Short communication

Simple procedure to eliminate concentrated sodium bicarbonate and carbonate with reusable strong cation-exchange cartridges for ion chromatographic analysis of formate and oxalate

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Abstract

A straightforward method with strong cation-exchange cartridges to eliminate bicarbonate and carbonate interference in IC analysis of trace formate and oxalate is described. The recoveries and detection limits for formate and oxalate were $101\pm4\%$ and 1.6 μM, $87\pm2\%$ and 0.8 μM, respectively, and independent of individual cartridges, pH and concentrations of interfering ions in the matrix. The cartridges were regenerated with 100 mM Na_2CO_3, 50 mM H_2SO_4 and water, and reused for at least 50 times. This method was applied to quantification of radiolysis products of γ-ray-irradiated bicarbonate and carbonate aqueous solutions with ion chromatography. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since bicarbonate and carbonate are the predominant anions in natural water with concentrations as high as 50 mM [1], the analysis of radiolysis products of bicarbonate and carbonate aqueous solutions is important for understanding radiation-induced reactions taking place in groundwater, relevant to nuclear waste repository. Only Draganic et. al. [2] have reported on the radiolysis products of aqueous solution of ammonium bicarbonate. In their study, formate and oxalate, the main products of radiolysis, were detected by unspecific and indirect methods. Such methods lack the sensitivies necessary to derive the clear mechanisms and kinetics of formate and oxalate formation.

The analysis of formate and oxalate, which are common in food products and biological fluids, has been extensively studied by ion chromatography [3,4]. However, high concentrations of sodium cations, bicarbonate and carbonate in the matrix lead to substantial interference, including carbonic acid, bicarbonate and system peaks which mask formate and oxalate ions, noise and baseline drift caused by CO_2 bubbles formed in low pH eluent, and the overload of the IC column. Chakraborty introduced an accurate fluorite calibration in the presence of strong interference from carbonate in IC [5], but this method is time-consuming and not suitable for direct conductivity detection. Both Robbins [6] and Carel and Thompsen [7] employed acidification with HCl

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or H_2SO_4, while Green and Woods [8] used a hydrogen-form cation-exchange preparatory column to convert bicarbonate and carbonate into CO_2. With a view to solve the problem of analysis in a matrix rich in interfering ions completely, the latter approach is more applicable than the acidification, but needs further adaptation to handle small volumes of samples and avoid diluting samples with eluent. Saari-Nordhaus and co-workers have reported on eliminating high concentrations of OH^-, H^+, Cl^-, SO_4^{2-} in sample matrix with solid-phase extraction cartridges or discs without the dilution of sample [9,10]; however, no similar attempt has been reported to eliminate bicarbonate and carbonate interference. Thus, this work aimed to develop a simple method to eliminate bicarbonate and carbonate interference in IC analysis of trace formate and oxalate, which includes a pretreatment using solid-phase extraction via strong cation-exchange (abbreviated as SCX hereafter) cartridges and processes to clean and regenerate the cartridges.

2. Experimental

2.1. Apparatus and experimental conditions

The analysis of formate and oxalate ions was performed on a Hitachi (Hitachi Ltd., Ibaraki, Japan) IC System which consisted of an L-7100 Pump, an L-7300 Column Oven, an L-7470 Conductivity Dectector, an L-7500 Integrator, a 100-μl sample loop and a Hitachi #2740 anion-exchange column (150×4.6 mm I.D.). The eluent was composed of 0.5 m*M* phthalic acid and 0.8 m*M* Tris(hydroxymethyl)aminomethane (abbreviated as Tris hereafter) (pH 6.1). The column temperature was 40°C, column pressure 35 kgf/cm^2, eluent flow-rate 1.5 ml/min.

Irradiation was performed in a 4.1-PBq ^{60}Co source. All solutions were made in deionized water obtained from a Milli-Q Jr. water-purification system (Nihon Millipore Ltd., Yonezawa, Japan). $NaHCO_3$ was 99.99% purity (Aldrich, Milwaukee, USA). All other chemicals were G.R. grade (Wako Pure Chemical Industries, Osaka, Japan).

