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A Simple Electrophoretic Method for the Simultaneous Determination of Chromium and Vanadium in Real and Environmental Samples

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Abstract

A very simple, selective and highly sensitive capillary electrophoretic method for the simultaneous determination of chromium(III) and vanadium(V) with Mo(VI)-P(V) reagent has been developed. A Mo(VI)-P(V) reagent reacted with a mixture of trace amounts of chromium(III) and vanadium(V) to form the stable heteropolyanions in 0.1M acetate buffer (pH 2.0) at room temperature($25\pm5\ ^0$C). Both anionic forms of chromium(III) and vanadium(V) can be determined simultaneously by capillary electrophoresis with direct UV detection at 254nm. The pre-column complex formation reaction is instantaneous and absorbance remains stable for 24h. Linear calibration curves were obtained in the concentration ranges of 0.06 – 60 mgL^{-1} and 0.05 – 80 mgL^{-1} of Cr(III) and V(V), respectively; the detection limits were 6.0 µg L^{-1} and 5.0 µg L^{-1} , respectively. The influence of several experimental parameters on both sensitivity and efficiency was investigated. The interference from over 50 cations, anions and complexing agents has been discussed at 1 mgL^{-1} of Cr and V, respectively. The unique selectivity and sensitivity of the method allowed its direct application to the determination of Cr and V in complex matrices of certified reference materials and synthetic seawater.. The developed was also used successfully in the determination of chromium and vanadium in environmental waters (tap and lake). The method has high precision and accuracy (s =±0.02 for 0.5 mg L^{-1}).

Keywords: *Capillary electrophoresis; Mo(VI)-P(V) reagent; chromium and vanadium; alloy; steel; environmental waters*

Introduction

Chromium and / or vanadium in trace amounts is important industrially[1], as a : biological nutrient[2], epidemiological preventive[3], toxicant[4], environmental pollutant[5] and occupational hazard[6]. Therefore, the accurate determination of the metal at trace and ultra-trace levels is important.

Simultaneous determination of chromium and vanadium in complicated matrices is a very difficult task that achieved using sophisticated and / or high cost instruments such as anodic stripping voltammetry with ICP-MS detection [7], ICP-AES [8], NAA [9], HPLC [10], XRF [11] and AAS [12]. However, the relatively high costs [7-12], high detection limits [10-12] and poor recoveries and precisions are common disadvantages.

Moreover, such methods must be combined with prior pre-concentration, ion exchange and / or solvent extraction separation techniques [8,10,11]. Hence the need for a simple, low cost, sensitive and highly selective method is clear.

Capillary Electrophoresis (CE) is being increasingly applied for the determination of metal ions,

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primarily because of its great flexibility and easy implementation [13]. Separations of metal ions that exist in a free, uncomplexed form are comparatively rare in the practice of CE because the absolute mobility values of most of the metal ions in their free form do not differ enough from one to another to envision electrophoretic separations of practical interest. Obviously, complexation presents the most valuable approach for performing metal speciation and offers a powerful means of manipulation and separation selectively.

The so called molybdenum blue method has been used for the colorimetric determination of inorganic oxoanions. A modified of the method is known as the Mo(VI) – Mo(V) reagent method[14]. However, from recent studies [15, 16] the formation of different types of polyoxometalate was possible. These studies showed that the so-called lacunary molybdophosphate complex $[H_3PMo_{11}O_{39}]^{4-}$ was kinetically stable at low concentration of Mo(VI) and P(V) in aqueous solutions [17, 18]. 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, $[H_3PMo_{11}O_{39}]^{4-}$ 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 simultaneous CE determination of chromium(III) and vanadium(V), because their yellow color complexes were kinetically stable and possessed different mobilities. The method was based on the reaction of non-absorbent Mo(VI) – P(V) reagent in 0.1 M acetate buffer of pH 2.0 with Cr(III) and V(V) to produce a highly UV-absorbent yellow complex product, followed by direct measurement of the absorbance in aqueous solution. With suitable masking, the reaction can be made highly selective and the reagent blank does not show any UV-absorbance.

Experimental Section

Instrumentation

The capillary electrophoresis experiments were performed with a P/ ACE-2050 system (Beckman Instruments, Fullerton, CA, USA) equipped with a UV detector. All separations were carried out on a fused-silica capillary of 40 × 47 cm × 50 µm i.d. Separation was performed with cathode at the injection side. Samples were injected in the hydrodynamic mode by applying pressure of 3.44 kPa. The temperature of the capillary was kept at 25 ^{0}C using thermoregulation equipment of the instrument. Electropherograms were recorded by varying the applied voltage (-5 to -25 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. pH measurement was made using a pH-mV meter model PHS – 3B with combination electrodes. A typical commercially available [13] CE instrumental system is shown in Figure 1.

