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Short communication

Quantitative determination of oxalate and other organic acids in drinking water at low μg/l concentrations

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Abstract

In this research, a recently developed ion chromatography method for organic acids was expanded to include oxalate. A major challenge was that oxalate elutes between inorganic anions such as sulfate, phosphate, bromide and nitrate, which are often present in much higher concentrations than oxalate. Optimization of the previously reported method made it possible to determine oxalate in these matrices. However, for those samples in which higher inorganic anion concentrations caused the oxalate peak to be obscured, a ''heart-cut'' column switching technique was used as an alternative. The method detection limit for oxalate was 9 μg/l with the direct approach and 6 μg/l for the ''heart-cut'' technique. These modifications represent a valuable supplement to a recently developed method for monitoring ozonation by-products in drinking water.

Keywords: Water analysis; Organic acids; Oxalate

1. Introduction

Organic acids such as acetic, formic and oxalic acid are known to be disinfection by-products when ozonation is applied during drinking water treatment [1–3]. Since these compounds are suspected to contribute to bacterial regrowth in drinking water distribution systems, there is considerable interest in being able to quantify these organic acids.

Currently, there are several different methods available for the quantification of organic acids. They include gas chromatography (GC) [4–9], high-performance liquid chromatography (HPLC) [10,11], capillary electrophoresis (CE) [12–15] and ion chromatography (IC) [16–27]. GC and HPLC methods [4–11] might be able to achieve the necessary sensitivities but typically involve time consuming sample preparation steps such as extraction and/or derivatization. CE [12–15] is a promising technique which has recently gained a lot of interest because it can achieve high separation efficiencies very quickly. However, a major drawback is the current predominant use of direct or indirect UV detection which results in a lack of sensitivity. The difficulty with all of these analyses lies in the fact that inorganic anions are typically present in mg/l concentrations whereas organic acids are present in low μg/l concentrations.

IC methods which are commonly applied to organic acid analysis are ion-exclusion chromatography [16–23] and anion-exchange chromatography [24–27]. In ion-exclusion chromatography, most inorganic anions elute in the system peak whereas anions of weaker acids are retained and separated. UV detection has traditionally been used in ion-

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exclusion chromatography resulting in relatively low sensitivities. The sensitivity of conductivity detection in ion-exclusion chromatography was recently improved by replacing mineral acids, the traditional eluent modifiers, with weaker acids such as benzoic or methanesulfonic acid [17,18] thus lowering the background conductivity. More recent papers [21–23] suggest to use polyols and sugars as eluent modifiers. Although this substitution led to a further increase in sensitivity, it should be noted that these studies were performed with model samples (spiked deionised water) only. The impact of sample matrices which will include significant quantities of, for example, carbonate on the separation of the organic acids were not considered in these fundamental studies. It is also anticipated that organic acids with low pK_a values such as oxalic acid (pK_a 1.27) might be difficult to separate from the system peak in these methods.

Anion-exchange methodology, and combinations of anion-exchange chromatography with other techniques, were used to determine organic acids in various types of water [24–27]. Recent suppressor technology is capable of significantly reducing the background conductivity caused by NaOH containing eluents thus allowing detection of organic acids at μg/l concentrations when using conductivity detection [26,27].

Recently, the authors introduced a fast IC method [27] based on anion-exchange chromatography which is capable of quantifying seven different organic acids in drinking water at low μg/l concentrations. As stated in that paper [27], this method did not allow for the determination of organic acids eluting after chloride, including oxalate. Depending on the concentration of certain inorganic anions (sulfate, bromide and phosphate), the oxalate peak could be obscured by those anions, making its quantification difficult. Considering that oxalate was found to be a major ozonation by-product, it was necessary to modify the procedure to ensure that oxalate could also be measured.

To solve this problem, two different approaches were attempted and are described herein. First, an optimization of the existing method was undertaken so that oxalate could be quantified in samples with lower mg/l concentrations of inorganic anions. Secondly, for samples with higher inorganic anion concentrations a combination of the existing method and a ''heart-cut'' column switching technique was studied.

