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Simultaneous electrophoretic determination of vanadium(V) and vanadium(IV) based on the complex formation with a Mo(VI)–P(V) reagent

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Abstract

A capillary electrophoretic (CE) method was developed for the sensitive determination of V(V) and V(IV). A Mo(VI)–P(V) reagent reacted with a mixture of trace amounts of V(V) and V(IV) to form the $[P(V^V Mo_{11})O_{40}]^{4-}$ and $[P(V^{IV} Mo_{11})O_{40}]^{5-}$ complexes in 0.1 M monochloroacetate buffer (pH 2.2). Since the V-substituted Keggin anions possessed high molar absorptivities in the UV region and the peaks due to their migrations were well separated in the electropherogram, the pre-column complex formation reaction was applied to the simultaneous CE determination of V(V) and V(IV) with direct UV detection at 220 nm. The calibration curves were linear over two orders of magnitude with detection limits of $5 \cdot 10^{-7}$ M for V(V) and $2 \cdot 10^{-7}$ M for V(IV). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Vanadium; Metal cations; Metal complexes

1. Introduction

Vanadium exists in the oxidation states of V(V) and V(IV) in natural and waste waters, and the speciation of vanadium has been the subject of extensive study [1]. Recently, capillary electrophoresis (CE) was applied to the simultaneous determination of V(V) and V(IV) as negatively charged complexes with ethylenediaminetetraacetic acid (EDTA), with detection limits of 0.1 and 0.4 µg/ml for V(V) and V(IV), respectively [2]. When diethylenetriaminepentaacetic acid (DTPA) was used as the chelating reagent, detection limits were in the

range of $2 \cdot 10^{-6}$ – $8 \cdot 10^{-6}$ M [3]. Despite many advantages with respect to simplicity and selectivity, the pre-column complexation methods do not satisfy all requirements for routine analysis, because of the decomposition of the V(V) and V(IV) chelates during CE separation in a capillary. The addition of the aminopolycarboxylic acids to the running buffer decreases the sensitivity because the chelating reagents also absorb in the UV region. New reagents that can form kinetically stable complexes with V(V) and V(IV) are being searched to improve the sensitivity of the pre-column CE method.

The so-called molybdenum blue method has been used for the colorimetric determination of inorganic oxoanions. A modification of the method is known as the Mo(VI)–Mo(V) reagent method [4]. How-

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ever, most of the work has been restricted to the determination of tetrahedrally-coordinated oxoanions which can act as the central heteroion in the Keggin and Dawson structures [5–7]. Considerable effort has been devoted to the development of new methods based on different types of polyoxometalate formation. We found that the reaction of Mo(VI) with trace amounts of Cr(III) or IO_4^- produced stable Anderson-type complexes in aqueous solution, and applied the complex formation to the simultaneous CE determination of Cr(III) and Cr(VI), and of IO_4^- and IO_3^- with direct UV detection [8,9]. Recently, a sensitive CE determination of P(V) was made possible, based on the formation of a Keggin-type $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ complex in the presence of CH_3CN as an auxiliary solvent [10].

Our ion-transfer voltammetric study showed that the so-called lacunary molybdophosphate complex, $[\text{H}_3\text{PMo}_{11}\text{O}_{39}]^{4-}$ was kinetically stable at low concentrations of Mo(VI) and P(V) in aqueous solution [11]. On the basis of these findings, we developed a voltammetric phosphate sensor based on the formation of the lacunary complex [12]. Recently, we found that trace amounts of V(V) and V(IV) produced readily the V-substituted complexes;

$[\text{P}(\text{V}^{\text{V}}\text{Mo}_{11})\text{O}_{40}]^{4-}$ and $[\text{P}(\text{V}^{\text{IV}}\text{Mo}_{11})\text{O}_{40}]^{5-}$ in such aqueous Mo(VI)–P(V) solutions [13]. A combination of these findings prompted us to develop a new analytical method with the use of a Mo(VI)–P(V) reagent, in which the lacunary molybdophosphate, $[\text{H}_3\text{PMo}_{11}\text{O}_{39}]^{4-}$ exists as predominant. In the Mo(VI)–P(V) reagent method, oxoanions to be determined are incorporated in the peripheral structure of the molybdophosphate complex.