2.2. Sample pretreatment

Samples were pretreated by Varian Bond Elut® SCX cartridges (Varian Associates, Harbor City, CA, USA) with column volume 1 ml, sorbent mass 100 mg and capacity 0.79 meq/g, then filtered through a 0.45-μm Millex-HV filter (Nihon Millipore Ltd., Yonezawa, Japan).

The procedure to eliminate $NaHCO_3$ and Na_2CO_3 by SCX cartridges includes three steps: (1) for a new cartridge, rinsing the cartridge consecutively with 5 ml of methanol, 5 ml of Milli-Q water, 5 ml of 100 m*M* Na_2CO_3, 2 ml of 50 m*M* H_2SO_4 and 5 ml of Milli-Q water or, for a used cartridge, regenerating the cartridge with 1 ml of 100 m*M* Na_2CO_3, 2 ml of 50 m*M* H_2SO_4 and 5 ml of Milli-Q water; (2) pushing 1 ml of sample through the cartridge, collecting the last 0.5 ml eluted fraction; and (3) ultrasonically degassing the collected fraction for 15 min. A cartridge was regenerated and reused at least 50 times.

3. Results and discussion

We analyzed the Milli-Q water eluted from conditioned cartridges to examine their cleanness. When SCX cartridges were conditioned with 5 ml of methanol and 5 ml of Milli-Q water consecutively, the eluted water was contaminated by Cl^-, SO_4^{2-} and two unknown cations from the cartridges. We further cleaned the cartridges with 100 m*M* Na_2CO_3, regenerated the absorbents into H^+ form with 50 m*M* H_2SO_4 and washed out SO_4^{2-} with Mill-Q water. As a result, all contaminants from SCX were eliminated, as shown in Fig. 1A.

Chromatograms of 23.4 μ*M* HCOONa and 26.9 μ*M* $(NH_4)_2C_2O_4$ in 50 m*M* Na_2CO_3 aqueous solutions before and after pretreatment are shown in Fig. 1B,C. Curve B illustrates the substantial interference caused by 50 m*M* Na_2CO_3. Curve C illustrates the effective removal of Na_2CO_3 by the SCX cartridges. Curve C also shows peaks for impurities from Na_2CO_3: two cations (impurities A and B), 0.6 μ*M* Cl^- and 1.5 μ*M* SO_4^{2-}, which are inside the ranges quoted by the manufacturer.
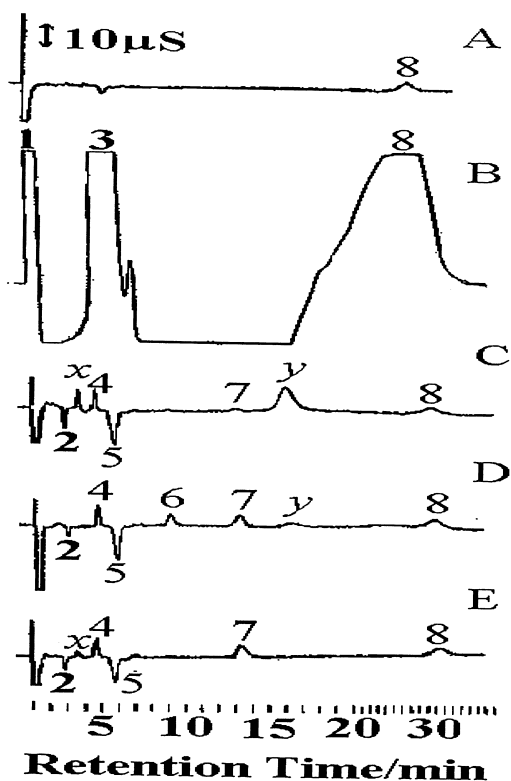
Fig. 1. Chromatograms of (A) Milli-Q water after pretreatment; (B,C) 23.4 μM HCOO$^-$ and 26.9 μM C$_2$O$_4^{2-}$ in 50 mM Na$_2$CO$_3$ before and after pretreatment; (D,E) γ-ray-irradiated N$_2$O-saturated 50 mM NaHCO$_3$ (absorbed dose, 1.1 kGy) and O$_2$-free 50 mM NaHCO$_3$ (absorbed dose, 102 Gy) after pretreatment. Peaks: (1) H$_2$CO$_3$; (2) unknown impurity A; (3) HCO$_3^-$; (4) Cl$^-$; (5) unknown impurity B; (6) NO$_3^-$; (7) SO$_4^{2-}$; (8) system peak; (x) HCOO$^-$; (y) C$_2$O$_4^{2-}$. Column, Hitachi #2740 (150$\pm$4.6 mm I.D.); eluent, 0.5 mM phthalic acid+0.8 mM Tris; flow-rate, 1.5 ml/min; column temperature, 40°C; conductivity detection; injection 100 μl.

