Determination of Trace Inorganic Anions in Weak Acids by Single-Pump Column-Switching Ion Chromatography

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Abstract

Ion chromatography has been proposed for the determination of three common inorganic anions (chloride, nitrate, and sulfate) in nine weak acids (tartaric acid, citric acid, formic acid, acetic acid, metacetonic acid, butyric acid, butanedioic acid, hexafluorophosphoric acid, and salicylic acid) using a single pump, two valves, a single eluent, and a single conductivity detector. The present system uses ion exclusion, concentrator, and anion-exchange columns connected in series via 6-port and 10-port valves in a Dionex ICS-2100 ion chromatograph. The valves were switched for the determination of three inorganic anions from weak acids in a single chromatographic run. Sample matrices of weak acids with a series of concentrations can be investigated. Complete separations of the previously mentioned anions are demonstrated within 40 min. Under the optimum conditions, the relative standard deviation values ranged from 1.3 to 3.8%. The detection limits of the three inorganic anions (S/N = 3) were in the range of 0.3–1.7 µg/L. The recoveries were in the range of 75.2–117.6%. With this system, automation for routine analysis, short analysis time, and low cost can be achieved.

Introduction

Developing a reliable method to determine trace anions in concentrated acids is quite necessary. Concentrated acids play an important role in many fields, especially in the fabrication of semiconductor devices. Purity requirements for these reagents are more stringent. Over the past decade, ion-exclusion chromatographic separation coupled to ion chromatographic separation (ICE–IC) method has become the most popular analytical technique for the determination of trace anions in concentrated acids, such as hydrofluoric acid (1–2), concentrated phosphoric acid (3–4), organic acids (5–9), and other weak acidic solutions (10–12). This technology, using a valve system, allows weak acids to be eluted off into the waste and switches the target ions (inor-ganic anions) to the analytical column. ICE–IC, also called column-switching ion chromatography, does not require any sample pretreatment (13–15).

The ICE–IC method previously described in literature consisted of two eluent systems: potassium hydroxide for ion exchange and deionized water for ion exclusion (16–19). Two pumps were necessary to provide the two different eluents regularly, adding more complexity and costs of the method. Therefore, a new method has been developed instead of the traditional column-switching system.

The new proposed method involves a simplified column-switching method for the determination of inorganic anions in concentrated weak acids. Compared to traditional column-switching method, only one pump was used in this system, so it is called single-pump column-switching. The IC suppressor in a self-regenerating system can change potassium hydroxide into water by the effects of anion-exchange membrane. So most of the time, the eluent from the outlet of conductivity cell is deionized water when the IC runs with the suppressor. It can be used as mobile phase for the ion-exclusion column. Thus, only one eluent system is needed providing the eluent both for anion-exchange column and ion-exclusion column, and only a single pump is used in this system. The method has been successfully applied to a wide range of samples such as organic acids, phosphate, and other weak acids.

Experimental

Reagents, solutions, and samples

Reagent-grade chemicals were used for standard and eluent preparation. Deionized (18.2 MΩ/cm) water was generated using a Millipore Milli-Q Plus system (Millipore, Milford, MA). Working standards were prepared by further diluting the 1000 mg/L standards to the range expected for the anions of interest. All standard solutions of inorganic anions were prepared from corresponding salts (Beijing Xinguang Chemical Reagent Factory, Beijing, China).

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Serial concentrations of the weak acids (0, 1, 5, and 10% by weight) were prepared by dissolving appropriate amounts of the analyte salts in deionized water, and the solutions were stored in the dark at 4°C. Tartaric acid (Guangzhou Chemical Reagent Factory, Guangzhou, China); citric acid (The First of Shanghai Reagent Factory, Shanghai, China); formic acid (The Second Yixing Chemical Reagent Factory, Yixing, China); acetic acid (Hangzhou Chemical Reagent Factory, Hangzhou, China); metacetonic acid (Shanghai Chemical Reagent Factory, Shanghai, China); butyric acid (Sinopharm Chemical Reagent Co., Shanghai, China); butanedioic acid (Shanghai Chemical Reagent Factory, Shanghai, China); hexafluorophosphoric acid (Yongtai Technology Co, Zhejiang, China); and salicylic acid (Shanghai New Chemical Research Institute, Shanghai, China) were used. Polyethylene containers were used for storage of the concentrated acid samples.