The present study was undertaken to apply the Mo(VI)–P(V) reagent method to the simultaneous CE determination of V(V) and V(IV), because the $[\text{P}(\text{V}^{\text{V}}\text{Mo}_{11})\text{O}_{40}]^{4-}$ and $[\text{P}(\text{V}^{\text{IV}}\text{Mo}_{11})\text{O}_{40}]^{5-}$ complexes were kinetically stable and possessed different mobilities. Since both complexes had high molar absorptivities in the UV region, the Mo(VI)–P(V) reagent method brought about an increase in the sensitivity by an order of magnitude.

2. Experimental

2.1. Instrumentation

The CE experiments were performed with a P/ACE MDQ system (Beckman Instruments, Fullerton, CA, USA) equipped with a built-in UV diode-array detector. All separations were carried out on a fused-silica capillary (GL Sciences, Tokyo, Japan) of 60 cm (50 cm effective length) \times 75 μm I.D. Separation was performed with cathode at the injection side. Samples were injected in the hydrodynamic mode by applying a pressure of $3.5 \cdot 10^3$ Pa. Between runs the capillary was washed at $1.4 \cdot 10^5$ Pa for 3 min with the running buffer. The temperature of the capillary was kept at 25°C using the thermoregulation equipment of the instrument. Electropherograms were recorded by varying the applied voltage (–5–30 kV). Optimum separation with minimal analysis time was obtained at the applied voltage of –15 kV. Lower applied voltage increased the analysis time and broadened the peak-shape. At higher applied voltage, the baseline became increasingly noisy, probably owing to the Joule heating effect. UV-visible spectra were recorded on a Hitachi Model U-3000 spectrophotometer.

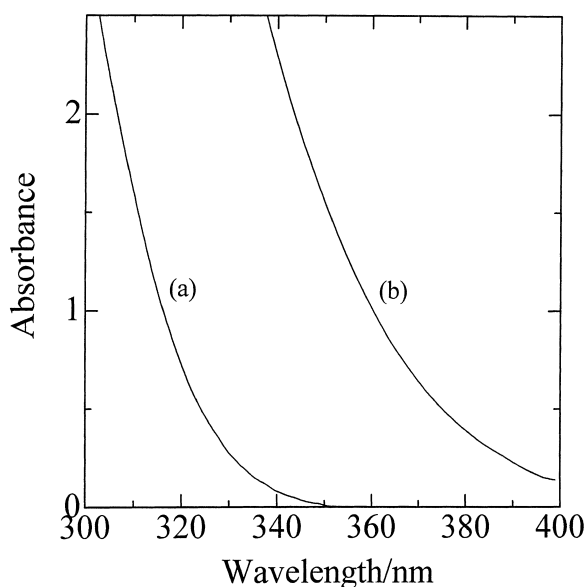


Fig. 1. UV-visible spectra for (a) 5.0 mM Mo(VI) and (b) 5.0 mM Mo(VI)+0.50 mM P(V) in an aqueous solution of pH 3.2. Path length; 1.0 cm.

2.2. Chemicals

A $1 \cdot 10^{-2}$ M V(V) stock solution was prepared by dissolving NH_4VO_3 in water. A stock solution of V(IV) was prepared by dissolving appropriate amount of $\text{VOSO}_4 \cdot n\text{H}_2\text{O}$ in 0.1 M H_2SO_4 ; the vanadium content was determined with a Shimadzu Model ICP-5000 inductively coupled plasma emission spectrometer. $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ were used to prepare Mo(VI) and P(V) stock solutions, respectively. All other reagents were of analytical grade and were used as received.

For the sake of brevity, the $[\text{H}_3\text{PMo}_{11}\text{O}_{39}]^{4-}$, $[\text{P}(\text{V}^{\text{V}}\text{Mo}_{11})\text{O}_{40}]^{4-}$ and $[\text{P}(\text{V}^{\text{IV}}\text{Mo}_{11})\text{O}_{40}]^{3-}$ complexes were sometimes referred to as PMo_{11} , $\text{PV}^{\text{V}}\text{Mo}_{11}$ and $\text{PV}^{\text{IV}}\text{Mo}_{11}$, respectively.