2. Experimental

Reagents, instrumentation and sample preparation were the same as described previously [27] unless noted otherwise.

2.1. Reagents

In order to account for different water matrices, organic acid standards in deionised water were fortified with different inorganic anions (NO_3^-: 50, 100 mg/l; SO_4^{2-}: 100, 200 mg/l; Br^-: 1, 10, 25, 50 mg/l; PO_4^{3-}: 1, 5, 10 mg/l).

All solutions, standards and samples were preserved by adding neat $CHCl_3$ to a final concentration of 0.1% (v/v) $CHCl_3$ in the solution (e.g., 50 μl of neat $CHCl_3$ into 50 ml solution). As shown before, organic acid solutions preserved in this manner can be stored for at least 1 week at 4°C [27].

2.2. Instrumentation

In addition to the earlier described configuration, a high-pressure 4-way injection valve (V2), a low-pressure 2-way valve (V3) and a concentrator column (TAC-1, 24×4 mm I.D.) were utilized for the ''heart-cut'' column switching technique. The installation is illustrated in Fig. 1.

2.3. Determination of oxalate in samples with low inorganic anion concentrations (NO_3^- <50 mg/l; SO_4^{2-} <200 mg/l; Br^- <25 mg/l; PO_4^{3-} <5 mg/l)

Samples were directly injected onto the IC system via a 740 μl sample loop, and the following eluent gradient (flow 1 ml/min) was applied: 7 m*M* NaOH for 10 min, linear increase to 125 m*M* NaOH for 13 min (17% NaOH 7 m*M*, 83% NaOH 150 m*M*), 125 m*M* NaOH for 12 min. This was followed by 7 m*M* NaOH for 10 min to re-equilibrate the columns for the next injection.

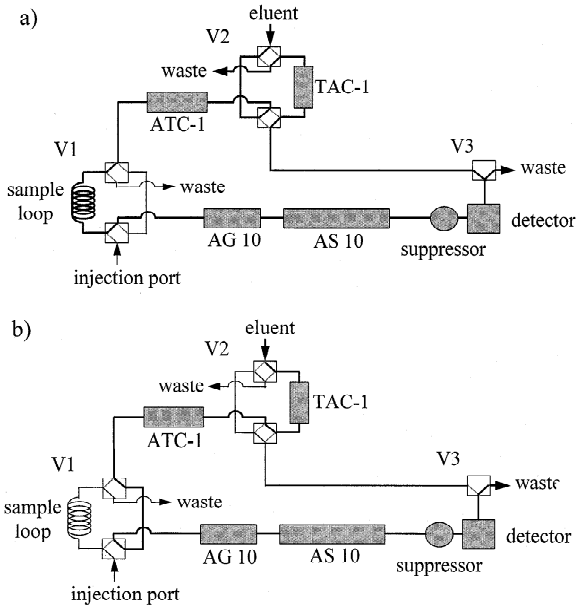

Fig. 1. System configuration during (a) sample preparation run and during (b) oxalate analysis run (V1 sample injection valve; V2 valve for reinjection of effluent trapped on concentrator column; V3 switching valve; ATC-1 anion trapping column; AG 10 guard column; AS 10 analytical column; TAC-1 concentrator column).

2.4. Determination of oxalate in samples with high inorganic anion concentrations

This two-step procedure consisted of a sample preparation run and an oxalate analysis run. The sample preparation run initially proceeded as described in Section 2.3. During the time window when oxalate was expected to be eluted (27.5–29.5 min) the effluent was collected onto a concentrator column by switching a 2-way-valve (V3, Fig. 1). At the end of the run, the system was re-equilibrated for 10 min to 50 m*M* NaOH, the starting concentration for the oxalate analysis run. The collected effluent from the sample preparation run, containing the oxalate, was then reinjected from the concentrator column onto the analytical column and analyzed using the following eluent gradient (flow: 1 ml/min): 50 m*M* NaOH, linear increase to 125 m*M* NaOH in 24 min, 125 m*M* for 5 min. This was followed by 7 m*M* NaOH for 10 min to re-equilibrate the system to the starting conditions of the next sample preparation run. The configuration of the different valves and columns is illustrated in Fig. 1.