Equipment

Most chromatographic separations were performed on a Dionex (Sunnyvale, CA) ICS-2100. The system consists of a pump, two valves (6-port and 10-port valve), and a DS6 conductivity cell.

All columns used in this study were manufactured by Dionex. An IonPac ICE-AS6 column (250 mm × 9 mm) was used for the ion-exclusion separation, followed by an AG11-HC column (50 mm × 4 mm) to concentrate anions prior to injection into the anion-exchange system. An AG11-HC guard column (50 mm × 4 mm) and AS11-HC separation column (250 mm × 4 mm) were used for the final separation. An electrochemical self-generating suppressor was used for eluent suppression with external water mode; deionized water was used as regenerant by pneumatic means, i.e., by putting the high-density polyethylene (HDPE) bottles in a chamber pressurized to 250 psi with nitrogen. Another Dionex DS6 conductivity detector was used to optimize the switching-time. Two valves' positions were programmed in by Chromeleon 6.5 (Dionex). Measurements were performed using a 200-μL sample loop. Chromeleon 6.5 software was used to acquire the data and control the instrumentation.

Polyether ether ketone (PEEK) tubes were used to connect all chromatographic hardware. The lengths of the connecting tubing were kept as short as possible to minimize system void volume.
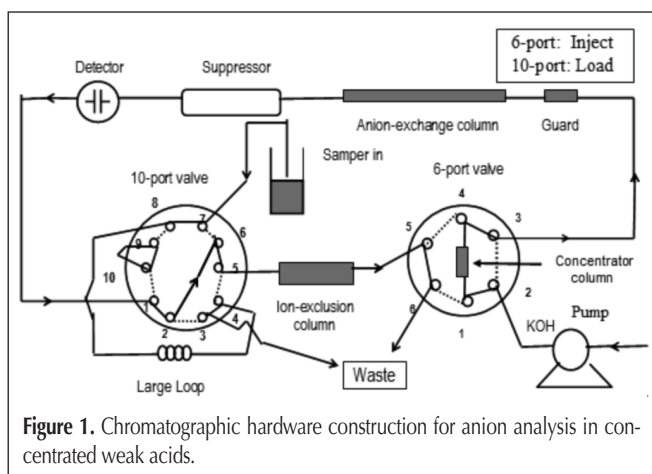
Chromatographic conditions

Suppressed IC with conductivity detection was performed with EG40 eluent generator, which provide a concentration of 25 mmol/L potassium hydroxide liquid. The suppressor current was set at 100 mV. All ion-exclusion separations were done on the IonPac ICE-AS6 column using liquid from the outlet of conductivity cell as the eluent. The flow rate was 0.55 mL/min.
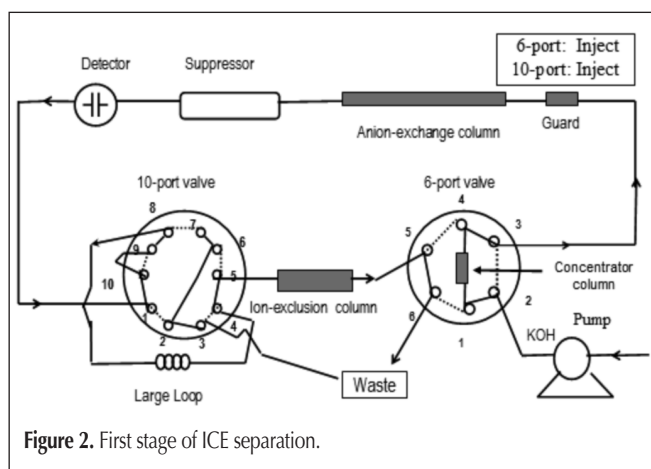
Experimental procedure

Analysis of trace anions in concentrated weak acids was accomplished in two steps: an ICE pretreatment, followed by injecting a portion of the ICE separation to an IC separation. Firstly, the analyte anions were separated from the weak acid matrix by ICE. A carefully selected fraction, called hereafter "cut window" fraction containing the major percentage of each analytes, was then sent to a concentrator column. The fractions preceding and following were directed to waste. The anions accumulated onto the concentrator were finally separated on an anion-exchange column and detected by conductivity after electrochemical suppression of the eluent. The schematic in Figure 1 illustrates how the chromatographic hardware was set up. This initial construction shows the 6-port valve in the "inject" position and the 10-port valve in the "load" position.

