filter (0.45 µm, 25 mm, VWR international, Darmstadt, Germany) were used. Tests for blank values, adsorption, and memory effects were investigated for comparison with the filter materials. All of the checked materials showed no blank signal, perchlorate losses, or memory effects for water or synthetic samples [1].

Instrumentation

The chromatographic instrument (Thermo Scientific Dionex DX-500) consisted of a gradient pump (Dionex GP50) with a flow of 0.25 mL/min, an autosampler (Dionex AS50) with 1000-µL-injection loop, a column thermostat set at 30 °C (Dionex Ultimate 3000 TCC-3000), an eluent generator (Dionex RFC-30) equipped with an eluent generator cartridge (Dionex EGC-III KOH), continuously regenerated trap column (Dionex CR-ATC), and a conductivity detector (Dionex CD-25). The entire flow path was metal free. For eluent suppression prior to conductivity detection a Thermo Scientific

AERS-500 was used at a current setting of 22 mA. Separation was performed on a Dionex AS20 column and guard column-set. Columns and suppressor were in the 2-mm format, and data acquisition and evaluation were done using the Dionex Chromeleon 6.70 chromatography software. The eluent (35 mmol/L KOH) was produced electrolytically in situ. Samples were injected with volumes between 500 and 1000 µL using partial loop injection for volumes below 1000 µL. The total runtime was 30 min for each sample. [1].

The electrical conductivity of the samples was measured using a WTW MultiLab 540 equipped with a TetraCon 325 conductivity cell.

Quality requirements for the separating system

As a typical analytical requirement, the column of choice should allow the elution of perchlorate in a reasonable time and with acceptable chromatographic efficiency. At the same time, the column's capacity should be high enough to allow the injection of high ionic strength samples without impairing the retention time characteristics of perchlorate. Due to perchlorate's tendency to adsorb at the stationary phase, EPA 314.0 explicitly recommends the use of columns with hydrophilic characteristics, to improve peak symmetry and peak integration. Specific quality requirements defined by EPA 314.0 will be discussed later.

Analysis

Statistical performance data were evaluated based on ISO standard methods [9, 10]. The calibrated working range was adjusted to 1.5–15 µg/L perchlorate with 10 different standard solutions and an injection volume of 750 µL. For routine analysis, a minimum of five concentration levels were calibrated each day of operation for the defined working range. All V_{x0} (variation coefficient of the procedure) values calculated were below 3.33%, thus fulfilling the requirements described in [11]. For both analyses, a first-order calibration was applied using peak-area data. All other samples and standards were injected in replicate ($n = 3$), and the resulting data was used for the following calculations. Single anion and mixed anion solutions of different concentrations were used for the experiments. Depending on the samples' ionic strength, defined by the concentrations of main components, such as chloride, nitrate, carbonate, and sulfate, perchlorate elutes on a drifting baseline and can be integrated as a 'rider peak' by the chromatography software. The evaluation of 'rider peaks' can be difficult and has the potential to lead to erroneous results [4]. If necessary, real-world samples were filtered through a disposable non-sterile cellulose acetate syringe filter.

Results and discussion

Chromatographic conditions

In order to comply with the analytical procedure described in EPA 314.0, we followed the recommendations and requirements as outlined in the method.

Determination of the peak Gaussian factor (PGF)

EPA 314.0 defines the PGF as an indicator for the analytical column's hydrophobicity. The PGF is determined according to Eq. (1) [2].

$$\mathrm{PGF} = 1.83 \cdot \frac{W_{(1/2)}}{W_{(1/10)}}, \tag{1}$$

where $W_{(1/2)}$ is the peak-width at peak-half height, and $W_{(1/10)}$ is the peak width at the peak's tenth height. For hydrophobic columns, leading to an asymmetric perchlorate peak, the PGF value will significantly deviate from the optimal symmetric peak with, PGF = 1. This value must be between 0.80 and 1.15 for a perchlorate solution at a concentration in the middle-to-upper part of the calibrated range. In this study, a column set was used consisting of Dionex IonPac AS20 equipment with a corresponding guard column, both in the 2-mm format. The resin is characterized as being of ultralow hydrophobicity [12], and the evaluated PGF (Table 1) showed that the requirements are fulfilled across the entire calibrated range.

