



Use of potassium-form cation-exchange resin as a conductimetric enhancer in ion-exclusion chromatography of aliphatic carboxylic acids

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ABSTRACT

In this study, a cation-exchange resin (CEX) of the K⁺-form, i.e., an enhancer resin, is used as a postcolumn conductimetric enhancer in the ion-exclusion chromatography of aliphatic carboxylic acids. The enhancer resin is filled in the switching valve of an ion chromatograph; this valve is usually used as a suppressor valve in ion-exchange chromatography. An aliphatic carboxylic acid (e.g., CH₃COOH) separated by a weakly acidic CEX column of the H⁺-form converts into that of the K⁺-form (e.g., CH₃COOK) by passing through the enhancer resin. In contrast, the background conductivity decreases because a strong acid (e.g., HNO₃) with a higher conductimetric response in an eluent converts into a salt (e.g., KNO₃) with a lower conductimetric response. Since the pH of the eluent containing the resin enhancer increases from 3.27 to 5.85, the enhancer accelerates the dissociations of analyte acids. Consequently, peak heights and peak areas of aliphatic carboxylic acids (e.g., acetic acid, propionic acid, butyric acid, and valeric acid) with the enhancer resin are 6.3–8.0 times higher and 7.2–9.2 times larger, respectively, than those without the enhancer resin. Calibrations of peak areas for injected analytes are linear in the concentration range of 0.01–1.0 mM. The detection limits (signal-to-noise ratio = 3) range from 0.10 μM to 0.39 μM in this system, as opposed to those in the range of 0.24–7.1 μM in the separation column alone. The developed system is successfully applied to the determination of aliphatic carboxylic acids in a chicken droppings sample.

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1. Introduction

Ion-exclusion chromatography (IEC) has been a useful analytical method mainly for the separation and determination of weak acids, e.g., carboxylic acids, bicarbonates, and silicates, and weak bases, e.g., ammonium ion, and amines [1–7]. Acids analyzed by IEC (i.e., analytes) can be classified into fully ionized species and partially ionized species, depending on ion-exclusion/penetration effect on pseudo Donnan's membrane effect between stationary phase and mobile phase, and hydrophobic adsorption to the resin phase [1].

Conductivity detection has been commonly used for IEC, because it is possible to simultaneously detect many kinds of ionized species by this detection technique. However, responses of partially ionized species are low due to their low dissociation in an acidic eluent [8]. Therefore, many researchers have attempted and reported [9–15]. In particular, postcolumn ion-exchange reactions are useful (1) for achieving linear calibrations in wide concentration ranges and (2) for carrying out sensitive detection by converting partially ionized species into fully ionized species. Tanaka and Fritz [9] have reported that the response of a bicarbonate by a combina-

tion of two different ion-exchange resin columns connected after a separation column is approximately ten times that by a single separation column; this result is attributed to the fact that the columns caused the conversion of the bicarbonate from a weak acid to a strong base. Further, Hayashi carried out sensitive conductimetric detection by accelerating the ionization of weak acids by using a (bis-[2-hydroxyethyl]-iminotris-[hydroxy methyl]-methane: Bis-Tris) buffer with a pH of 6.5 connected after a separation column [11]. Guillén et al. [12] have applied this method to the determination of organic acids in brandy samples.

The purpose of this study is to develop a postcolumn conductimetric enhancement system by using a cation-exchange resin (CEX) in the alkali metal form, packed in a switching valve of the ion chromatograph Tosoh IC-2001 [16]. This CEX functions as a conductimetric enhancer for a weak acid used as a sample in IEC, because the CEX converts from a species with low conductivity (e.g., CH₃COOH) into that with high conductivity (e.g., CH₃COOK). Conversely, the resin functions as a conductimetric suppressor for strong acids used as eluents, because it converts from a species with high conductivity (e.g., HNO₃) into that with low conductivity (e.g., KNO₃). Consequently, the conductimetric responses of weak acid analytes improve with the use of the CEX.

This paper reports that a CEX of the K⁺-form is an effective conductimetric enhancer for the IEC of monocarboxylic acids in terms

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of sensitive detection, calibration linearity, and its applicability to the determination of aliphatic carboxylic acids in a chicken droppings sample.

2. Experimental conditions

2.1. Reagents

Standard solutions of aliphatic carboxylic acids were purchased from Wako Pure Chemicals (Osaka, Japan), and they were dissolved in deionized water obtained from a Milli-Q reagent grade water system (Millipore).

2.2. Separation column and enhancer resin

The separation column was a weakly acidic CEX (Tosoh TSKgel Super IC-A/C, 150 mm × 6 mm ID) of the H⁺-form.

The enhancer resin was Tosoh TSKsuppress IC-A (200 μm particles). The resin was converted from the H⁺-form into the alkali metal form by an SR-2W Recipro shaker (TAITEC, Koshigaya, Japan) in a 0.5 M salt solution (e.g., LiCl, Na₂SO₄, and K₂SO₄) for 1 h. The enhancer resin was filled into a bottle connected just before the switching valve.