The concentrated acid sample was loaded via manual injection into the sample loop (the large loop). At least four loop volumes were pushed through the large loop to ensure that the sample had been filled in. Meanwhile the eluent was flowing through the 6-port valve, concentrator column, guard column, anion-exchange column, suppressor, detector (conductivity cell), 10-port valve, ion-exclusion column, then to the waste.

The concentrated weak acid sample was delivered from the large loop to the ion-exclusion column with the eluent from the outlet of conductivity cell (deionized water) by switching the 10-port valve to the "inject" position. The first portion of the ICE separation was sent to waste (Figure 2). Next, the concentrator column was placed in line with the ICE column, and the "cut" portion was preconcentrated on the concentrator column by placing the 6-port valve in the "load" position (Figure 3). The time of "cut window" was optimized in order to obtain the highest recovery for the separated common inorganic anions.

Finally, the concentrator column was placed before the anion-exchange column by placing the 6-port valve in the "inject" posi-

Figure 1. Chromatographic hardware construction for anion analysis in concentrated weak acids.

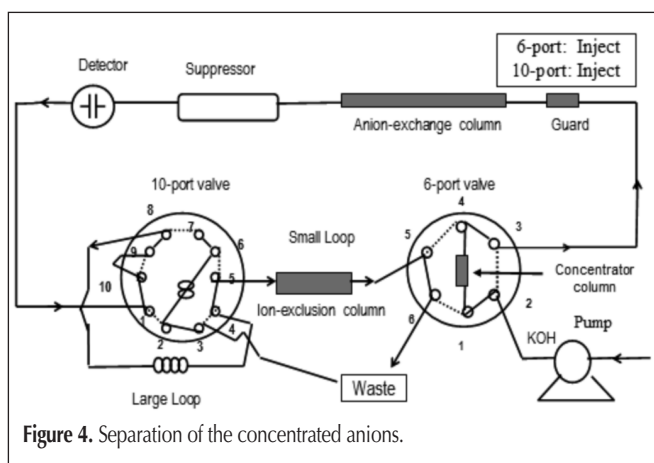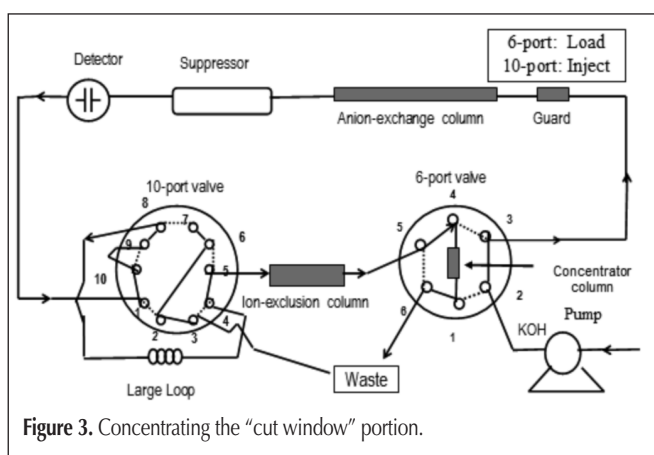**Figure 2.** First stage of ICE separation.

tion, and the concentrated anions were separated by analytical column. While the IC separation was in progress, the 10-port valve was still in the "inject" position. The eluent from the outlet of conductivity cell was keeping on rinsing the ion-exclusion column, ensuring that the weak acid reserved on ICE-AS6 can be totally washed down to the waste and that the column was refreshed (Figure 4). There is a concern that the desired inorganic anions that had been separated through the anion-exchange column would be eluted into the ion-exclusion column again. However, the eluent would become deionized water again after all the desired ions were washed up through the anion-exchange column. Hence, when all the ions were washed to waste, making the whole analysis procedure completed and the system ready for next sample.

