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Short communication

New approach to determining each component of a two-component overlapping peak by single-column anion ion chromatography

Hong Yu

Department of Chemistry, Harbin Normal University, Harbin, 150080, Heilongjiang Province, China

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Abstract

A new approach to determining each component of a two-component overlapping peak in single-column anion ion chromatography analysis is described. In single-column anion ion chromatography analysis, if the sample is the same as the eluent, the sample peak will not appear. If the sample is not the same as the eluent and the limiting equivalent conductance of the sample is different from that of the eluent, the sample peak will appear. Therefore, one component of a two-component overlapping peak can be determined with the other component as eluent. The method was tested by the overlapping peak of molybdate and tungstate and of tartaric and citric acids. A minor rearrangement of the detection equation for ion chromatography is also described in this paper.

Keywords: Detection, LC; Peak overlap; Molybdate; Tungstate; Tartaric acid; Citric acid

1. Introduction

Ion chromatography is a powerful analytical tool for the analysis of ionic and polar substances. It can be subdivided into two types: single-column ion chromatography [1] and dual-column ion chromatography [2]. The first type can use many kinds of eluents. This enables determination of substances which are difficult to separate. Two-component overlapping peaks sometimes appear in single-column anion ion chromatographic analysis. Simultaneous determination of the components by single-column ion chromatography requires a high-efficiency column and a suitable eluent, but success is not always achieved. An approach to determining each component of a two-component overlapping peak is proposed in this paper. The method is tested by the overlapping peak of molybdate and tungstate and of tartaric and citric acids.

2. Theory

Gjerde et al. [3] have developed an equation for the conductivity change accompanying elution of an anion in ion exchange chromatography and this equation can be applied in the rearranged manner shown below.

In single-column anion ion chromatography, the conductance of the eluent is given by the following equation:

$$G_B = \frac{(\lambda_{E^+} + \lambda_{E^-})C_E I_E}{10^{-3} K} \quad (1)$$

The conductance of the eluent and sample during a peak elution will be:

$$G_S = \frac{(\lambda_{E^+} + \lambda_{E^-})(C_E - C_S)I_E}{10^{-3} K} + \frac{(\lambda_{E^+} + \lambda_{S^-})C_S I_S}{10^{-3} K} \quad (2)$$

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Subtraction of these two equations gives the change in conductance when a sample peak is eluted:

$$\Delta G = G_S - G_B = \frac{(\lambda_{E^-} + \lambda_{S^-})I_S - (\lambda_{E^+} + \lambda_{E^-})I_E}{10^{-3}K} C_S \quad (3)$$

where ΔG is the detector response, K the cell constant, λ the limiting equivalent conductance of cation or anion, C the normality, I the degree of electrolytic dissociation, and E^+, E^-, E, S^- and S represent the eluent cation, eluent anion, eluent, sample anion and sample, respectively.

According to Eq. (3), if the sample is the same as the eluent, $\Delta G = 0$ and the sample peak will not appear. If the sample is not the same as the eluent and limiting equivalent conductance of the sample is different from that of the eluent, then $\Delta G \neq 0$ and the sample peak will appear. Therefore, one component of a two-component overlapping peak can be determined with the other component as eluent.

3. Experimental

3.1. Reagents

Analytical grade sodium molybdate, sodium tungstate, *p*-hydroxybenzoic acid, tartaric acid, citric acid, potassium biphthalate, sodium chloride, potassium nitrate and sodium sulphate were obtained from a variety of suppliers. Doubly deionized water was used for the preparation of aqueous solutions.

3.2. Equipment

A Shimadzu Model HIC-6A ion chromatograph was used, comprising a Model LP-6A pump, a conductivity detector Model CDD-6A, an autosample injector Model SIL-6B, a C-R5A integrating recorder, a system controller Model SCL-6B and 100 mm×4.6 mm I.D. Shim-pack IC-A1 anion-exchange column. In all experimentations, 50-μl samples were injected. The flow-rate was maintained at 1.0 ml min^{-1}. The recorder full-scale was set to 2 μs cm^{-1}.