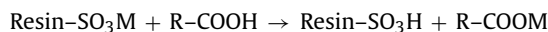
2.3. Enhancement process

All IEC measurements were carried out using the Tosoh IC-2001 ion chromatograph, which consists of an eluent pump, auto-sample injector, conductimetric detector, column oven, and suppression system. In this study, the suppression system was used as the enhancer system for the conductivity detection of aliphatic carboxylic acids in IEC. Therefore, we refer to the valve as the “enhancer valve.”

A summarized description of the enhancement procedure is schematically shown in Fig. 1. The enhancer valve consists of a six-port electronic rotary valve equipped with three grooves for packing the resin. Since the enhancer valve is switched before each injection, a new resin is always used for enhancement in analyzing each sample. While the first groove (a) is used for measuring the sample, the resin used is discharged to the drain from the second groove (b). Simultaneously, a new resin is filled into the third groove (c) in order to measure the next sample [16].

The filling and discharging of the resin and the washing of the groove are carried out by means of water pressure achieved using a syringe pump. The resin that is used in the groove is a strongly acidic cation exchanger of the alkali metal (M)-form; therefore, the

chemical reaction occurring in the enhancer valve is as follows:



Since the resin used for enhancement in the groove is disposable, no regeneration of the enhancer resin is required, and by-products and high molecular weight of matrix in a real sample do not damage the enhancer valve. The small volume of the grooves (200 μL) in the enhancer valve helps to eliminate band broadening; at the same time, the volume of the grooves is sufficient for measuring one sample.

2.4. Analytical conditions

Acids added to the eluent were 0.5 mM nitric acid (HNO₃, pH 3.24), 0.5 mM perchloric acid (HClO₄, pH 3.27), 0.25 mM sulfuric acid (H₂SO₄, pH 3.27), and 0.55 mM phosphoric acid (H₃PO₄, pH 3.27). The flow rate of the eluent was 0.6 mL min⁻¹. The temperature of the column oven was 40 °C. Further, the injection volume was 30 μL.

2.5. Preparation of sample

A chicken droppings sample was obtained from a chicken farm in Gunma Prefecture, Japan. After the decomposition of 0.1 g of the sample in 50 mL of distilled-deionized water using a microwave, the sample was filtered using a syringe filter (0.45 μm). At the time of determining the aliphatic carboxylic acids in the sample, a strongly acidic CEX column of the H⁺-form, TSKgel OApak-P (60 mm × 6 mm ID), was connected before the separation column in order to unify counter-cations to H⁺ in the sample.

3. Results and discussion

3.1. Selection of enhancer resin

Three different strongly acidic CEXs of the alkali metal form were compared in terms of their conductimetric enhancement effects on the aliphatic carboxylic acids after ion-exclusion chromatographic separation. CEXs of the Li⁺-form, Na⁺-form, and K⁺-form were tested as enhancer resins. Fig. 2 shows typical ion-exclusion chromatograms of five aliphatic carboxylic acids; the K⁺-form CEX was used as the enhancer resin and the eluent was 0.55 mM phosphoric acid. From the chromatograms, it could be observed that the signals of analyte acids with the enhancer were considerably stronger than those without it.

Table 1 summarizes enhancement ratios of analytical signals obtained with and without the enhancer in the 0.55 mM phosphoric acid eluent. The enhancement ratios of five aliphatic carboxylic acids with the K⁺-form CEX were the highest in this study, though the background conductivity obtained with the K⁺-form CEX (61.0 μS cm⁻¹) was higher than those obtained with the Li⁺-form (40.6 μS cm⁻¹) and Na⁺-form (48.7 μS cm⁻¹) CEXs. Analytical signals of all acids, except for formic acid, with K⁺-form CEX were 6.3–8.0 times higher and 7.2–9.2 times larger, respectively, than those in the case of acids without K⁺-form CEX. This would be attributed to the fact that the limiting equivalent conductivity of K⁺ is higher than those of Li⁺ and Na⁺ [17]. From these results, it was concluded that the K⁺-form CEX was the most suitable enhancer resin among all resins considered in this study.

3.2. Selection of acid added to eluent

The role of acid in the eluent used for carrying out the IEC of aliphatic carboxylic acids with the K⁺-form enhancer resin was investigated. As mentioned earlier, the acids added to the eluent

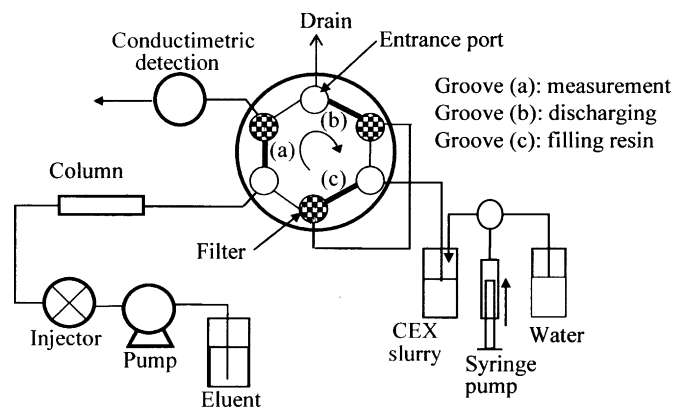


Fig. 1. Configuration of enhancer valve in Tosoh IC-2001. The details are described in the text.

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