3. Results and discussion

3.1. UV–visible spectroscopic study

3.1.1. Formation conditions of a lacunary $[\text{H}_3\text{PMo}_{11}\text{O}_{39}]^{4-}$ complex

Fig. 1a shows UV–visible spectra for an aqueous solution of 5.0 mM Mo(VI) (pH 3.2). With the addition of 0.50 mM P(V) to the Mo(VI) solution in the pH range of 1–4, as shown in Fig. 1b, the Mo(VI)–P(V) solution turned to pale-yellow. Our ion-transfer voltammetric study demonstrated the formation of PMo_{11} as a predominant species [11,13]. It should be noted that the Keggin-type $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ complex is not formed at any appreciable amount at these weak acidities [10]. In the following, the formation conditions of PMo_{11} were investigated with the absorbance change at 360 nm.

The effect of the P(V) concentration on the formation of PMo_{11} was investigated by varying the P(V) concentration while keeping $[\text{Mo}(\text{VI})]=5.0$ mM at pH 3.2. As shown in Fig. 2, the formation of PMo_{11} became maximal at the P(V) concentration of 0.50 mM. With further increase of the P(V) concentration, the absorbance value was decreased, probably because of the degradation of PMo_{11} into $\text{A}[\text{H}_6\text{PMo}_9\text{O}_{34}]^{3-}$ [14].

3.1.2. Formation conditions of $\text{PV}^{\text{V}}\text{Mo}_{11}$ and $\text{PV}^{\text{IV}}\text{Mo}_{11}$

With the addition of $1 \cdot 10^{-4}$ M V(V) to the 5.0 mM Mo(VI)–0.50 mM P(V) system (pH 3.2), as shown in Fig. 3a, the formation of $\text{PV}^{\text{V}}\text{Mo}_{11}$ was ascertained by the appearance of an orange–yellow solution. In contrast to the Mo(VI)–P(V)–V(V) system, the addition of $1 \cdot 10^{-4}$ M V(IV) to the Mo(VI)–P(V) system produced a dark-blue solution (Fig. 3b). Although PMo_{11} is subjected to chemical reduction to the so-called heteropoly-blue species, the ion-transfer voltammetric study has demonstrated the formation of $\text{PV}^{\text{IV}}\text{Mo}_{11}$ without any redox reaction [13]. In both systems, the absorbance values increased with time, and attained to constant values in about 10 min. After the absorbance-increase period, the $\text{PV}^{\text{V}}\text{Mo}_{11}$ and $\text{PV}^{\text{IV}}\text{Mo}_{11}$ complexes were kinetically stable in solution, as evidenced by no absorbance change.

In order to obtain the formation conditions of $\text{PV}^{\text{V}}\text{Mo}_{11}$ and $\text{PV}^{\text{IV}}\text{Mo}_{11}$, the absorbance value at 480 or 550 nm was plotted against pH for the 5.0 mM Mo(VI)–0.50 mM P(V) system containing $1 \cdot 10^{-4}$ M V(V) or V(IV); no absorption due to excess

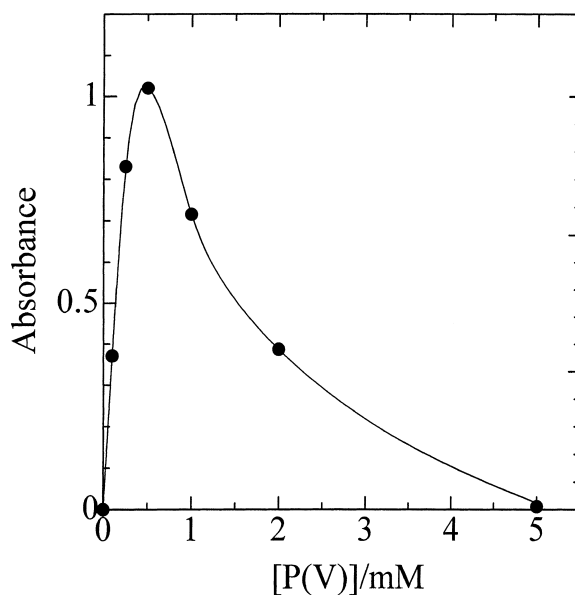


Fig. 2. Variation of the absorbance value at 360 nm as a function of the P(V) concentration in a 5.0 mM Mo(VI) solution of pH 3.2. Path length; 1.0 cm.

