

Highly sensitive determination of hydrazine ion by ion-exclusion chromatography with ion-exchange enhancement of conductivity detection

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Abstract

An ion-exclusion chromatography method with ion-exchange enhancement of conductivity was developed for the selective separation and sensitive determination of hydrazine ion from alkali/alkaline earth metal cations and ammonium ion. Hydrazine ion was separated by ion-exclusion/penetration effect from other cations on a weakly basic anion-exchange column in the OH⁻ form (TSKgel DEAE-5PW). Moreover, two different ion-exchange resin columns were inserted between the separating column and conductimetric detector in order to improve the sensitivity of hydrazine ion. The first enhancement column packed with a strongly basic anion-exchange resin in the SO₄²⁻ form (TSKgel SAX) for hydrazine ion can convert from N₂H₅OH to (N₂H₅)₂SO₄. Moreover, the second enhancement column packed with a strongly acidic cation-change resin in the H⁺ form (TSKgel SCX) can convert to H₂SO₄. As a result, the sensitivity of hydrazine ion using two conductivity enhancement columns could be 26.8-times greater than using the separating column alone. This method was effectiveness also for the enhancement of ammonium ion (6.1-times) and sodium ion (1.2-times). The calibration graph of hydrazine ion detected as H₂SO₄ was linear over the concentration range of 0.001–100 ppm ($r^2 = 0.9988$). The detection limit of hydrazine ion in this system was 0.64 ppb. Therefore, hydrazine ion in real boiler water sample could be accurately determined, avoiding the interference of other cations.

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1. Introduction

Hydrazine ion is a strong reducing agent in order to remove solved oxygen scavenger in boiler waters and hot-water systems [1]. Hydrazine ion as well as its derivatives has been also employed application in industry, agriculture, explosives and other field. However, hydrazine has been reported to be a toxic material which has to be treated with precaution [2]. Therefore, the monitoring system of hydrazine with high sensitive detection has been developed to determine trace levels of hydrazine in environmental

samples such as the boiler, river and industrial waters [3]. Many methods for the determination of hydrazine have been proposed including colorimetric [4], spectrophotometric [5,6], potentiometric [7], chemiluminescence [8], and titrimetric [9]. These could achieve the highly sensitive detection for hydrazine and its derivatives in the environments. However, some of these methods are sensitive to the interference of coexisted substances and/or require many procedures for pretreatment of samples.

Ion-exclusion chromatography has developed into a very useful technique for separating small weak acids or weak bases [10]. It is possible to determine a target sample without the interference of other samples. Ion-exclusion chromatographic separation of weak bases has been a packed column with a basic cation-exchange resin in the OH⁻

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form as a separating column, in order to convert from salts to bases, [11–15]. Especially, the method is effectiveness for separating of very weak bases, such as ammonium ion ($pK_b = 4.75$) or hydrazine ion ($pK_b = 5.77$), due to its large penetration effect to the resin-phase based on the effect of Donnan equilibrium membrane. Commonly, the detection of analytes separated has been carried out by the conductivity detector. However, the conductivity responses are low due to its low limiting equivalent ionic conductance [16].

Previously, Tanaka et al. reported the high sensitive determination of ammonium ion in biological nitrification–denitrification process water by ion-exclusion chromatography with ion-exchange enhancement of conductivity detection [17]. Ammonium ion was selectively separated by ion-exclusion effect from other cations on a strongly basic anion-exchange resin in the OH^- form with water eluent. The sensitivity was dramatically improved by two ion-exchange enhancement columns sited between the separating column and detector. However, measurement at ppb level of sample was difficult due to the high detection limit (530 ppb).

The purpose in this study is to achieve a sensitive detection of ppb level of hydrazine ion by the ion-exclusion chromatography with the conductivity enhancement columns, including the separation from ammonium ion and alkali metal/alkaline earth metal cations.