Results and Discussion

Optimization of chromatographic conditions

In traditional ICE–IC method, the conditions of ion-exclusion and ion-exchange separation can be discussed individually. But in a single-pump column-switching system, there was only one eluent system. The flow rate of ICE separation and IC separation must be the same. So the conditions of ICE and IC must be considered together. Based on experiments, the flow rate was an important factor to the ICE separation. In this part of study, the

Figure 3. Concentrating the "cut window" portion.

Figure 4. Separation of the concentrated anions.

flow rate was set at 0.55 mL/min. The IonPac ICE-AS6 column can separate common inorganic anions from weak acids successfully. By changing the concentration of potassium hydroxide, the IonPac AS11-HC column can also separate the three inorganic anions, although the set flow rate is only 0.55 mL/min. If the flow rate was below 0.55 mL/min, it must take a longer time for ICE separation. Otherwise, if the flow rate was above 0.55 mL/min, the resolution of inorganic anions and weak acids was not ideal. By comprehensive consideration, the chromatographic conditions were set as follows: the flow rate was 0.55 mL/min and the concentration of potassium hydroxide for anion-exchange separation was 25 mmol/L.

The eluent from the outlet of the conductivity cell was collected for further detection, comparing the conductivity and pH value of the eluent with those of deionized water. The results indicated that there was no difference between them. Thus, the eluent from the outlet of the conductivity cell can be used as mobile phase for ion-exclusion column.

This indicated the same conductivity and pH value as the deionized water. Thus, the eluent from the outlet of the conductivity cell can be used as mobile phase for ion-exclusion column.

Optimization of column-switching conditions

In this experiment, a conductivity cell was directly fixed after ICE-AS6 column without electrochemical suppression. Signals from the ion-exclusion column eluents were recorded. Figure 5 illustrates the signals from the unsuppressed conductivity for the ICE separation. Because inorganic ions we detected are strong acid ions, they cannot be reserved onto the resin and will be eluted out at the same time in front of the large amount of concentrated weak acids. Hence, there is a small peak on the chromatogram at approximately 7.0 min before large peaks at approximately 11.0 min.

The "cut window" from the ICE separation was optimized for a given flow rate (0.55 mL/min). It was important to ensure a complete capture of the anions of interest and avoid an excessive

Figure 5. Ion-exclusion separation of 10 mg/L of each anions from 10,000 mg/L tartaric acid. Peak 1 = three inorganic anions (10 mg/L each); Peak 2 = tartaric acid (10,000 mg/L). Sample volume: 200 µL; ICE column: IonPac ICE-AS6 (250 × 9 mm); Concentrator column: IonPac AG11-HC (50 × 4 mm); IC column: IonPac AG11-HC (50 × 4 mm), AS11-HC (250 × 4 mm); Detection: conductivity; Eluent: deionized water (25 mmol/L KOH after suppressor self-regenerating process); flow rate: 0.55 mL/min.

capture of the sample matrix. An extra conductivity cell was directly fed between ICE-AS6 column and 6-port valve without electrochemical suppression in order to record the signals from ion-exclusion column. The "cut window" time was established according to these ICE chromatograms in which the concentrated acid samples were injected into the ICE column. In this experiment, for all weak acids a time window from 7.5 to 10.5 min was selected.

Figure 6 shows sample chromatogram obtained after IonPac ICE-AS6 column. Pure citric acid concentration was 10,000 mg/L, spiked with chloride, sulfate, and nitrate at the 10 mg/L level. "Cut window" time was between 7.5–10.5 min. The peaks marked 3 that come out after citric acid (peak 2) in Figure 6 were due to recirculation of the eluted inorganic anions from the anion-exchange column into the ion-exclusion column. Therefore, common inorganic anions were fed twice into the IonPac ICE-AS6 column, firstly from the sample loop and secondly from the eluent after ion-exchange column. Figure 6 also shows that the total analysis time of single-pump column-switching system can be less than 40 min.