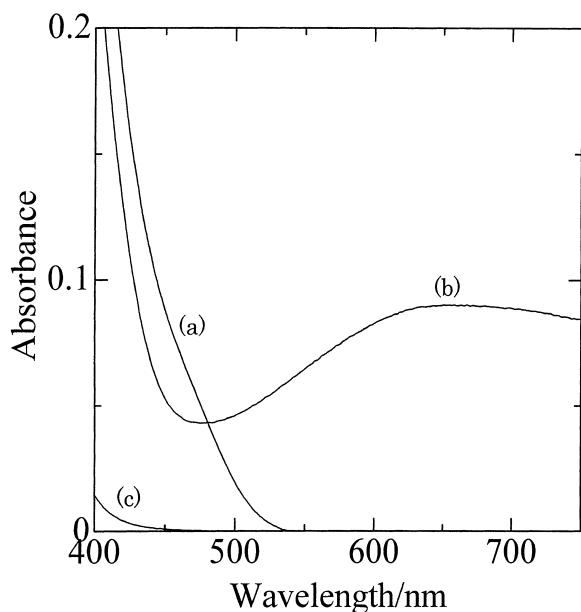


Fig. 3. UV-visible spectra for a 5.0 mM Mo(VI)–0.50 mM P(V) system (pH 3.2) containing (a) $1 \cdot 10^{-4}$ M V(V); (b) $1 \cdot 10^{-4}$ M V(IV); (c) none. The absorption spectra were recorded after standing for 10 min at room temperature. Path length; 1.0 cm.

of PMo_{11} or V(IV) occurs at the wavelengths. As shown in Fig. 4a, the absorbance value at 480 nm (for $\text{PV}^{\text{V}}\text{Mo}_{11}$) attained a maximum around pH 2.2. On the other hand, the absorbance value at 550 nm (for $\text{PV}^{\text{IV}}\text{Mo}_{11}$) was practically unchanged in the pH range of 2–3.5 (Fig. 4b). On the basis of these findings, the pre-column complexation was made in the 5.0 mM Mo(VI)–0.50 mM P(V) system at pH 2.2.

Fig. 5 shows the whole spectra of $\text{PV}^{\text{V}}\text{Mo}_{11}$ and $\text{PV}^{\text{IV}}\text{Mo}_{11}$. A wavelength of 220 nm, where the maximum absorbance was obtained, was chosen as best for the sensitive determination of V(V) and V(IV).

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 5.0 mM Mo(VI), 0.50 mM P(V), $1 \cdot 10^{-4}$ M V(V) and $1 \cdot 10^{-4}$ M V(IV). On the basis of the spectrophotometric observations, the test

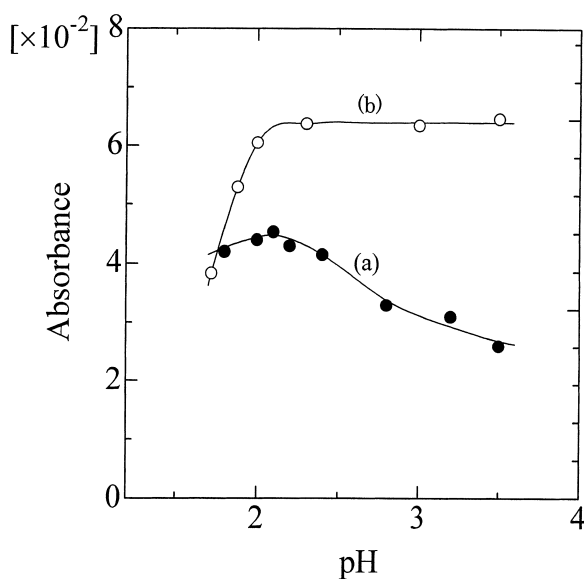


Fig. 4. Variation of the absorbance value as a function of pH for a 5.0 mM Mo(VI)–0.50 mM P(V) system containing $1 \cdot 10^{-4}$ M (a) V(V); (b) V(IV). (a) 480 nm; (b) 550 nm. Path length; 1.0 cm.