The separating column used in this study was a polymethacrylate-based weakly basic anion-exchange resin column (Tosoh TSKgel DEAE-5PW). A weakly anion-exchanger (tertiary amine functional groups) in the column is partially protonation and dissociation by OH^- in water eluent, and thus weak bases are easily penetrated into the resin-phase in the column rather than that in a strongly basic anion-exchange column [15]. The resolution of weak bases can be expected to be consequently improved.

The enhancement columns of conductivity detection used two sorts of ion-exchange columns. The first enhancement column was a strongly basic anion-exchange resin TSKgel SAX column formed by an anion that has a high limiting equivalent ionic conductance (e.g., Cl^-). The effect converts from a weak electrolyte (e.g., NH_4OH) to a strong electrolyte (e.g., NH_4Cl) by an anion-exchange reaction [17]. The second enhancement column was a strongly acidic cation-exchange resin TSKgel SCX column formed by H^+ that has the highest limiting equivalent ionic conductance of cations. This can greatly emphasize the conductivity response, because analytes convert to strong acids (e.g., HCl) by a cation-exchange reaction passing through the column.

In this paper, we report the feature of this system in terms: (1) the ion-exclusion chromatography of hydrazine from other cations on a weakly basic anion-exchange resin column with water eluent, (2) the effect of two ion-exchange enhancement columns of conductivity detection, (3) the linearity of analytes in the optimum condition, and (4) the application to the boiler water samples.

2. Experimental

2.1. Apparatus

The ion chromatograph (Tokyo, Japan) consisted of Tosoh LC-8020-Model II chromatographic data processor, DP-8020 dual pump operated at flow rate of 1 ml/min, SD-8022 on-line degasser, CO-8020 column oven operated at 40°C and CM 8020 conductimetric detector. The injection volume was 100 μl .

2.2. Reagents

All reagents were of analytical reagent-grade, purchased from Wako (Osaka, Japan) and were dissolved in distilled and deionized water for the preparation of standard solutions and eluents. The stock solutions of basic compounds used in this study were prepared by dissolving 0.1 M with distilled and deionized water. Appropriate amounts of analyte bases at the concentration of 0.1 M each were diluted with water as necessary.

2.3. Boiler water

Boiler water samples were collected from boiler system at the factory area of Tosoh (Shunan, Japan). Each analyte sample was analyzed after filtration through a 0.20 μm membrane filter.

2.4. Procedure of the enhancement system with conductivity detection

A separating column used in this study was a polymethacrylate-based weakly basic anion-exchange resin in the OH^- form, Tosoh TSKgel DEAE-5PW (150 mm \times 7.5 mm i.d.). This was because the separation of ammonium and hydrazine ions using a strongly basic anion-exchange resin column was insufficient in the water eluent. As shown in Fig. 1, two sorts of ion-exchange enhancement columns were employed and inserted between a separating and a conductivity detector. The first enhancement column was a polystyrene–divinylbenzene-based strongly basic anion-exchange resin in the SO_4^{2-} form, TSKgel SAX (50 mm \times 4.6 mm i.d.) and second a polystyrene–divinylbenzene-based strongly acidic cation-exchange resin in the H^+ form, TSKgel SCX (50 mm \times 4.6 mm i.d.). All columns were specially packed by Tosoh and were equilibrated with eluting water for 30 min before chromatographic runs.