Effects of the matrix concentration

In this part of the study, solutions containing different concentrations of weak acids (0, 1, 5, and 10%, w/v), each spiked with chloride, sulfate, and nitrate at 10 mg/L level, were subjected to be analyzed by the proposed procedure. It indicates that the first peak was not affected by the variable concentrations of weak acids in this study. However, the second one was gradually masked as the matrix peak gets broader under increasing concentrations of weak acids. Thus, no matter at what concentrations of weak acids, the switching-time was already between 7.5–10.5 min.
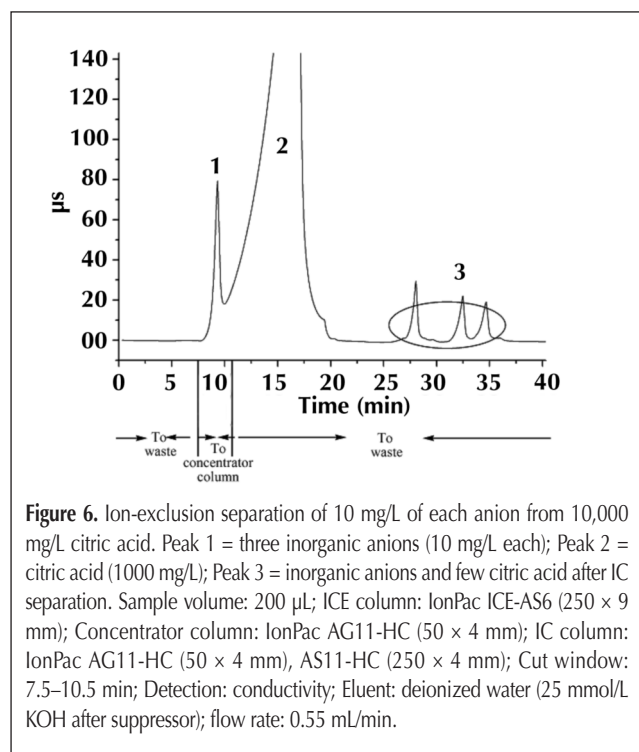
High back pressure in the position of the suppressor

In this single-pump column-switching system, there is an ICE column after the conductivity cell, leading to a high pressure (~550 psi) after the suppressor. The micro-membrane suppressor may result in the leakage of eluent, and only little flow rate suppressed eluent go to the ion-exclusion column. The anion self-regenerating suppressor (ASRS) from Dionex can not endure such high pressure because of the leakage of the suppressor. However, a pressure-durable, tailor-made suppressor from Xiamen University can solve this problem. Thus, it can be used under high back pressure. In our system, we chose the ASRS suppressor made by Xiamen University, which has similar characteristics (suppressed capacity, dead volumne, etc.) as the commerical micro-membrane suppressor, such as the Dionex suppressor, and resolved the problem of high back pressure in the position of the suppressor.

System blank

A blank was determined by performing all the steps of the analysis with deionized water as the sample. This result was then applied as a correction to all subsequent sample measurements. The blank value is consisted of the impurities from the sample pretreatment and the chromatographic system.

The eluent from the outlet of the conductivity cell was injected into another IC chromatographic system directly. The results showed that the aimed ions (chloride, nitrate, and sulfate) were all not detected. So there were no anions disturbances of the liquid from the outlet of the conductivity cell. It also proved that the eluent from the outlet of the conductivity cell can be used as the mobile phase of ion-exclusion column.