4. Results and discussion

4.1. Overlapping peak of molybdate and tungstate

Because of their similarity the separation of molybdate and tungstate is difficult. When 1.0 m*M* *p*-hydroxybenzoic acid (pH 7.0–8.5) was employed as eluent for separation of molybdate and tungstate, an overlapping peak was obtained and their simultaneous determination was not achieved. When molybdate was determined with sodium tungstate as eluent and tungstate was determined with sodium molybdate as eluent, the determination of molybdate and tungstate in the same sample was achieved.

Fig. 1 shows an ion chromatogram of molybdate, chloride, nitrate and sulphate obtained with a solution of 1.0 m*M* sodium tungstate as eluent. Chloride, nitrate and sulphate do not interfere with the determination of molybdate. The peak heights obtained from a series of samples consisting of 100 μg ml^{-1} molybdate and various concentration of tungstate indicate that tungstate does not interfere with the determination of molybdate as the concentration of

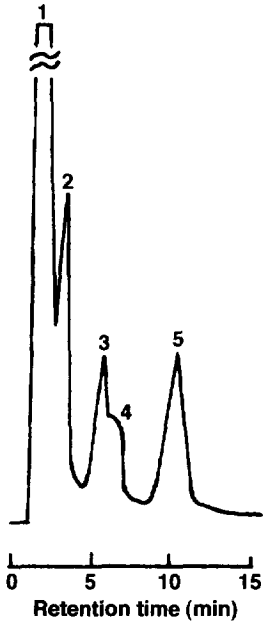

Fig. 1. Chromatogram obtained with 1.0 m*M* sodium tungstate as eluent. Peaks: 1 = injection peak, 2 = chloride (20 μg ml^{-1}), 3 = sulphate (20 μg ml^{-1}), 4 = nitrate (50 μg ml^{-1}), 5 = molybdate (200 μg ml^{-1}).

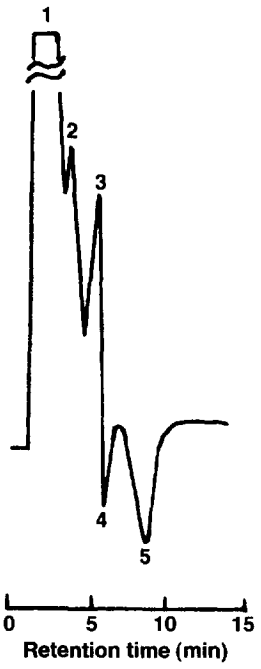

Fig. 2. Chromatogram obtained with 1.0 m*M* sodium molybdate as eluent. Peaks: 1 = injection peak, 2 = chloride (40 μg ml^{-1}), 3 = sulphate (40 μg ml^{-1}), 4 = nitrate (100 μg ml^{-1}), 5 = tungstate (200 μg ml^{-1}).

tungstate in the samples is less than 20 times that of molybdate. The injection peak is larger with higher concentration of tungstate in the samples. If the concentration of tungstate is >2000 μg ml^{-1}, the injection peak interferes with the determination of molybdate.

Fig. 2 shows a chromatogram of tungstate, chloride, nitrate and sulphate obtained with 1.0 m*M* sodium molybdate as eluent. Chloride, nitrate and sulphate do not interfere with the determination of tungstate. The peak heights from a series of samples consisting of 100 μg ml^{-1} tungstate and various concentrations of molybdate indicate that molybdate does not interfere with the determination of tungstate as the concentration of molybdate in the samples is less than 20 times that of tungstate. If the concentration of molybdate is >2000 μg ml^{-1}, the injection peak interferes with the determination of tungstate.

Molybdate is determined with 1.0 m*M* sodium tungstate as eluent. The detection limit for molybdate is 3.55 μg ml^{-1} ($S/N=2$), the relative standard deviation is 1.04% ($n=6$), the calibration curve follows the equation $H=0.11C+1.62$ (H = peak height, C = concentration) with a correlation coefficient of 0.998 ($n=6$) and the quantitative range is 3.55–1500 μg ml^{-1}.

Tungstate is determined with 1.0 m*M* sodium molybdate as eluent. The detection limit for tungstate is 5.03 μg ml^{-1}, the relative standard deviation is 1.66%, the calibration curve follows the equation $H=0.078C-0.35$ with a correlation coefficient of 0.998 and the quantitative range is 5.03–1500 μg ml^{-1}.