3. Results and discussion

3.1. Ion-exclusion chromatographic separation of hydrazine ion

A 0.1 ml sample containing 1 ppm NaCl , 1 ppm NH_4Cl , and 1 ppm $\text{N}_2\text{H}_5\text{Cl}$ was injected to test the separation

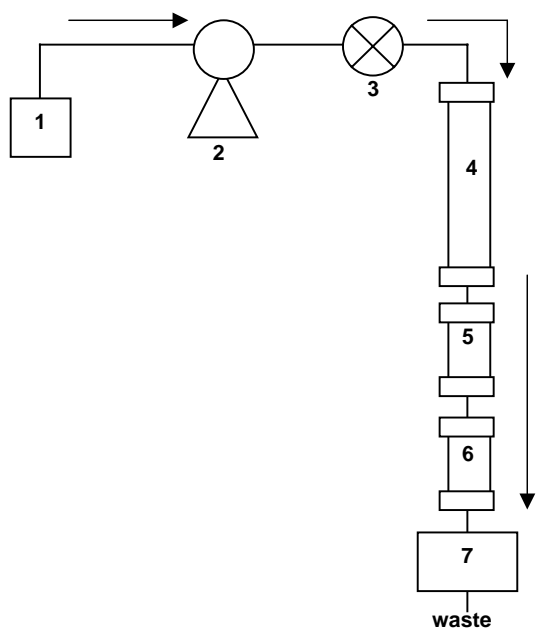


Fig. 1. Schematic illustration of the proposed system. Identities: 1, eluent; 2, pump; 3, injector; 4, separating column; 5, first enhancement column; 6, second enhancement column; 7, conductivity detector.

ability of the system used. In the elution with water, the weakly basic anion-exchange column in the OH^- form converts NaCl , NH_4Cl and $\text{N}_2\text{H}_5\text{Cl}$ to NaOH , NH_4OH and $\text{N}_2\text{H}_5\text{OH}$, respectively. Good resolution of the sample bases was obtained depending on the degree of ion-exclusion/penetration effect for each other to the resin-phase of the separating column as shown in Fig. 2A

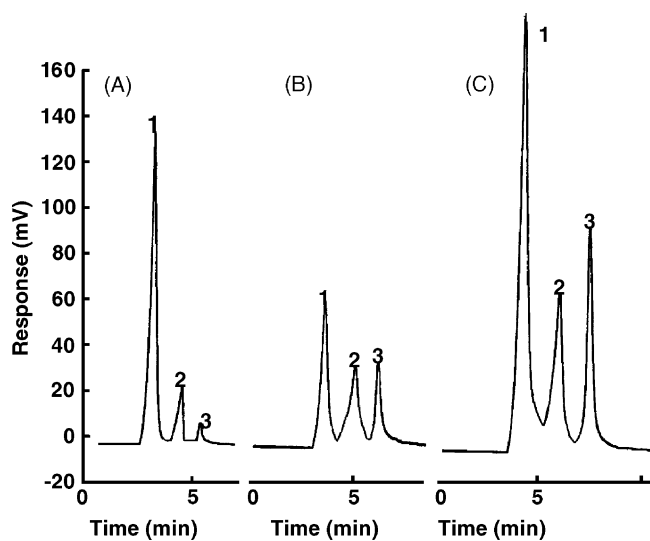
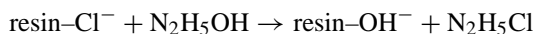


Fig. 2. Comparison of ion-exclusion chromatograms of some cations with and without first and second enhancement columns. The construction of column: (A) separating column (OH^- form) alone; (B) (A) + first enhancement column (SO_4^{2-} form); (C) (B) + second enhancement column (H^+ form). Sample concentrations: 1 ppm for each. Peaks: 1, sodium ion; 2, ammonium ion; and 3, hydrazine ion. Eluent was distilled and deionized water at 1 ml/min of the flow-rate. Injection volume was 0.1 ml.

[16]. However, the conductances of weak base such as NH_4OH ($\text{p}K_{\text{b}1} = 4.75$) and $\text{N}_2\text{H}_5\text{OH}$ ($\text{p}K_{\text{b}1} = 5.77$) were consequently low.