Quality-assurance (QA) requirements

Evaluation of trueness and precision

EPA 314.0 states that seven replicates of a synthetic perchlorate standard ($\rho = 25$ µg/L) must be analyzed in order to calculate the average recovery and the corresponding repeatability. The requirements are fulfilled if the recovery falls with the limit of ± 10% and if the repeatability coefficient is less than 10%.

In this study, we evaluated both parameters at even lower concentrations (1.5 and 15 µg/L) with a larger number of replicates ($n = 10$). The QA data obtained in subsequent experiments were within the ± 10% and average recoveries were 106% (1.5 µg/L) and 100.4% (15 µg/L). The corresponding variation coefficients were 5.15% (1.5 µg/L) and 0.436% (15 µg/L).

Table 1 Derived PGF for standard solutions

Parameter	Value									
ClO_4^-[µg/L]	1.5	3.0	4.5	6.0	7.5	9.0	10.5	12.0	13.5	15.0
PGF	1.0	1.0	0.97	0.97	0.96	0.96	0.96	0.96	0.96	0.96

Perchlorate recovery in an independent control sample

Following EPA 314.0 the recovery for a check standard must be between 90 and 110%. In our evaluation, recovery was checked at low concentration levels, reflecting the analytical needs of the upcoming ISO standard. For the analysis of a solution containing 7.5 µg/L perchlorate, being analyzed each day of system operation during a 3 month period, an average recovery of 98% with a standard deviation of 2.6% was found.

Evaluation of the method detection limit (MDL)

EPA 314.0 requires the determination of the Method Detection Limit (MDL). It is based on the analysis of seven spiked solutions. The EPA MDL experiment was carried out on a 2 µg/L perchlorate level with a resulting MDL at 0.53 µg/L with a variation coefficient of 8.4%. In order to support the ISO method development work, we used the performance data of the calibration function for the working range from 1.5 to 15 µg/L. Our results showed a variation coefficient of 1.0% according to [9]. For the MDL comparison reasons we applied the algorithms for the calculation of the limit of quantification as outlined in [10]. The calculated data of 0.98 µg/L was below 1.5 µg/L safeguarding the lowest calibration concentration statistically.

Influence of matrix ions on the chromatographic performance

Perchlorate retention time shift

The possible influence of matrix ions on the perchlorate brutto retention time (*RT*) was tested for the applied chromatographic conditions spiking perchlorate solutions ($\rho = 1.5$ µg/L) with chloride, carbonate, sulfate,, or nitrate individually, resulting in final concentrations between 10 and 250 mg/L. The 250 mg/L levels represented corresponding target values for chloride and sulfate according to the European Drinking Water Directive [13]. Perchlorate showed a *RT* of about 20 min in the matrix-free solution. The impact of the increasing single ion concentrations on the retention of perchlorate was low, with a maximum decrease below 1.5% for the 250 mg/L addition of nitrate.

In a second experiment, samples containing 10 µg/L perchlorate were spiked with a mixture of chloride, sulfate, nitrate, and hydrogen carbonate, resulting in a final concentration of between 100 and 1000 mg/L for each of the anions. A concentration dependent retention time decrease was observed with a maximum decrease of 4.2% for the highest concentration levels added (Table 2). The observed retention time deviation is well below the limit permitted by recent ion chromatography standard methods, which allow a maximum deviation of ± 10% within a single batch of experiments [14].

Perchlorate recovery in mixed matrix ion solutions

Recoveries were evaluated for ten 10 µg/L perchlorate solutions containing a mixture of chloride, sulfate, nitrate, and hydrogen carbonate, at concentrations between 100 and 1000 mg/L, each. The perchlorate peak-area signal obtained of an unspiked 10 µg/L standard solution, serving as a reference for the calculation of the recovery rates. Perchlorate showed decreased recoveries for samples containing more than 100 mg/L of matrix ions, falling outside the EPA 314.0 recovery acceptance range of 80–120% [3] (Table 2).