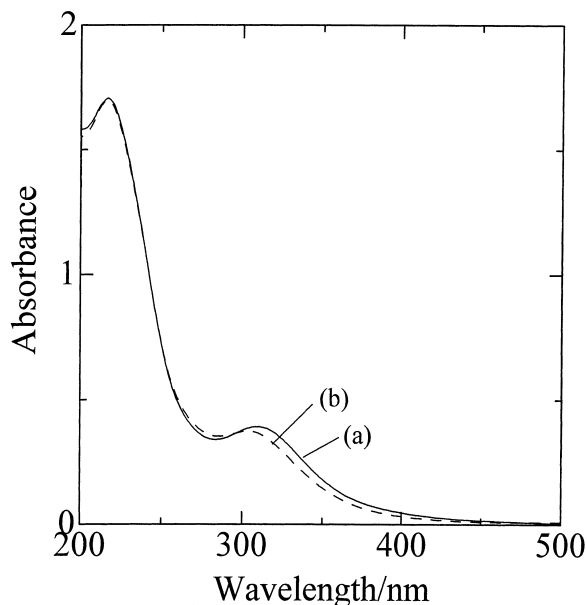


Fig. 5. UV-visible spectra for a 2.0 mM Mo(VI)–0.2 mM P(V) system containing $2 \cdot 10^{-4}$ M (a) V(V); (b) V(IV) in an aqueous solution of pH 2.2. Path length; 1.0 mm.

solution was left standing for 10 min at room temperature, and the electropherogram was recorded. The selection of an appropriate buffer was extremely important for the separation of V(V) and V(IV). When citrate, tartrate, malonate and monochloroacetate buffers were compared, the best results regarding the sensitivity and peak shapes were obtained with the use of a 0.1 M monochloroacetate buffer as both sample and running buffers. The addition of the

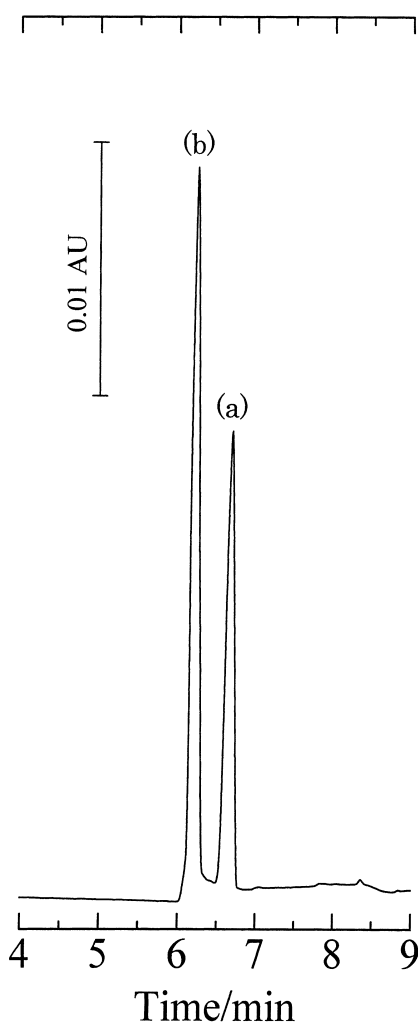


Fig. 6. An electropherogram for a test solution consisting of a 5.0 mM Mo(VI)–0.50 mM P(V)–0.1 M monochloroacetate buffer (pH 2.2) containing $1 \cdot 10^{-4}$ M V(V) and $1 \cdot 10^{-4}$ M V(IV). The running buffer; 0.1 M monochloroacetate buffer (pH 2.2). (a) $PV^V Mo_{11}$; (b) $PV^{IV} Mo_{11}$.

Mo(VI)–P(V) reagent to the running buffer is not required, because the $PV^V Mo_{11}$ and $PV^{IV} Mo_{11}$ complexes are so kinetically stable and no degradation occurs during migration in the capillary.