3.2. Use of anion-exchange enhancement column

A strongly basic anion-exchange column was sited between the separating column and the detector in order to obtain a more sensitive detection of NH_4OH and $\text{N}_2\text{H}_5\text{OH}$. This column is called the first enhancement column. The purpose is to convert from the NH_4OH and $\text{N}_2\text{H}_5\text{OH}$ to a more highly ionized form and thus to increase the conductivity. For example, when the anion-exchange column is in the Cl^- form, the exchange reaction for $\text{N}_2\text{H}_5\text{OH}$ is as follows:



Several anionic forms were tested and compared for the anion-exchange column TSKgel SAX, in order to evaluate the performance of the first enhancement column. The anion-exchange resin in the SO_4^{2-} form was higher than those in the other anionic forms because the ionic equivalent conductance of SO_4^{2-} (80) is higher than those of Cl^- (76), Br^- (78), I^- (77), and NO_3^- (71) [16]. Although $\text{Fe}(\text{CN})_6^{4-}$ (111) has higher ionic equivalent conductance than that of SO_4^{2-} , the detector response of ammonium and hydrazine ions obtained on the anion-exchange resin in the $\text{Fe}(\text{CN})_6^{4-}$ form were lower than that in the SO_4^{2-} form. This might be mainly due to the unstable nature of $(\text{NH}_4)_4\text{Fe}(\text{CN})_6$ and $(\text{N}_2\text{H}_5)_4\text{Fe}(\text{CN})_6$ formed in the anion-exchange reaction on TSKgel SAX.

From these results, an anion-exchange resin in the SO_4^{2-} form was judged to be the most useful as a first enhancement column. The peak areas of a 1 ppm standard sample detected with the use of this column gave the increase of conductivity response 1.70-times for ammonium ion and 4.16-times for hydrazine ion larger than that detected without enhancement column as shown in Fig. 2B.

On the other hand, the peak areas of sodium ion gave lower conductivity response than that detected on separating column alone due to the conversion to Na_2SO_4 which is a weak electrolyte.

3.3. Effect of cation-exchange enhancement column in the H^+ form

As described in Section 3.2, the $(\text{NH}_4)_2\text{SO}_4$ and $(\text{N}_2\text{H}_5)_2\text{SO}_4$ eluted from the first enhancement column have larger detector responses than the NH_4OH and $\text{N}_2\text{H}_5\text{OH}$ eluted from the separating column alone. However, the ionic equivalent conductance of H_2SO_4 (430) is much higher than that $(\text{NH}_4)_2\text{SO}_4$ (153) and $(\text{N}_2\text{H}_5)_2\text{SO}_4$ (139). Therefore, a more sensitive detection of weak bases should result from using a cation-exchange in the H^+ form as second enhancement column. The cation-exchange reaction in the column converts both $(\text{NH}_4)_2\text{SO}_4$ and $(\text{N}_2\text{H}_5)_2\text{SO}_4$ to H_2SO_4 that is the much higher conductivity response.

The chromatogram in Fig. 2C shows the effect of second enhancement column. The use of two enhancement columns could obtain 6.10-times for ammonium ion and 26.8-times for hydrazine ion enhancement in the detector response. The conductivity response of sodium ion with two enhancement columns could be detected the peak area of the 1.21-times enhancement greater than that without them.

3.4. Calibration curves

Fig. 3 shows the calibration curves of ammonium ion and hydrazine ions with conductimetric detection eluted by ion-exclusion chromatographic separation with and without two ion-exchange enhancement columns.

The calibration graphs for analyte cations with the separating column alone were nonlinear over the range of 0.05–10 ppm for ammonium ion and 0.05–5 ppm for hydrazine ion because the NH_4OH and $\text{N}_2\text{H}_5\text{OH}$ are very weak bases. It has been well known that a conductivity detector has a nonlinear detector response to weak bases obtained in ion-exclusion chromatography. The calibration graphs of analytes monitored in the first enhancement column were linear in the range of 0.01–25 ppm for ammonium ion and 0.01–50 ppm for hydrazine ion. The calibration graphs for analytes obtained in the second enhancement column were linear in the range of 0.001–100 ppm for ammonium ion and hydrazine ion (ammonium ion: $r^2 = 0.9995$ in 0.001–0.1 ppm and 0.9997 in 0.001–100 ppm; hydrazine ion: $r^2 = 0.9996$ in 0.001–0.1 ppm and 0.9991 in 0.001–100 ppm). These results could be demonstrated the advantage using two enhancement columns.