Matrix conductivity threshold (MCT)

The MCT is a laboratory-specific quality criterion and serves as a decision aid as to whether the sample can

Table 2 Sample data for neat and fortified perchlorate samples ($\rho = 10$ µg/L, average of three replicates)

MI mg/L	Cond µS/cm	RT_a min	RT_b min	Area $(A)_a$ µS min	Area $(A)_b$ µS min	Height $(H)_a$ µS	Height $(H)_b$ µS	Recovery_a µg/L	Recovery_b µg/L	$PD_{(A/H)a}$ %	$PD_{(A/H)b}$ %
0	< 1	19.74	21.32	0.01913	0.02042	0.03665	0.03771				
100	910	19.62	21.24	0.01615	0.01850	0.02972	0.03250	84.8	90.6	4.11	5.12
200	1740	19.52	21.16	0.01349	0.01630	0.02203	0.02590	70.7	79.8	17.3	16.2
300	2550	19.36	21.12	0.01061	0.01290	0.01577	0.01930	55.5	63.2	28.9	23.4
400	3340	19.76	21.06	0.00752	0.01010	0.01128	0.01410	39.3	49.4	27.7	32.3
500	4100	19.29	21.05	0.00302	0.00481	0.00680	0.00921	15.8	23.6	14.9	3.55
600	4890	19.23	20.98	0.00195	0.00321	0.00472	0.00669	10.2	15.7	20.8	11.4
700	5620	19.08	20.88	0.00133	0.00261	0.00346	0.00537	7.0	12.8	26.4	10.2
800	6370	19.03	20.83	0.00069	0.00163	0.00222	0.00371	3.6	8.0	40.5	18.9
900	7130	19.01	20.62	0.00026	0.00107	0.00102	0.00247	1.4	5.2	51.2	20.0
990	7770	18.91		0.00019		0.00083		1.0		56.1	
1000	7860		20.62		0.00057		0.00156		2.8		32.5

MI, Matrix ion concentration for each anion; Cond, conductivity; RT, retention time; *a*, data series 1; *b*, data series 2; *A*/*H*, peak-area to height ratio; $PD_{(A/H)}$, peak-area to peak-height-ratio be injected directly, or if dilution or sample preparation should be applied. EPA 314.0 describes two methods to establish the MCT: a regression method and the method of the highest acceptable conductance level. EPA 314.0 suggests determining the MCT on a perchlorate concentration level that is five times higher than the RL. In the EPA method, the MCT experiments were conducted on a 25 μg/L perchlorate level corresponding to perchlorate RLs of 3–5 μg/L [3]. In this study, the evaluations were performed on a concentration level of 10 μg/L perchlorate, reflecting potentially lower concentrations to be addressed by the ISO standard. The experiments were repeated using identical chromatographic conditions with an unused IonPac AS20 column set. Both data sets demonstrated a similar retention time, recovery, and MCT. Table 2 summarizes the results of these data sets.

MCT regression method

The regression method is based on a series of standard solutions of identical perchlorate concentration with different concentrations for chloride, sulfate, and carbonate, including one matrix free standard solution. The electrical conductivity of each of the solutions is measured. This study's sample regime included 11 solutions, 10 with varying concentrations of chloride, sulfate, carbonate, plus nitrate—as an extension to the EPA method—reflecting the composition of samples from agricultural environments. Each ion was added at concentrations between 100 and 1000 mg/L matrix ions (MI). While chloride, sulfate, and carbonate can be removed with SPE cartridges [1], nitrate remains in the sample and could interfere with the perchlorate peak. Figure 1 compares chromatograms obtained from untreated samples with different concentrations of MI.