The electropherogram is shown in Fig. 6. Peak a is due to $[P(V^V Mo_{11})O_{40}]^{4-}$, and peak b is due to $[P(V^{IV} Mo_{11})O_{40}]^{5-}$ which migrates faster through the capillary than $[P(V^V Mo_{11})O_{40}]^{4-}$, because the former carries the greater negative charge of -5 . Both peaks were sharp and well separated.

The respective peak areas were plotted against the buffer pH and the results are shown in Fig. 7. The peak area for $PV^V Mo_{11}$ was greatest around pH 2.2, and the corresponding value for $PV^{IV} Mo_{11}$ was practically constant in the pH range of 2–3. As a result, a pH of 2.2 was chosen as being optimal for the simultaneous CE determination of V(V) and V(IV).

3.3. Recommended procedure

At first, a complexing reagent consisting of 50 mM Mo(VI)–5.0 mM P(V)–1 M monochloroacetate buffer (pH 2.2) was prepared. An appropriate amount of a sample to be analyzed is placed in a 20-ml volumetric flask and then 2 ml of the Mo(VI)–P(V) reagent is added. After the solution is diluted to the mark with distilled water, it is left standing for 10 min at room temperature. Before the CE measurement, the capillary was filled with 0.1 M monochloroacetate buffer (pH 2.2), and a 0.1 M NaCl solution is introduced for 3 s as a leading electrolyte for the transitional isotachopheresis effect [15]. The sample solution was introduced into the capillary for 15 s, and calibration curves were constructed by varying the concentrations of V(V) and V(IV). The peak areas showed a linear dependence on the concentration of V(V) or V(IV) in the range of $5 \cdot 10^{-7}$ – $1 \cdot 10^{-4}$ M. The correlation coefficients are >0.998 . The detection limits for a signal-to-noise ratio of 3 were $5 \cdot 10^{-7}$ M for V(V) and $2 \cdot 10^{-7}$ M for V(IV). The reproducibility was investigated by making 10 runs with both vanadium species present at $1 \cdot 10^{-4}$ M. The relative standard deviations of peak areas and migration times were better than 2.5 and 1.2%, respectively.

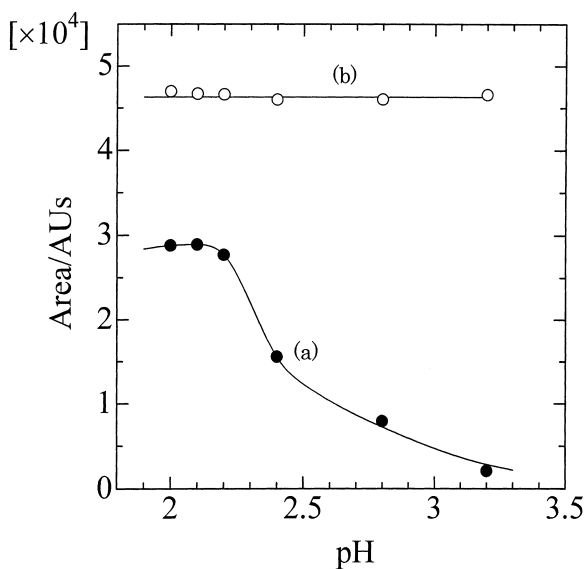


Fig. 7. Relationship between the sample pH and the peak area for (a) $PV^V Mo_{11}$ and (b) $PV^{IV} Mo_{11}$. The test solution; 5.0 mM $Mo(VI)$ –0.50 mM $P(V)$ –0.1 M monochloroacetate buffer containing $1 \cdot 10^{-4}$ M $V(V)$ and $1 \cdot 10^{-4}$ M $V(IV)$. The running buffer; 0.1 M monochloroacetate buffer (the buffer pH was adjusted to be the same as the sample buffer).