3. Results and discussion

3.1. Direct analysis of samples with non-interfering concentrations of inorganic anions

In order to achieve sufficient separation of oxalate from inorganic anions, the IC performance had to be at its optimum. It was found that the status of the guard column played a major role. Over time, impurities originating from the different sample matrices were deposited on the guard column, leading to significant broadening of the oxalate peak whereas the earlier eluting acids were not affected to the same extent. Guard column clean ups with HCl (1 *M*), EDTA (40 m*M*) and NaOH (1 *M*) improved the performance temporarily, however regular guard column replacement (every 3–6 months depending on sampling loads and sample matrices) gave the best results.

Proper maintenance of the ATC-1, the column used to purify the eluents, was also found to be critical. Before running each sample queue, the ATC-1 was regenerated off-line thus minimizing the possible introduction of additional impurities onto the guard and analytical columns.

Another factor influencing the quality of the chromatograms was the type of eluent container used. Plastic containers provided the best reproducibility of retention times for the late eluting peaks, including oxalate.

Consideration of these factors made it possible to extend the previously introduced IC method to include oxalate. After establishing a calibration curve ($y=2.21\cdot10^5x+3.82\cdot10^5$, $r^2=0.9999$) the method detection limit for oxalate was determined to be 9 μg/l ($c=13$ μg/l, $n=8$) [28]. The reproducibility of the procedure was acceptable, with a recovery of 93% and a corresponding standard deviation of 7% ($c=63$ μg/l, $n=8$).

This optimized direct injection IC method has been applied successfully to different types of drinking water samples on a routine basis. One example of which is shown in Fig. 2 for a sample obtained

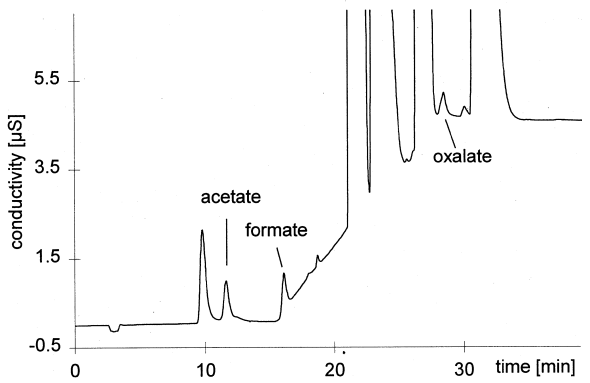

Fig. 2. Drinking water sample taken after ozonation in a full scale water treatment plant (60 µg/l oxalate).

following ozonation in a drinking water treatment plant.

3.2. "Heart-cut" column switching technique

Although the method described above may be used for samples with inorganic anion concentrations which are typical for those encountered in drinking water, there are some sample matrices which will exceed the capability of this method, especially for the measurement of oxalate. In order to investigate the extent of these matrix effects, organic acid standards in deionized water were spiked with single inorganic anions in varying concentrations and measured by the direct IC method. It was found that the oxalate peak could be obscured by inorganic anion peaks from NO_3^-, Br^-, PO_4^{3-} or SO_4^{2-}. Oxalate quantification became impossible when the concentration of a single inorganic anion exceeded 50 mg/l for NO_3^-, 25 mg/l for Br^-, 5 mg/l for PO_4^{3-} or 200 mg/l for SO_4^{2-}. It should be noted that these limits are only estimates for a particular sample type (spiked deionized water) and that concentrations of inorganic anions affecting oxalate quantification might be lower in real samples due to the combined effect of several inorganic anions.

As an alternative, the "heart-cut" column switching technique was evaluated for the quantification of oxalate in samples in which inorganic anion concentrations were high enough to interfere with the oxalate determination by the direct IC method. After initial experiments a two-stage procedure consisting of a sample preparation run and an analytical run was chosen. The sample preparation run utilized the same instrument conditions that were applied as described for the direct injection IC method. When oxalate eluted, the effluent was collected onto a concentrator column. The isolated oxalate was then eluted from the concentrator column and readsorbed onto the analytical column by the application of a completely different gradient specifically developed for the separation of oxalate (Fig. 3).