Analytical performance

Under the previously selected conditions, some parameters such as linear range, precision (relative standard deviation, RSD) ($n = 6$), limits of detection (LOD) (signal-to-noise ratio, S/N = 3),
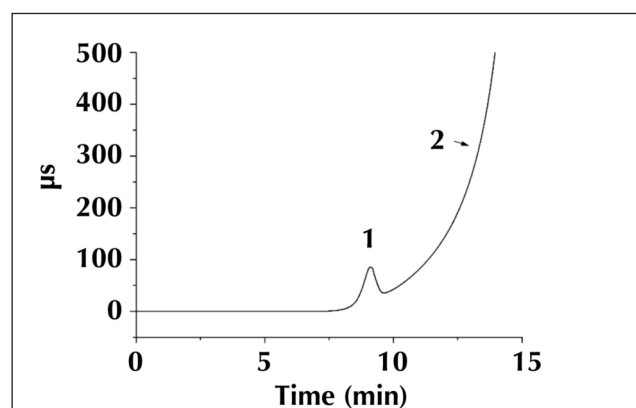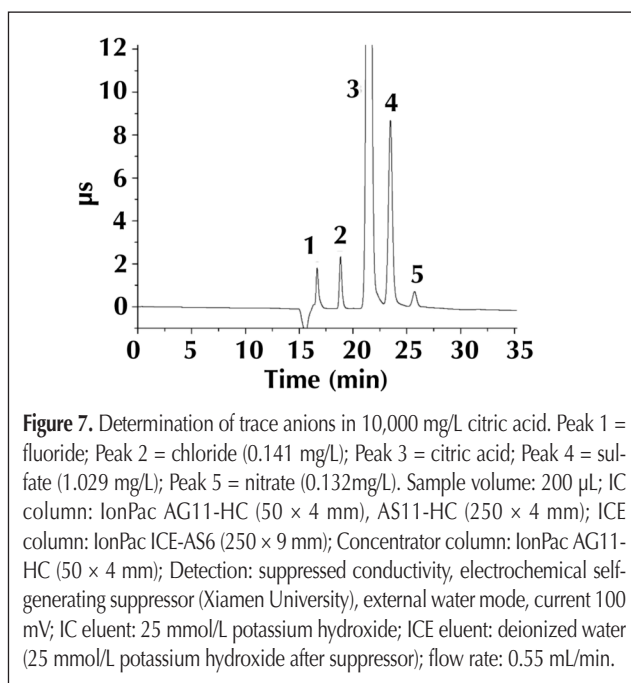

Figure 6. Ion-exclusion separation of 10 mg/L of each anion from 10,000 mg/L citric acid. Peak 1 = three inorganic anions (10 mg/L each); Peak 2 = citric acid (1000 mg/L); Peak 3 = inorganic anions and few citric acid after IC separation. Sample volume: 200 µL; ICE column: IonPac ICE-AS6 (250 × 9 mm); Concentrator column: IonPac AG11-HC (50 × 4 mm); IC column: IonPac AG11-HC (50 × 4 mm), AS11-HC (250 × 4 mm); Cut window: 7.5–10.5 min; Detection: conductivity; Eluent: deionized water (25 mmol/L KOH after suppressor); flow rate: 0.55 mL/min.

Figure 7. Determination of trace anions in 10,000 mg/L citric acid. Peak 1 = fluoride; Peak 2 = chloride (0.141 mg/L); Peak 3 = citric acid; Peak 4 = sulfate (1.029 mg/L); Peak 5 = nitrate (0.132mg/L). Sample volume: 200 µL; IC column: IonPac AG11-HC (50 × 4 mm), AS11-HC (250 × 4 mm); ICE column: IonPac ICE-AS6 (250 × 9 mm); Concentrator column: IonPac AG11-HC (50 × 4 mm); Detection: suppressed conductivity, electrochemical self-generating suppressor (Xiamen University), external water mode, current 100 mV; IC eluent: 25 mmol/L potassium hydroxide; ICE eluent: deionized water (25 mmol/L potassium hydroxide after suppressor); flow rate: 0.55 mL/min.

Table I. Analytical Performance of the Proposed Method

Analyte	Linear equation	Linear range (mg/L)	Correlation coefficient (R)	LOD (µg/L)	LOQ (mg/L)	RSD (%, $n = 6$)
Cl-	$y = 3.7165x + 0.5407$	0.02–20	0.9992	0.3	0.02	3.8
SO_4^{2-}	$y = 2.8382x + 0.5901$	0.02–20	0.9996	0.4	0.02	2.6
NO_3^-	$y = 2.0621x + 0.0386$	0.02–20	0.9998	1.7	0.02	1.3