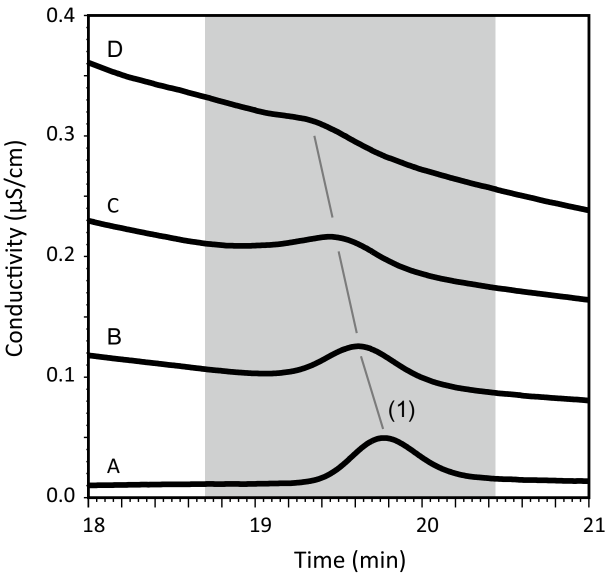

Fig. 1 Influence of matrix ions (MI) on a 10 μg/L perchlorate signal; A (0 mg/L MI); B (100 mg/L MI); C (200 mg/L MI); D (400 mg/L MI); (1) 10 μg/L perchlorate; signal offset of 10% was applied

The matrix impact can be visualized using the percentage difference in ratios of peak area and peak height ($\text{PD}_{(A/H)}$) which is calculated by the following equation: (2) [2, modified]

$$\text{PD}_{(A/H)} = \frac{|(A/H)_{\text{MF}} - (A/H)_{\text{MI}}|}{(A/H)_{\text{MF}}} \cdot 100\% \qquad (2)$$

with A representing the peak area and H reflecting the peak height of the respective perchlorate peak. MF stands for the matrix-free solution and MI for the spiked sample or standard.

The correlation of the $\text{PD}_{(A/H)}$ data plotted against the conductivity data results in a linear regression function. This function can be used to calculate the MCT as long as the calculated coefficient of determination (R^2) is above 0.95. As a convention, EPA 314.0 sets the decision value for the highest acceptable conductance at $\text{PD}_{(A/H)} = 20\%$. Figure 2 shows a plot using data series 1 (Table 2).

The MCT concept assumes that the $\text{PD}_{(A/H)}$ changes with increasing MI concentrations. Based on a decreasing peak-height value, the $\text{PD}_{(A/H)}$ value can be expected to increase with higher matrix ion concentrations. Our observations did not confirm this prognosis for the tested 500–700 MI solutions, resulting in $\text{PD}_{(A/H)}$-values below that of the 400 MI solution (Table 2). Linearity (within the meaning of EPA 314.0) was obtained between 0 and 300 mg/L of matrix ions, and the respective MCT resulted to about 2000 μS/cm corresponding to roughly 250 mg/L of each spiked anion (Fig. 2). Applying the procedure of EPA 314.0, a conductivity of below 2000 μS/cm would result in a $\text{PD}_{(A/H)}$ below 20% and would therefore allow the evaluation of signals after direct sample injections [3].

Highest conductance level method

Alternatively, EPA 314.0 permits the MCT to be set at a conductivity level of a spiked solution with a $\text{PD}_{(A/H)}$ value below the defined decision value of 20%. Using the data elaborated for this study, this was the case for the 200 MI solution with a $\text{PD}_{(A/H)}$ of 18%, and a conductivity of about 1750 μS/cm (Fig. 2, Table 2). Accordingly, all samples showing conductivity below 1750 μS/cm should be suitable for direct injection, and sample with conductivities above would need to be treated (e.g., diluted). In contrast to this prognosis the results of our work showed poor perchlorate recovery below 80%, even for samples starting at a concentration of about 100 mg/L MI or 1000 μS/cm.

