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Short communication

Capillary electrophoretic determination of Ga(III) based on the formation of a heteropolyoxomolybdate complex

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Abstract

A novel capillary electrophoretic (CE) method was developed for the determination of Ga(III). The so-called Anderson-type $[GaMo_6O_{24}H_6]^{3-}$ complex was readily formed by the reaction of Mo(VI) with Ga(III) in 0.050 M monochloroacetate buffer (pH 2.0) and the precolumn complex-formation reaction was applied to the CE determination of Ga(III) with direct UV detection at 240 nm. The peak area was linearly dependent on the concentration of Ga(III) in the range of $5.0 \cdot 10^{-7}$–$5.0 \cdot 10^{-5}$ M. Owing to the high molar absorptivity of the Anderson anion, a detection limit of $2.0 \cdot 10^{-7}$ M (signal-to-noise ratio=3) was achieved. The advantage of the present method is that the presence of large excesses of Al(III) and In(III) does not cause interference.
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1. Introduction

Gallium has been used in the semiconductor industry, and there is an increasing concern about its potential toxicity [1]. Various instrumental techniques, such as atomic absorption spectrometry [2–4], liquid chromatography [5], UV–visible spectrophotometry [6,7] and voltammetry [8,9], have been used for the determination of Ga(III) at trace levels. Because the chemical properties of Ga(III), Al(III) and In(III) are very similar, their binary and ternary mixtures may result in serious errors. Simple and

selective analytical methods are required for the determination of Ga(III).

We have recently developed novel CE methods for the determination of various oxoanions, based on the formation of heteropolyoxometalate complexes. The sensitive CE methods for the determination of P(V) and As(V) were developed through the formation of the corresponding Keggin complexes in aqueous–CH_3CN media [10,11]. The formation of heteropoly-blue complexes was used as the basis for the simultaneous CE determination of P(V) and As(V) [12]. Besides, the formation of the $[P(V^VMo_{11})O_{40}]^{4-}$ and $[P(V^{IV}Mo_{11})O_{40}]^{5-}$ complexes was applied to the simultaneous determination of V(V) and V(IV), with the use of a Mo(VI)–P(V) complexing reagent [13]. Similarly, trace amounts of

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Sb(III) and Bi(III) were determined simultaneously through the formation of the $[P(Sb^{III}W_{11})O_{40}]^{6-}$ and $[P(Bi^{III}W_{11})O_{40}]^{6-}$ complexes [14].

We first applied the formation of the Anderson-type $[Cr^{III}Mo_6O_{24}H_6]^{3-}$ or $[I^{VII}Mo_6O_{24}]^{5-}$ complex to the CE analyses of Cr(III) and Cr(VI), or of I(VII) and I(V) [15,16]. Until then, the Anderson complexes had been thought to be formed only at high concentrations of Mo(VI) and heteroions.

In the present study, we found that a trace amount of Ga(III) reacted readily with Mo(VI) to form an Anderson complex at room temperature. On the basis of the precolumn formation of the Anderson complex, we developed a new CE method, which made it possible to determine Ga(III) in samples containing large excesses of Al(III) and In(III).

2. Experimental

2.1. Instrumentation

Separations were made on a P/ACE MDQ apparatus (Beckman Instruments, Fullerton, CA, USA) equipped with a built-in UV diode-array detection system. A fused-silica capillary (GL Sciences, Tokyo, Japan) of 60 cm (50 cm effective length)×75 µm I.D. was used. The reversed polarity mode of CE system (cathodic injection and anodic detection) was applied. The samples were injected in the hydrodynamic mode by applying a pressure of $3.5 \cdot 10^3$ Pa for 10 s. Before each run, the capillary was washed with the running buffer at $1.4 \cdot 10^5$ Pa for 3 min. The temperature of the capillary was maintained at 30 °C using the thermoregulation equipment of the instrument. The optimum applied voltage was −15 kV, and measurements were performed with a direct UV detection at 240 nm. The absorption spectra were recorded with a Hitachi model U-3000 spectrophotometer.