3.4. Interference from foreign ions

The interference from foreign ions was examined with the proposed method. The results are summa-

Table 1
Effect of foreign ions on the determination of $V(V)$ and $V(IV)$

Ion	Concentration (M)	Relative error (%)	
		V(V)	V(IV)
Cr(III)	$1 \cdot 10^{-4}$	–1.4	+0.4
Mn(II)	$1 \cdot 10^{-4}$	–0.9	–0.8
Fe(III)	$1 \cdot 10^{-4}$	–1.5	–1.5
Co(II)	$1 \cdot 10^{-4}$	–2.6	+0.6
Ni(II)	$1 \cdot 10^{-4}$	–0.1	+2.0
Cu(II)	$1 \cdot 10^{-4}$	+2.3	–1.2
Zn(II)	$1 \cdot 10^{-4}$	+1.1	–0.4
Al(III)	$1 \cdot 10^{-4}$	+0.5	+0.3
Ga(III)	$1 \cdot 10^{-4}$	–0.5	+0.4
Si(IV)	$1 \cdot 10^{-4}$	–1.5	+2.2
Ge(IV)	$1 \cdot 10^{-4}$	–0.1	+0.1

Sample: 5.0 mM $Mo(VI)$ –0.50 mM $P(V)$ – $5 \cdot 10^{-5}$ M $V(V)$ – $5 \cdot 10^{-5}$ M $V(IV)$ –0.1 M monochloroacetate buffer (pH 2.2). Running buffer: 0.1 M monochloroacetate buffer (pH 2.2). Voltage: –15 kV.

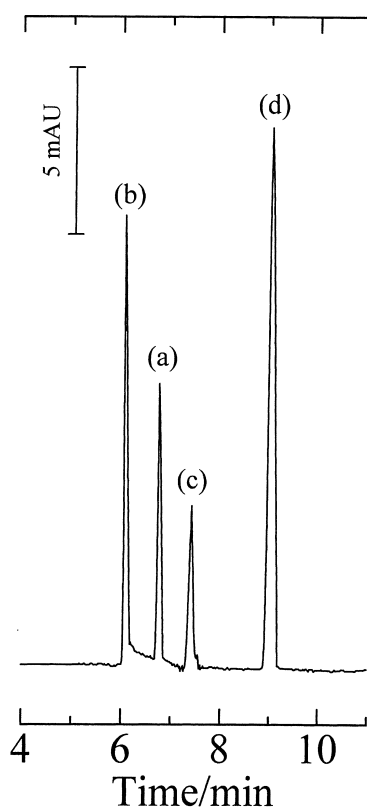


Fig. 8. An electropherogram for a solution consisting of a 5.0 mM $Mo(VI)$ –0.50 mM $P(V)$ –0.1 M monochloroacetate buffer (pH 2.2) containing $5 \cdot 10^{-5}$ M $V(V)$, $5 \cdot 10^{-5}$ M $V(IV)$, $1 \cdot 10^{-4}$ M $Fe(III)$, $1 \cdot 10^{-4}$ M $Cr(III)$ and $1 \cdot 10^{-4}$ M $Ga(III)$. The running buffer; 0.1 M monochloroacetate buffer (pH 2.2). (a) $PV^V Mo_{11}$; (b) $PV^{IV} Mo_{11}$; (c) $[P(Fe^{III} Mo_{11})O_{40}]^{6-}$; (d) $[Cr^{III} Mo_6 O_{24} H_6]^{3-}$ + $[Ga^{III} Mo_6 O_{24} H_6]^{3-}$.

riized in Table 1. Under the recommended conditions, the $Mo(VI)$ – $P(V)$ reagent can react with $Fe(III)$ to form a $Fe(III)$ -substituted molybdophosphate anion, $[P(Fe^{III} Mo_{11})O_{40}]^{6-}$, and with $Cr(III)$ and $Ga(III)$ to form the corresponding Anderson-type heteropolyanions, $[XMo_6 O_{24} H_6]^{3-}$ [$X=Cr(III)$, $Ga(III)$]. Their presence causes no serious errors, because the mobilities of the $[P(Fe^{III} Mo_{11})O_{40}]^{6-}$ and $[XMo_6 O_{24} H_6]^{3-}$ complexes are different from those of the $[P(V^V Mo_{11})O_{40}]^{4-}$ and $[P(V^{IV} Mo_{11})O_{40}]^{5-}$ complexes (Fig. 8). However, the presence of these metal ions at much greater concentrations may cause negative errors, owing to a lack of $Mo(VI)$.

The remaining Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Al(III), Si(IV) and Ge(IV) ions do not interfere because no complex formation occurs under the recommended conditions.

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