We examined a series of formate and oxalate standard aqueous solutions (1–30 μM). The peak area counts of both formate and oxalate linearly responded to their concentrations, with slope $(1.90\pm0.01)\times10^2$ area counts μM^{-1}, linear correlation coefficient 0.987, intercept $(3\pm3)\times10^2$ area counts for formate, and $(1.92\pm0.05)\times10^3$ area counts μM^{-1}, linear correlation coefficient 0.997, intercept $(-1\pm1)\times10^3$ area counts for oxalate, respectively. Since the concentration and pH of bicarbonate and carbonate may be changed signifi-

cantly by irradiation, and a cartridge can only be used for about 50 times, we examined the influence of pH and the concentration of the bicarbonate and carbonate matrix, as well as individual cartridges on the percent recoveries of 20.0 μM formate and 20.7 μM oxalate. Every sample was pretreated and analyzed in triplicate. As shown in Table 1, both concentration and pH of the matrix as well as individual cartridges had little effect on the percent recoveries of formate and oxalate, the averages of which were 101$\pm$4% and 87$\pm$2%, respectively. On the basis of twice standard deviation of the average recoveries, the detection limits for formate and oxalate with this pretreatment procedure are 1.6 and 0.8 μM, respectively. The recovery of oxalate was lower than 90%, since some oxalate was retained by the absorbent, which was verified by the continuing increase of its percent recovery when the regeneration of cartridges did not include the step to wash out the retained oxalate with 1 ml of 100 mM Na$_2$CO$_3$.

Chromatograms of γ-ray-irradiated N$_2$O-saturated 50 mM NaHCO$_3$ (absorbed dose, 1.1 kGy) and O$_2$-free 50 mM NaHCO$_3$ (absorbed dose, 102 Gy) after pretreatment are shown in Fig. 1D, and E, respectively. In the former, oxalate was present at 5.5 μM, NO$_3^-$ (a radiolysis product of N$_2$O) at 8.4 μM, and SO$_4^{2-}$ (an impurity from NaHCO$_3$) at 4.0 μM, which is twice as much as the value quoted by the manufacturer. In the latter, formate was present at 5.0 μM, SO$_4^{2-}$ at 4.0 μM, and oxalate was absent. These results demonstrate the applicability of quantifying formate, oxalate and other inorganic ions such as NO$_3^-$ and SO$_4^{2-}$ in concentrated bicarbonate and carbonate aqueous solutions with ion chromatography after sample pretreatment with SCX cartridges.

This pretreatment procedure is an improvement over the previous reports [8–10]. First, samples are pushed through the cartridges directly rather than eluted with large volumes of water, which saves time and avoids diluting samples. Second, CO$_2$ is evacuated with an ultrasonic water bath instead of an evaporation process, which avoids losing volatilizable components. Third, solid-phase extraction cartridges are usually supposed to be for single use, but we successfully regenerated SCX cartridges with Na$_2$CO$_3$, H$_2$SO$_4$ and water for multiple use, thus greatly reducing expense.

Table 1
The percent recoveries of formate and oxalate after pretreatment with SCX

Condition	Recovery of formate (%)	Recovery of oxalate(%)
pH 9.1		
$[NaHCO_3+Na_2CO_3]=0$ m*M*	105±4	88±5
$[NaHCO_3+Na_2CO_3]=25$ m*M*	105±3	87±2
$[NaHCO_3+Na_2CO_3]=50$ m*M*	97±5	89±2
[NaHCO_3+Na_2CO_3]=50 mM		
pH 8.3	95±5	85±2
pH 9.1	97±5	89±2
pH 11.3	102±6	86±2
50 mM Na_2CO_3, pH 11.3		
SCX 1	102±6	86±2
SCX 2	100±3	85±1
SCX 3	99±4	84±5
Average	101±4	87±2

Acknowledgements

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