2.2. Chemicals

A stock solutions of Ga(III) was prepared by dissolving $Ga(NO_3)_3$ in distilled water. A stock solution of Mo(VI) was prepared with $Na_2MoO_4 \cdot 2H_2O$. The ammonium salt of the Anderson complex, $(NH_4)_3[GaMo_6O_{24}H_6] \cdot 5H_2O$ was prepared

according to the literature method [17]. All other reagents were of analytical grade and were used as received.

3. Results and discussion

3.1. UV–visible spectra

As shown in Fig. 1a, a UV spectrum of $3.0 \cdot 10^{-4}$ M Mo(VI) in an aqueous solution of pH 3.5 exhibited an absorption maximum at 216 nm, due to the formation of a mixture of $[Mo_8O_{26}]^{4-}$ and $[Mo_7O_{24}]^{6-}$ [18]. On the addition of $5.0 \cdot 10^{-5}$ M $Ga(NO_3)_3$ to the Mo(VI) solution, the absorbance value was increased at wavelengths of 240–300 nm (Fig. 1b), indicating the formation of a complex of Mo(VI) with Ga(III). The heteropolyanion exhibited an absorption maximum around 240 nm; the absorbance increase at wavelengths <240 nm was due to the absorption of NO_3^- (Fig. 1c). The complex formation occurred in the pH range of 2–4, and the absorbance value attained to a constant value in a few minutes in the whole pH range. For comparative purposes, Fig. 1d shows UV spectra for a $5.0 \cdot 10^{-5}$ M
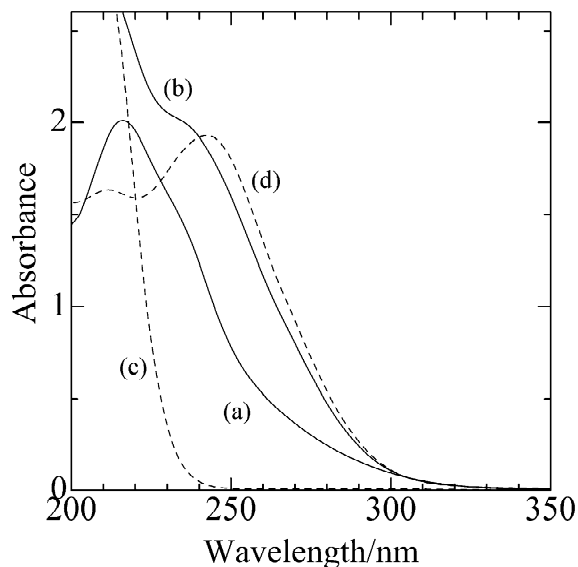

Fig. 1. UV–visible spectra for (a) $3.0 \cdot 10^{-4}$ M Mo(VI); (b) (a)+ $5.0 \cdot 10^{-5}$ M Ga(III); (c) $1.5 \cdot 10^{-4}$ M NO_3^-; (d) $5.0 \cdot 10^{-5}$ M $[GaMo_6O_{24}H_6]^{3-}$ in aqueous solution (pH 3.5). Path length; 1.0 cm.

solution of $(NH_4)_3[GaMo_6O_{24}H_6] \cdot 5H_2O$ at pH 3.5. As expected, the absorption maximum was found to be 240 nm. When the measurement was made again after standing the solution for 24 h at 25 °C, the absorption spectrum was unchanged, indicating that $[GaMo_6O_{24}H_6]^{3-}$ is kinetically stable. On the basis of these results, a wavelength of 240 nm was chosen as optimum for the CE determination of Ga(III).

A Mo(VI)–Al(III) system also produced the corresponding Anderson complex, although the equilibrium in the Mo(VI)–Al(III) system was reached so slowly and the maximum absorbance was attained after heating at 80 °C for ~60 min. It must be added that no complex formation occurred for the Mo(VI)–In(III) system.