3.5. Detection limits and reproducibility

Detection limits of 1 ppm ammonium ion and 1 ppm hydrazine ion calculated at signal to noise of 3 in the three column system were ranged from 0.55 ppb, and that of hydrazine ion was 0.64 ppb.

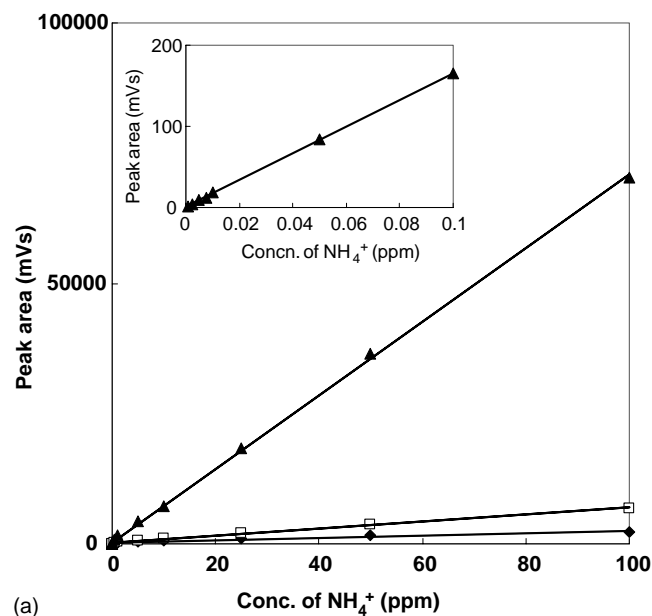
The reproducibility in the repeated chromatographic runs ($n = 10$) and day-to-day (3 days; 10 runs per day) were investigated by injecting 1 ppm of sample concentrations. The relative standard deviations (R.S.D.) obtained were pretty good as summarized in Table 1. Additionally, R.S.D. of the

Table 1

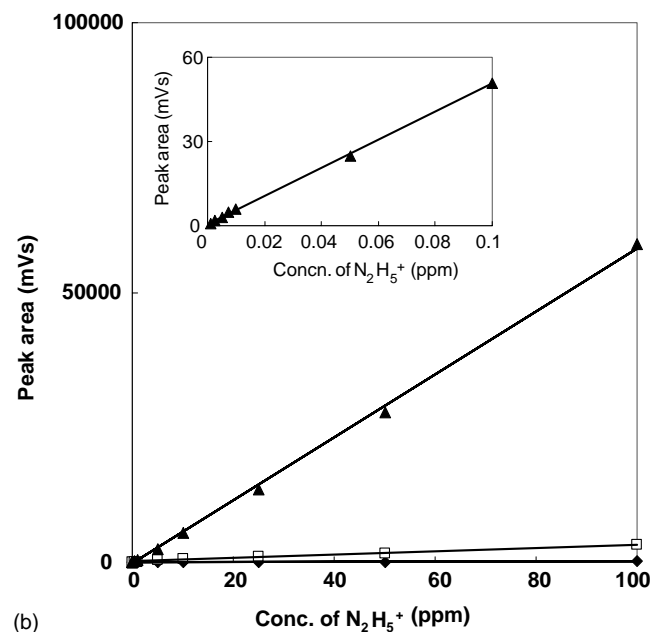
Relative standard deviation (R.S.D.) of the retention time and peak area in the repeated chromatographic runs of some cations in the ion-exclusion chromatography with two enhancement columns^a

Sample cations	One day ($n = 10$)		Day-to-day (3 days; 10 runs per day)	
	Retention time (%)	Peak area (%)	Retention time (%)	Peak area (%)
Sodium ion	0.18	2.43	0.63	2.53
Ammonium ion	0.20	2.69	0.76	2.66
Hydrazine ion	0.20	1.87	0.68	1.75

^a Conditions were the same as in Fig. 2.