The organic acids eluting in the sample preparation run were quantified using the same calibration curves obtained from the direct injection IC method. In order to quantify oxalate, which elutes in the

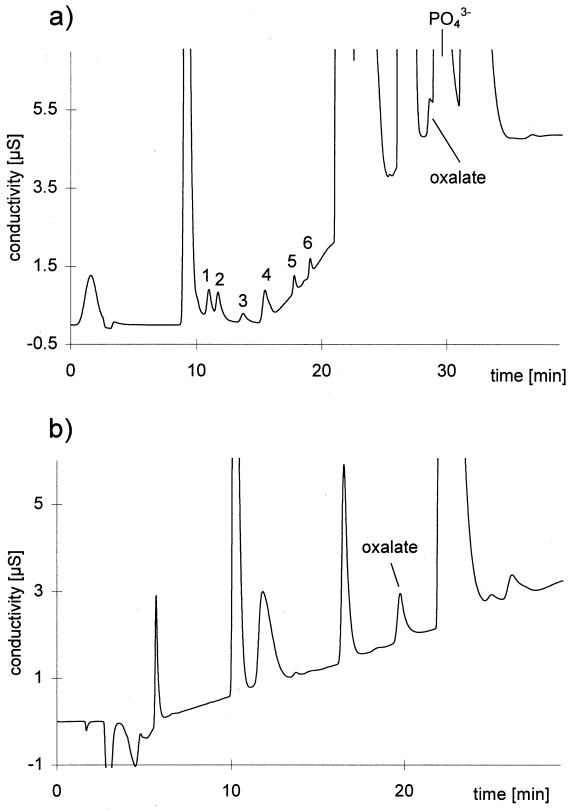

Fig. 3. Tap water fortified with 10 mg/l phosphate and spiked with organic acids (c=50 µg/l each); (a) sample preparation run [1=acetate (coelutes with lactate and glycerate), 2=glycolate (coelutes with propionate), 3=butyrate, 4=formate, 5=pyruvate (coelutes with oxalacetate), 6=α-ketobutyrate]; (b) analytical run.

analytical run, a new calibration curve was established ($y=1.88\cdot10^5x-1.41\cdot10^5$, $r^2=0.9938$). Subsequently, the method detection limit of oxalate was determined to be 6 μg/l ($c=6$ μg/l, $n=8$) [28] and the reproducibility proved to be good with a 91% recovery and a corresponding standard deviation of 3% ($c=63$ μg/l, $n=7$).

It should be noted that depending on the sample matrix the cutting window for oxalate may require adjustment. Large quantities of inorganic anions can alter eluent properties with the consequence that the retention time of a compound of interest, here oxalate, might shift. Detailed procedures for finding the optimum cutting window for a specific matrix have been described by Killgore and Villasenor [29].

The main advantage of the instrumental configuration shown in Fig. 1, was that it accommodated both applications (the direct method and the ''heart-cut'' column switching technique) on one instrument without having to do any manipulations on the instrument itself. The advantage of the ''heart-cut'' column technique is that it can accommodate the quantification of organic acids including oxalate in a wide range of sample matrices. However the direct IC method is a lot faster and was therefore utilized whenever the sample matrix allowed it.

4. Conclusions

The methodology described herein supplements a recently published IC method [27] thus enabling the determination of oxalate concentrations in addition to those of other organic acids (β-hydroxybutyrate, acetate, glycolate, formate, butyrate, pyruvate and α-ketobutyrate) at low μg/l concentrations. The option of applying the ''heart-cut'' column technique in addition to the direct IC method enabled the determination of oxalate and other organic acids in a wide range of drinking water sample matrices. Furthermore, detection limits in the low μg/l range make this method suitable for monitoring organic acid ozonation by-products in drinking water.

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