3.2. Optimization of the CE conditions

In order to optimize the CE conditions, the following measurements were made for a test solution consisting of $2.0 \cdot 10^{-3}$ *M* Mo(VI), $1.0 \cdot 10^{-5}$ *M* Ga(III) and $1.0 \cdot 10^{-5}$ *M* Al(III). Among monochloroacetate, malonate, tartrate and citrate buffers, the use of 0.050 *M* monochloroacetate buffer as both sample and running buffers gave the best results regarding the sensitivity and peak shapes.

3.2.1. Effect of pH

Fig. 2 shows an electropherogram recorded immediately after the preparation of the test solution (pH 2.0); two peaks, denoted (a) and (b), were well-separated. Peak (a) was ascribed to $[GaMo_6O_{24}H_6]^{3-}$, and peak (b) to $[AlMo_6O_{24}H_6]^{3-}$. The peak area due to the migration of $[GaMo_6O_{24}H_6]^{3-}$ was reproducible even if the test solution was introduced into the capillary immediately after the preparation. On the other hand, peak (b) grew slowly as time passed, attaining to a maximum value when the electropherogram was recorded after the test solution was heated at 80 °C for 60 min. These results are in good agreement with the spectrophotometric observations. No peaks due to isopolymolybdate anions were observed within 10 min.

Fig. 3 shows migration times of $[GaMo_6O_{24}H_6]^{3-}$ and $[AlMo_6O_{24}H_6]^{3-}$ as a function of the buffer pH. In the pH range of 2–3.5, the Anderson anions
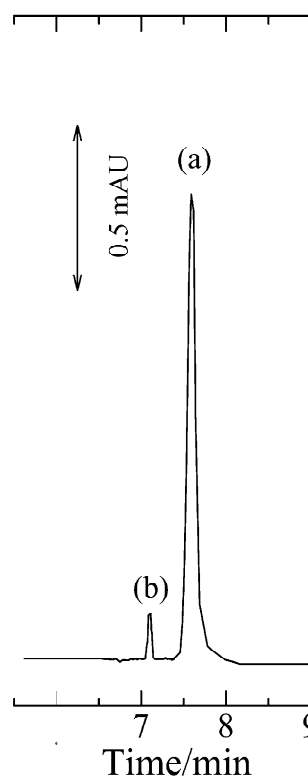

Fig. 2. Electropherograms for a $2.0 \cdot 10^{-3}$ *M* Mo(VI)$-1.0 \cdot 10^{-5}$ *M* Ga(III)$-1.0 \cdot 10^{-5}$ *M* Al(III)–0.050 *M* monochloroacetate buffer (pH 2.0) system. The running buffer; 0.050 *M* monochloroacetate buffer (pH 2.0). (a) $[GaMo_6O_{24}H_6]^{3-}$; (b) $[AlMo_6O_{24}H_6]^{3-}$.

showed well-shaped migration peaks. As the pH was lowered, both peaks were well separated, probably owing to the difference of the acid-dissociation constant of the Anderson anions. In conclusion, a buffer pH of 2.0 was chosen as optimum.