Table II. Results of Determination in Real Samples*

Anions	Found† (mg/L)	Added (mg/L)	Total (mg/L)	Recovery (%)
Tartaric acid ($t = 21.72$)				
Cl- ($t = 18.74$)	0.076	0.1	0.1866	110.6
SO_4^{2-} ($t = 23.17$)	0.713	1.0	1.645	93.2
NO_3^- ($t = 25.08$)	0.163	0.25	0.390	90.8
Citric acid ($t = 21.36$)				
Cl-	0.141	0.25	0.3542	85.3
SO_4^{2-}	1.029	1.0	1.811	78.2
NO_3^-	0.132	0.25	0.4143	112.9
Formic acid ($t = 21.35$)				
Cl-	0.212	0.25	0.4193	82.9
SO_4^{2-}	0.127	0.25	0.3418	85.9
NO_3^-	0.079	0.1	0.1816	102.6
Acetic acid ($t = 21.52$)				
Cl-	0.175	0.25	0.3803	82.1
SO_4^{2-}	0.165	0.25	0.3670	80.8
NO_3^-	0.077	0.1	0.1657	88.7
Metacetonic acid ($t = 21.68$)				
Cl-	0.224	0.25	0.5068	113.1
SO_4^{2-}	0.256	0.25	0.4728	86.7
NO_3^-	0.098	0.1	0.2121	114.1
Butyric acid ($t = 21.74$)				
Cl-	0.728	1.0	1.513	78.5
SO_4^{2-}	0.057	0.1	0.1441	87.1
NO_3^-	0.055	0.1	0.1699	114.9
Butanedioic acid ($t = 21.79$)				
Cl-	0.281	0.25	0.575	117.6
SO_4^{2-}	0.056	0.1	0.1323	76.3
NO_3^-	0.062	0.1	0.1486	86.6
Hexafluorophosphoric acid ($t = 22.56$)				
Cl-	1.221	1.0	1.973	75.2
SO_4^{2-}	0.104	0.1	0.2108	106.8
NO_3^-	0.179	0.25	0.3763	78.9
Salicylic acid ($t = 21.83$)				
Cl-	0.161	0.25	0.3653	81.7
SO_4^{2-}	N.D.‡	–	–	–
NO_3^-	0.052	0.1	0.1603	108.3

* Mean ± standard deviation, $n = 6$, t = Retention time (min).
† Corrected for system blank.
‡ N.D. = not detectable.

and limits of quantification (LOQ) of the proposed method were investigated. Calibration curves were obtained by preparing a series of standard solutions with the concentration range of 0.02–20 mg/L. Each analyte exhibited good linearity with correlation coefficient $R ≥ 0.9992$ in the studied range. The reproducibility of the peak area was studied by six repetitive determinations of 1 mg/L standard, and the RSD were not more than 3.8%. The LOD, estimated based on S/N = 3, were in the range of 0.3–1.7 µg/L for the three anions, and the lower limit of the linear range (20 µg/L) was selected as the LOQ of the three anions (LOQ were not estimated based on S/N). Table I summarizes the analytical data. The data are valid when concentrations of the organic acid are from 0 to 25,000 mg/L.

Analysis of real samples

To evaluate the feasibility of the proposed method for determining inorganic anions in real weak acid samples, nine organic acid samples (concentration is 10,000 mg/L) were tested under the optimal experimental conditions. The results are shown in Table II. The results demonstrated that the recoveries of spiked samples were between 75.2–117.6%. The typical chromatograms are shown in Figure 7. As we can see in Figure 7 and Table II, the resolution was good between the small amount of organic acids, which switched in the concentrator column and the three anions. By single-pump column-switching system, interferences from substrates of organic acids were eliminated successfully.

Conclusions

This proposed method allows the accurate and precise determination of trace inorganic anions in weak acids with a relatively short analysis time and low costs without any sample pretreatment. Compared to the traditional column-switching method, single-pump column-switching applies only one pump, which reduced equipments and consumption of solvents and made the system simpler and more convenient for rapid and automated analysis. The recoveries obtained in the range of 75.2–117.6% were satisfactory. The results of this study indicate that single-pump column-switching would be applicable as a quality control test for high-purity applications.

Acknowledgments

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