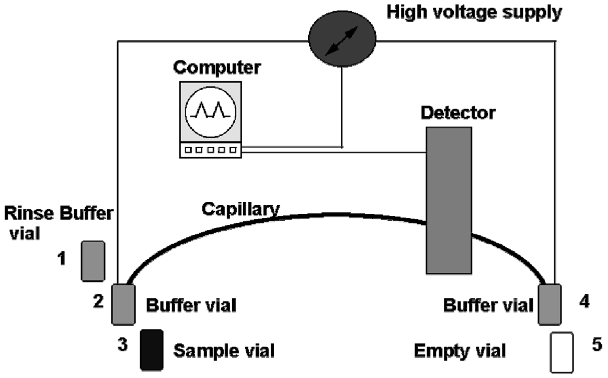

Figure 1. **Typical CE separation system**

Reagents and solutions

All chemicals used were of analytical-reagent grade or the highest purity available. Doubly distilled water, which is non-absorbent under UV-radiation, was used throughout.

Glass vessels were cleaned by soaking in acidified solution of $KMnO_4$, followed by washing with concentrated HNO_3, and were rinsed several times with high purity distilled water. Stock solutions and environmental water samples (1000-mL each) were kept in a polypropylene bottle containing 1-mL of concentrated HNO_3.

A stock solution of 50 mM Mo(VI) and 5 mM P(V) was prepared by dissolving requisite amounts of $Na_2MoO_4.\ 2H_2O$ and $NaH_2PO_4.\ 2H_2O$, respectively. The solutions were stable for at least one month when stored in a bottle at 4 ^{0}C. A stock solution of 1M acetate buffer (running buffer) (pH 2.0) was prepared by appropriate amounts of CH_3COOH and CH_3COONa solution and its pH was adjusted to 2.0 by a pH meter.

A 100 mL amount of stock standard solution of 1 mgmL^{-1} of Cr(III) was prepared by dissolving 769.63 mg of $Cr(NO_3)_3$. $9H_2O$ in doubly distilled water and a 100 mL amount of stock solution (1mg mL^{-1}) of V(V) was prepared by dissolving 229.6 mg of NH_4VO_4 in doubly distilled water containing 1-2mL of nitric acid(1+1). More dilute standard solutions were daily prepared from these stock solutions as and when required. The following working solutions were used:. 2 mg mL^{-1} of EDTA and 20.0 mg mL^{-1} of As^{III} and a 100-mL stock solution(1mg mL^{-1}) of Cr^{VI} or V^{IV} was prepared from $K_2Cr_2O_7$ or $VOSO_4$. nH_2O, respectively. Also, a 5% solution of NH_4OH.

Other solutions: Solutions of a large number of inorganic ions and complexing agents were prepared from their Analar grade or equivalent grade water soluble salts.

Homogenized and finally powdered certified reference materials from Beijing NCS Analytical Instruments CO. Ltd, Beijing, P.R. China, were used as received.

Procedure

A volume of 01-1.0mL of a aqueous solution containing 0.5 – 800 µg of vanadium(V) and 0.6 – 600 µg of chromium(III) in a 10-mL calibrated flask was mixed with a 1-mL of 50 mM of Mo(VI) and 1-mL of 5 mM P(V) followed by the addition of 3-7-mL (preferably 5-mL) of 1M acetate buffer (pH 2.0). The mixture was diluted to up to mark with double distilled water and it was left standing for 20 min at room temperature (25±5 ^{0}C). Before CE measurement, the capillary was filled with 0.1M acetate buffer (pH 2.0) (running buffer), and a 0.1M NaCl solution was introduced for 3s as a leading electrolyte for the transitional isotachophoresis effect[19]. The sample was introduced into capillary for 3-20 s (preferably 10s) and the absorbance was measured by a UV-detection at 254 nm. The Mo(VI) – P(V) reagent does not show any absorbance at UV-region in the absence of V(V) and Cr(III).

The concentrations of V(V) and Cr(III) were evaluated from the peak heights of the signal by using the calibration curves prepared with the standard solutions.

Results and Discussion

Optimization of the CE System

Preliminary tests were carried out with the aid of different flow assemblies to select the optimal CE conditions. In order to optimize the CE conditions, the influence of the hydrodynamic and chemical parameters on the magnitude of the peak height, the shape of the peak and reproducibility of the results were studied for a test solution consisting of 5.0 mM Mo(VI), 0.5 mM P(V), 10 mgL^{-1} of both V(V) and Cr(III). Table1 shows the results optimization of working conditions.