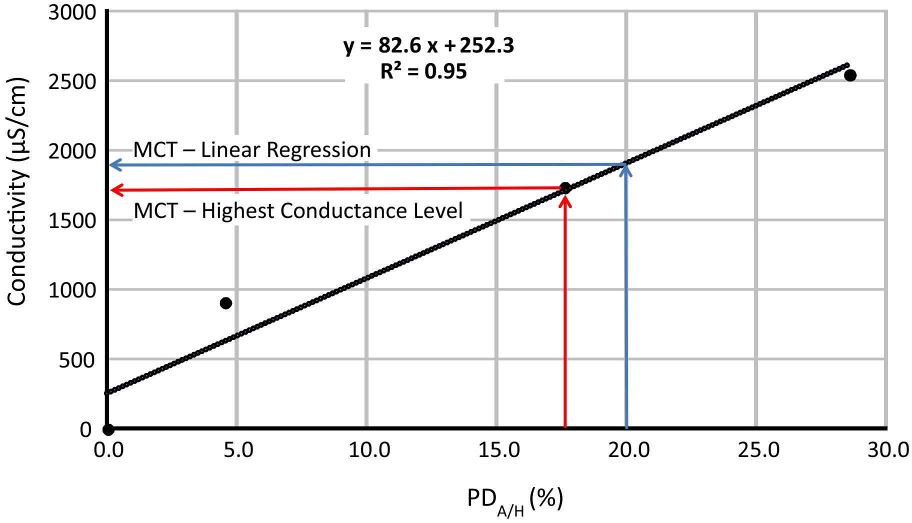

Fig. 2 Estimation of the MCT using a 2 mm Dionex IonPac AS 20 column set; 10 µg/L perchlorate

Confirmation of the RL using a mixed matrix ion solution

The analysis of a perchlorate solution at the RL, being spiked with matrix ions at a concentration within ± 10% of the MCT, is required to confirm the RL according to EPA 314.0. The perchlorate recovery rate for this sample should fall in the range between 70 and 130%. Otherwise the experiment should be repeated with solutions with a lower MCT—a suggestion is to lower MCT in increments of 10% until the recovery requirement is met. This study followed the concept described in ISO/TS 13530 [10]. According to that specification, the RL need to be verified with real-world samples. Samples with perchlorate values below the elaborated limit of determination of 0.33 µg/L were chosen and spiked with perchlorate to achieve a nominal concentration of 1.5 µg/L (RL). The samples were then analyzed both directly and after being treated (Table 3).

The RL was determined according to [10] with a relative result uncertainty of approximately 33%. The first requirement checks the measured value considering the relative result uncertainty. Consequently, all results must be within RL ± 33% or (1.5 ± 0.495) µg/L (Table 3). This was the case for all tested matrices with results below 1.995 µg/L.

The second verification requirement compares the measured repeatability standard deviation with a calculated test standard deviation s_{calc} also regarding the 33% uncertainty according to Eq. (3) [10, modified]

$$s_{\text{calc}} = \frac{\text{RL}\sqrt{n}}{3t_{f;\alpha}}, \tag{3}$$

where s_{calc} is the calculated test value, RL is the reporting limit, n is the number of replicates, and $t_{f;a}$ is the table value of the t-distribution for $f = n - 1$ and $P = 95\%$. For RL = 1.5 µg/L, $n = 3$ and $t_{f;a} = 4.303$ the following applies: $s_{\text{calc}} = 0.201$ µg/L.

s_{calc} represents the maximal acceptable value for repeatability standard deviation (s_x). The RL is considered to be verified as long as s_x is less than or equal to s_{calc}. This was the case for all tested matrices with s_x below 0.201 µg/L (Table 3).

Influence of single matrix ions on $PD_{(A/H)}$ and perchlorate recovery

Hence the impact of increasing single anion concentrations between 10 and 250 mg/L for chloride, nitrate, carbonate, and sulfate on the recovery of 1.5 µg/L perchlorate solutions was investigated. The initial identification of the major interfering ion could be less labor intensive and faster alternative to the MCT evaluation. Test protocols of real-world samples (e.g., drinking and surface water) include the routine analyses of common anions such as sulfate, chloride, and nitrate. Understanding the impact of either of these anions on the recovery of perchlorate would simplify the decision if matrix elimination is needed for an appropriate perchlorate determination.

Table 4 summarizes the results. The perchlorate signal obtained of an unspiked 1.5 µg/L perchlorate standard solution served as reference for the calculation of the recovery rates.

Following the EPA 314.0 concept, all of the calculated $PD_{(A/H)}$-values below 20% indicate no need for sample

Table 3 Data for the verification of the perchlorate RL of 1.5 µg/L (average of three replicates)

Sample	Matrix	Treatment	TDA	Cond	Perchlorate	
			(mg/L)	(µS/cm)	Mean (µg/L)	s_x (µg/L)
1	Ground water	untreated	168	459	1.59	0.0115
		SPE treated			1.59	0.1340
2	Drinking water	untreated	113	713	1.46	0.0100
		SPE treated			1.67	0.0681
3	Drinking water	untreated	45	257	1.92	0.0569
		SPE treated			1.62	0.0321
4	Drinking water	untreated	110	705	1.65	0.0200
		SPE treated			1.58	0.0917
5	Surface water	untreated	55	311	1.92	0.0800
		SPE treated			1.71	0.0950