The method has been used in the determination of molybdenum and tungsten in the heteropoly acids of molybdenum, tungsten and silicon. The solutions of the heteropoly acid were prepared by dissolving 0.2500 g of the heteropoly acid in deionized water to a volume of 500 ml. The pH of each solution was adjusted to 9.0 with sodium hydroxide solution and the solutions were passed through a 0.45-μm membrane filter before the ion chromatography analysis. The molybdate in the solutions was determined with 1.0 m*M* sodium tungstate as eluent and tungstate was determined with 1.0 m*M* sodium molybdate as eluent. The results of analysis and recoveries of sample are listed in Table 1 and are the average

Table 1
The results of analysis and recoveries of heteropoly acid sample

Sample	Concentration in the solutions of heteropoly acid (μg ml^{-1})		Concentration added (μg ml^{-1})		Total concentration found (μg ml^{-1})		Recovery (%)		Concentration in heteropoly acid (%)		Mol Ratio Mo:W
	MoO_4^{2-}	WO_4^{2-}	MoO_4^{2-}	WO_4^{2-}	MoO_4^{2-}	WO_4^{2-}	MoO_4^{2-}	WO_4^{2-}	Mo	W	
$H_4[SiMo_6W_6O_{40}]\cdot nH_2O$	170.8	260.3	100.0	100.0	268.9	362.4	98.1	102.1	20.50	38.61	6:5.90
$H_4[SiMo_4W_8O_{40}]\cdot nH_2O$	110.8	338.1	100.0	100.0	212.5	438.7	101.7	100.6	13.30	50.16	4:7.88

value of three determination. The relative average deviations were less 2.00%.

4.2. Overlapping peak of tartaric acid and citric acid

Potassium biphthalate was employed as eluent for the separation of tartaric and citric acids; however, an overlapping peak was obtained and their simultaneous determination was not achieved. Tartaric acid was determined with citric acid as eluent and citric acid was determined with tartaric acid as eluent.

Fig. 3 shows a chromatogram of tartaric acid, chloride, nitrate and sulphate obtained with a solution of 1.0 m*M* citric acid (pH 4.0) as eluent. Chloride, nitrate and sulphate do not interfere with the determination of tartaric acid. The peak heights obtained from a series of samples consisting of 50 $\mu g\ ml^{-1}$ tartaric acid and various concentrations of citric acid indicate that citric acid does not interfere with the determination of tartaric acid as the concentration of citric acid in the samples is less than 20 times that of tartaric acid. The system peak is larger with higher concentration of citric acid in the sample. If the concentration of citric acid is over 1000 $\mu g\ ml^{-1}$, the system peak interferes with the tartaric acid peak.

Fig. 4 shows a chromatogram of citric acid, chloride, nitrate and sulphate obtained with 1.0 m*M* tartaric acid (pH 4.0) as eluent. Chloride, nitrate and sulphate also do not interfere with determination of citric acid. The peak heights obtained from a series of samples consisting of 50 $\mu g\ ml^{-1}$ citric acid and various concentrations of tartaric acid indicate that tartaric acid does not cause interference for the determination of citric acid as the concentration of tartaric acid in the samples is less than 10 times that of citric acid. If the concentration of tartaric acid is over 500 $\mu g\ ml^{-1}$, the system peak interferes with the citric acid peak.