(a)



(b)

Fig. 3. Comparison of calibration curves of ammonium and hydrazine ions with and without first and second enhancement columns. Concentration ranges in calibration graphs: large = 0.001–100 ppm; small = 0.001–0.1 ppm. Analyte samples: (A) ammonium ion, and (B) hydrazine ion. The construction of column: (◆) separating column alone; (□) separating column + first enhancement column; (▲) separating column + first enhancement column + second enhancement column. Other chromatographic conditions as in Fig. 2.

peak areas in the concentration range 5 and 50 ppb of hydrazine ion, which are about 10- and 100-times above the detection limit, were 2.3% in 5 ppb and 1.8% in 50 ppb in the repeated chromatographic runs ($n = 10$). Therefore, this three column system was applicable to determination of the low level concentration of hydrazine ion included in boiler water sample.

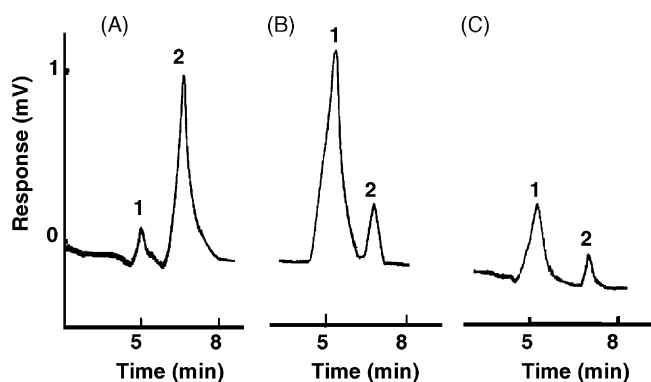


Fig. 4. Ion-exclusion chromatograms of ammonium and hydrazine ions in boiler water. Boiler water samples (see Table 2): (A) sample 1, (B) sample 2, and (C) sample 3. Peaks: 1, ammonium ion; 2, hydrazine ion. Other conditions as in Fig. 2.

Table 2
Determination of hydrazine ion in several boiler waters on the proposed system^a

Boiler sample	Concentration (ppb) ^b	Concentration (ppb)	Added (ppb)	Found (ppb)	Recovery (%)
1	54.7	53.8	50	47.5	95.0
2	23.5	21.4	50	48.8	97.5
3	18.0	19.1	50	48.4	96.8

^a Conditions were the same as in Fig. 2.

^b Colorimetric method.

3.6. Application to boiler water samples

The ion-exclusion method was applied to the determination of hydrazine ion in several boiler waters. Fig. 4 shows the ion-exclusion chromatograms of boiler waters collected at three different positions in Tosoh. The sensitive conductivity detection of ppb level of hydrazine ion from all boiler water samples could be achieved, separating from ammonium ion added in order to control pH of boiler water. The concentrations of hydrazine calculated in this method almost agreed with those in colorimetric method carried out by Tosoh as summarized in Table 2. No matrix limitation problems (e.g., pH value and salt content) for this method were obtained because there were no difference of analytical results between calibration and spiked methods.

4. Conclusions

This proposed method was the selective separation of ammonium and hydrazine ions from alkali/alkaline earth metal cations by the ion-exclusion chromatography on a weakly basic anion-exchange resin and the sensitive conductimetric determination by the enhancement columns. The good linearity of calibration curves over the concentration range of 0.001–100 ppm of the bases detected as H₂SO₄ was obtained by using the system. The results indicated that the present method was possible to accurately determine a lower concentration of hydrazine ion in the boiler water.

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