TDA, Total dissolved anions; Cond, Conductivity; s_x, repeatability standard deviation

Table 4 Impact of single anions on perchlorate recovery [ρ(perchlorate) = 1.5 µg/L]

Matrix ion concentration	Carbonate		Chloride		Nitrate		Sulfate	
	$PD_{(AH)}$ (%)	Recovery (%)	$PD_{(AH)}$ (%)	Recovery (%)	$PD_{(AH)}$ (%)	Recovery (%)	$PD_{(AH)}$ (%)	Recovery (%)
10	0.626	103	7.52	100	11.3	94.9	1.46	102
25	1.67	99.6	9.19	94.5	6.26	109	0.418	84.1
50	1.46	95.7	4.18	101	0.626	110	10.9	85.7
75	8.56	87.7	9.81	96.5	11.1	87.8	7.72	93.6
100	0.626	86.9	7.93	89.5	3.34	106	1.46	90.3
125	3.97	80.7	13.2	97.4	5.85	96.5	2.92	77.8
150	6.26	76.1	3.97	98.2	10.6	81.1	2.92	70.3
175	10.0	75.1	12.1	98.2	3.97	102	6.89	78.7
200	12.9	63.2	9.6	92.8	12.3	75.3	2.71	77.8
225	21.3	64.3	14	86.1	6.68	82.4	7.52	79.9
250	12.9	57.0	10	74.1	8.14	65.8	10.2	82.8

preparation [3]. The results of this study, however, indicate significant false negative results for concentrations above 125 mg/L for the individual anions. This could be explained by a well-known overloading effect in IC by which the peak of the minor component is influenced such that it broadens and flattens out (Fig. 1). As a result, the peak area decreases, and calculated concentrations are lower than the expected values.

Perchlorate recoveries were above 75% in all ion solutions with concentrations equal to or below 125 mg/L. Chloride and nitrate caused perchlorate recovery below 80% for concentrations above 200 mg/L, respectively. The influence of carbonate and sulfate was characterized by a continuous decrease in perchlorate recovery with increasing ion concentrations. Perchlorate recovery fell below 80% for their concentrations above 125 mg/L (Fig. 3). Consequently, samples showing concentrations above 125 mg/L of either of the mentioned anions would require a dedicated sample treatment (dilution or SPE).

Real-world sample analyses

An international interlaboratory trial (ILT) was organized by ANSÉS (Nantes, France) in support of the new ISO standard [7], with 25 participating laboratories. The calibrated working range was adjusted from 2 to 20 µg/L. At first, all unprocessed samples were analyzed. Then, the samples were treated to remove chloride, hydrogen carbonate, and sulfate by SPE or dilution before injection. In addition the concentrations of chloride, nitrate, and sulfate were determined by ion chromatography. Results are presented in Table 5.

The results confirmed the conclusions made for the single ion analyses (Table 4 and Fig. 3). The untreated mineral water and river water samples, with single ion