Tartaric acid is determined with 1.0 m*M* citric acid

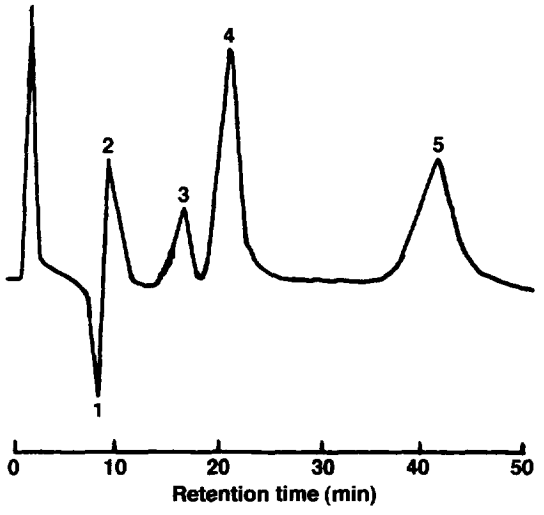

Fig. 3. Chromatogram obtained with 1.0 m*M* citric acid (pH 4.0) as eluent. Peaks: 1 = system peak, 2 = chloride (10 $\mu g\ ml^{-1}$), 3 = tartaric acid (50 $\mu g\ ml^{-1}$), 4 = nitrate (20 $\mu g\ ml^{-1}$), 5 = sulphate (20 $\mu g\ ml^{-1}$).

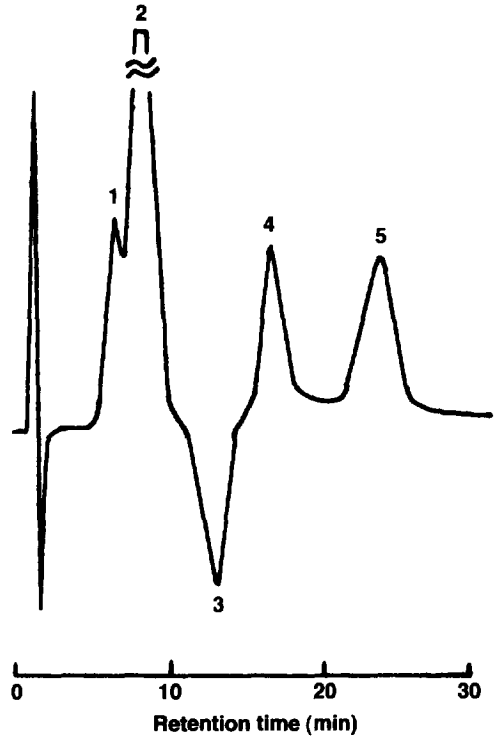

Fig. 4. Chromatogram obtained with 1.0 m*M* tartaric acid (pH 4.0) as eluent. Peaks: 1 = chloride (20 $\mu g\ ml^{-1}$), 2 = system peak, 3 = citric acid (100 $\mu g\ ml^{-1}$), 4 = nitrate (20 $\mu g\ ml^{-1}$), 5 = sulphate (20 $\mu g\ ml^{-1}$).

Table 2
The results of analysis and recoveries of drinking water sample

	Concentration in drinking water ($\mu g\ ml^{-1}$)	Concentration added ($\mu g\ ml^{-1}$)	Concentration found ($\mu g\ ml^{-1}$)	Recovery (%)
Tartaric acid	0.00	100.0	98.6	98.6
Citric acid	0.00	100.0	104.2	104.2

(pH 4.0) as eluent. The detection limit for tartaric acid is 1.44 $\mu g\ ml^{-1}$, the relative standard deviation is 2.97%. The calibration curve follows the equation $H=0.39C-2.96$ with a correlation coefficient of 0.997 and the quantitative range is 1.44–500 $\mu g\ ml^{-1}$.

Citric acid is determined with 1.0 m*M* (pH 4.0) tartaric acid as eluent. The detection limit for citric acid is 1.83 $\mu g\ ml^{-1}$, the relative standard deviation is 2.56%, the calibration curve follows the equation $H=0.24C-2.18$ with a correlation coefficient of 0.998 and the quantitative range is 1.83–500 $\mu g\ ml^{-1}$.

The method was applied to analyze a drinking water sample spiked with tartaric and citric acids. The results of analysis and recoveries of sample are listed in Table 2 and are the average value of three determination. The relative average deviations were less 2.00%.

5. Conclusions

Two-component overlapping peaks sometimes appear in single-column anion ion chromatography analysis. An approach to determining each component of a two-component overlapping peak in single-column anion ion chromatography analysis has been developed. One component of a two-component overlapping peak is determined with the other component as eluent. The method was tested by the overlapping peak of molybdate and tungstate and of tartaric and citric acids. This provided the possibility for determining a pair of difficult separating substances. A minor rearrangement of the detection equation for ion chromatography is also described.

References

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