3.2.2. Effect of Mo(VI) concentration

In order to optimize the Mo(VI) concentration in a sample solution to be determined, test solutions were prepared by varying the Mo(VI) concentration ($2.0 \cdot 10^{-4} - 2.0 \cdot 10^{-3}$ *M*) while keeping [Ga(III)]$=5.0 \cdot 10^{-5}$ *M* in 0.050 *M* monochloroacetate buffer (pH 2.0), and the electropherogram was recorded immediately after the preparation. With an increase of the Mo(VI) concentration, the peak area corresponding to $[GaMo_6O_{24}H_6]^{3-}$ was accordingly increased, and the optimum concentration of Mo(VI) was found to be $2.0 \cdot 10^{-3}$ *M*. With a further increase of the
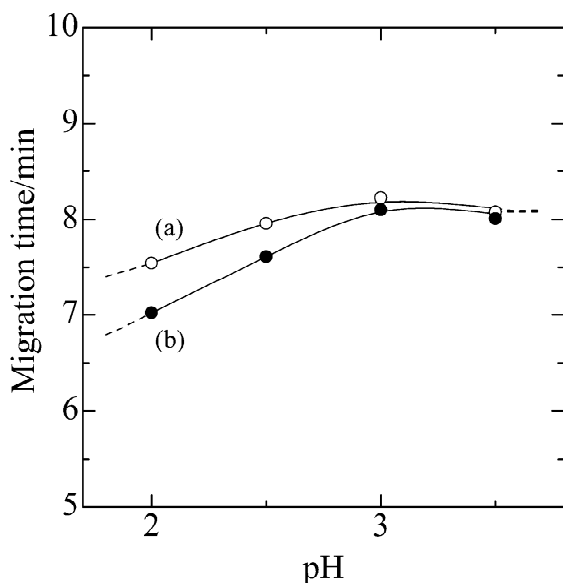
Fig. 3. Migration times as a function of pH. Samples; $2.0 \cdot 10^{-3}$ M Mo(VI)$-1.0 \cdot 10^{-5}$ M Ga(III)$-1.0 \cdot 10^{-5}$ M Al(III)-0.050 M monochloroacetate buffer. The running buffer; 0.050 M mono-chloroacetate buffer (the buffer pH was adjusted to be the same as the sample buffer). (a) $[GaMo_6O_{24}H_6]^{3-}$; (b) $[AlMo_6O_{24}H_6]^{3-}$.

Mo(VI) concentration, the linear range of the cali-bration curve was expanded to higher concentrations of Ga(III), but the detection limit was unchanged.

On the basis of these findings, the $2.0 \cdot 10^{-3}$ M Mo(VI)–0.050 M monochloroacetate buffer (pH 2.0) system was chosen as a compromise for the CE determination of Ga(III), and a calibration curve was constructed by varying the Ga(III) concentration. The peak area showed a linear dependence on the Ga(III) concentration in the range of $5.0 \cdot 10^{-7}$–$5.0 \cdot 10^{-5}$ M; the correlation coefficients were >0.998 and the detection limits were $2.0 \cdot 10^{-7}$ M. The peak area was satisfactorily reproducible with an RSD value ($n=5$) of 1.6%.

3.3. Recommended procedure

At first, a Mo(VI) reagent consisting of $4.0 \cdot 10^{-2}$ M Mo(VI)–1.0 M monochloroacetate buffer (pH 2.0) is prepared, and the capillary is filled with 0.050 M monochloroacetate buffer (pH 2.0) before sample injection. Since $[GaMo_6O_{24}H_6]^{3-}$ does not decom-pose during the migration in the capillary, the addition of Mo(VI) to the running buffer is not required.

An appropriate amount of a test solution is taken in a 20-ml volumetric flask containing 1.0 ml of the Mo(VI) reagent, and the solution is diluted to the mark with distilled water. The CE measurement is made by introducing the sample solution into the capillary. The amount of Ga(III) is determined from the calibration curve.

The present method can be applied to the de-termination of Ga(III) in samples containing large excesses of Al(III) and In(III). Since the formation reaction of $[AlMo_6O_{24}H_6]^{3-}$ proceeds very slowly, the presence of Al(III) in concentrations of up to $5.0 \cdot 10^{-3}$ M does not interfere with the determination of Ga(III) in the concentration range of $5.0 \cdot 10^{-7}$–$5.0 \cdot 10^{-5}$ M. Since no complex-formation of Mo(VI) with In(III) occurs, In(III) belonging to the same group as Al(III) and Ga(III) in a periodic table does not interfere.

3.4. Interference from foreign ions

The effect of other foreign ions on the determi-nation of Ga(III) was studied for the $2.0 \cdot 10^{-3}$ M Mo(VI)–0.050 M monochloroacetate buffer (pH 2.0) system containing $1.0 \cdot 10^{-5}$ M Ga(III). Oxoanions such as PO_4^{3-}, AsO_4^{3-}, SiO_4^{4-} and GeO_4^{4-} can form the corresponding Keggin-type heteropolyanions. However, their presence causes no serious errors, because the mobilities of the Keggin anions are different from that of $[GaMo_6O_{24}H_6]^{3-}$. The pres-ence of NaCl in concentrations up to 0.10 M did not interfere.

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