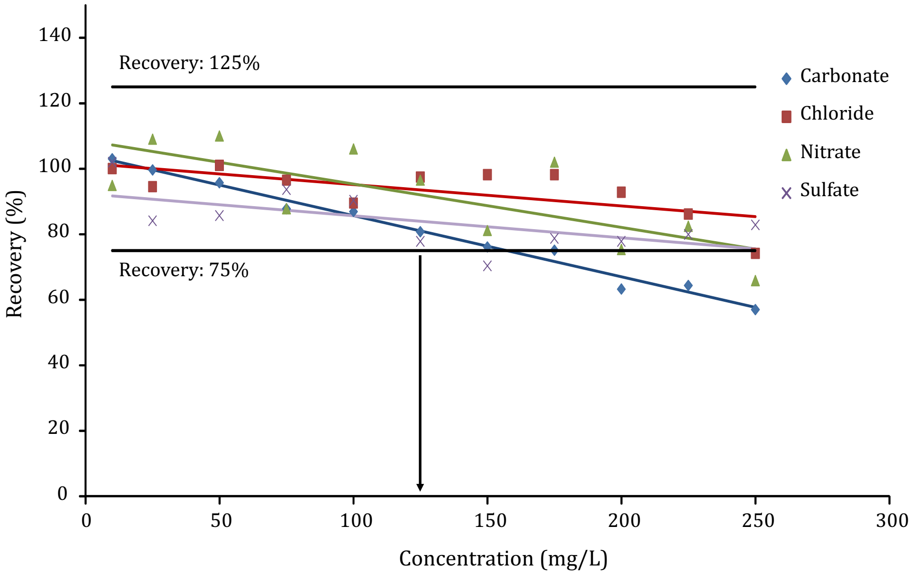

Fig. 3 Impact of individual anion concentrations on the recovery of perchlorate (ρ = 1.5 µg/L)

concentrations above 125 mg/L showed significantly lower perchlorate concentrations. Consequently, only the results obtained after sample preparation (dilution or SPE) were reported to the organizers. All reported results were accepted for the final statistics. All reported data were within 2–6% from the ILT's calculated mean value, proofing the applicability of the simplified method.

Conclusion

An isocratic ion chromatographic method with suppressed conductivity detection was applied to the routine perchlorate determinations at low µg/L levels. The applicability of the EPA 314.0 MCT concept was tested. In contrast to the EPA method, a 2 mm format Dionex IonPac AS20 column set, modified eluent concentration, and an injection volume of 750 µL was applied. The experiments in this study were performed at lower concentration levels, and the results obtained complied with or surpassed quality-control requirements specified in EPA 314.0.

The RL was verified according to ISO/TS 13530 [10] for untreated and treated real-world samples, in contrast to the EPA procedure where standard solutions are used. For the evaluation of the MCT 10 µg/L, perchlorate solutions were used (EPA 314.0 used 25 µg/L). In contrast to EPA, nitrate was added to the mixed matrix ions matrix to represent a composition of real-world samples. Despite the fact that all quality-control requirements were passed, this study did not confirm any benefit from the MCT regression method and the highest conductance method. According to the presented results, the rather complex MCT evaluation is not needed to evaluate

Table 5 Results for untreated and treated interlaboratory trial samples

ILT sample	Matrix ion				Perchlorate		
	SO_4^{2-}	Cl^-	NO_3^-	DF	Untreated	SPE treated	Ratio
	mg/L	mg/L	mg/L		µg/L	µg/L	%
Ground water	5.6	10	2.6	1	5.41	5.29	102
Drinking water	25	99	9.4	1	14.8	15.1	98
Mineral water	400	45	0.5	1	2.58	3.61	71
River water	330	800	16	1	16.1	20.1	80
Swimming pool water	210	150	13	25	205	201	102

DF sample dilution factor applied, *Ratio* (Untreated/SPE treated)·100%

if the chosen chromatographic conditions are suitable to determine trace levels of perchlorate and if sample preparation is needed. Hence, the impact of the major matrix anions on perchlorate recovery was investigated. None of the tested single matrix ion solutions provided a $PD_{(A/H)}$ above 20%, although significant reduced perchlorate recovery was obtained. Samples with individual matrix anion concentrations of below 125 mg/L would allow the direct injection, and those above this value would need to be prepared accordingly. This strategy was applied to samples of an international interlaboratory trial, and the results reported confirmed this simplified strategy.

Authors' contributions

MAS, DJ, UN, UKD, and FS contributed to the conception, discussion, and conclusions, and the manuscript. MAS and UN contributed to the collection of the analytical data and interpretation of data. DJ supplied the background information on IC separation mechanism, sample preparation, column characteristics, and data evaluation. FS conducted the statistical evaluations. All authors read and approved the final manuscript.

Author details

[1] Hessian State Laboratory, Glarusstr. 6, 65185 Wiesbaden, Germany. [2] Thermo Fisher Scientific, Im Steingrund 4-6, 63303 Dreieich, Germany. [3] Hochschule RheinMain, Am Brückweg 26, 65428 Rüsselsheim, Germany. [4] Hessian State Laboratory, Glarusstr. 6, 65203 Wiesbaden, Germany.

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