Table 1. **Selected chemical and CE parameters obtained with optimization experiments**

Parameter	Studied range	Selected value
Wavelength filters (λ_{max}) / nm	200, 214, 254, 280	254
Acidity / M H_2SO_4	$1 \times 10^{-4} – 3\times10^{-3}$	$5 \times10^{-4} – 16\times10^{-4}$ (preferably 1×10^{-3} M)
pH of running buffer (0.1M acetate buffer)	1.95 – 2.30	2
Length,cm(effective length, cm)× I.D. µm	47 × 40cm (25-75) µm	47 × 40cm × 50 µm
Applied pressure for ample injection / kPa	3 – 4	3.44
Applied voltage kV	-5 - -25	-15
Injection time of sample / sec	3 – 20	10
Injection time of 0.1 NaCl / sec	2 – 10	3
Concentration of reagent (M)		
CH_3COOH	0.05 – 1.0	0.1
CH_3COONa	0.05 – 1.0	0.1
Mo(VI)	$1 \times 10^{-2} - 1 \times 10^{-4}$	5×10^{-3}
P(V)	$1 \times 10^{-3} - 1 \times 10^{-4}$	5×10^{-4}
NaCl	0.05 – 1.0	0.1

Preliminary experiments have shown that a proper choice of a migration buffer is important for the separation of Cr(III) and V(V). Tartrate, formate, citrate, acetate, malonate and monochloro acetate buffer solutions of pH 2-4 were examined, and the best results regarding the sensitivity and peak shapes were obtained with the use of a 0.1M acetate buffer as both sample and running buffers. The effect of the buffer pH on the electropherogram is shown in Figure 4. At pH 2.0 (Figure 2), the first peak is due to $[P\ (V^{v}\ Mo_{11})\ O_{40}]^{4-}$ and the second is due to the $[P(Cr^{III}Mo_{12})\ O_{40}]^{3-}$ anion; no peaks due to free isopolymolybdate species were observed. The addition of the Mo(VI)-P(V) reagent to the running buffer is not required, because the $[P(V^{V}Mo_{11})O_{40}]^{4-}$ and $[P(Cr^{III}Mo_{12}\ )\ O_{40}]^{3-}$ complexes were so kinetically stable and no degradation occurred during migration in the capillary. The electropherogram is shown in Figure 2 peak (a) is due to $[P(V^{V}Mo_{11})O_{40}]^{4-}$, and peak (b) is due to $[P(Cr^{III}Mo_{12})O_{40}]^{3-}$ which migrates faster through the capillary than $[P(Cr^{III}Mo_{12})\ O_{40}]^{3-}$, because the former carries the greater negative charge of -4. Both peaks were sharp and well separated.

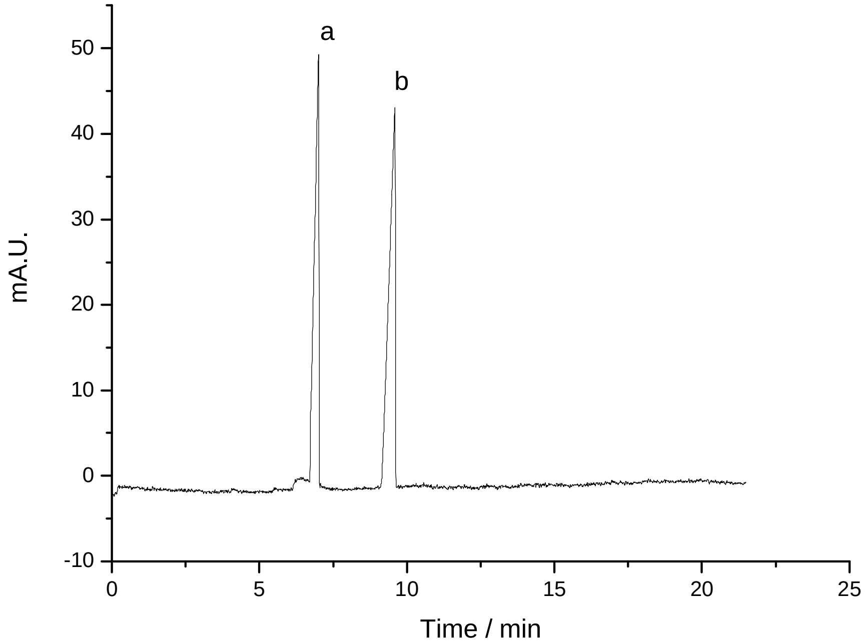

Figure 2. **An electropherogram for a test solution consisting of a 5.0 mM Mo(VI) – 0.5 mM P(V) – 0.1M acetate buffer (pH 2.0) containing 10.0 mgL^{-1} V(V) and 10.0 mgL^{-1} Cr(III). The running buffer; 0.1M acetate buffer (pH 2.0) (a) V(V) and (b) Cr(III) at 254 nm (applied Voltage = - 15 kV)**

Figure 3 shows the whole spectra of $PCr^{III}Mo_{12}$ and $PV^{V}Mo_{11}$. Different wavelengths (e.g. 200, 214, 220, 254, 280, 300nm etc.) were tested, 254nm was found to be best wavelength for the system.

The respective peaks heights were plotted against the buffer pH and the results are shown in Figure 4. The peaks height for $[P(V^{V}Mo_{11})O_{40}]^{4-}$ was greatest around pH 1.95 – 2.30 the corresponding value for $[P(Cr^{III}Mo_{12})O_{40}]^{3-}$ was practically constant in the pH range of 1.75 – 3.0. As a result, a pH 2.0 was chosen as being optional for the simultaneous CE determination of Cr(III) and V(V) at 254 nm.

After standing for some period (20 min) at room temperature, the test solution was introduced into a capillary thermo stated at 25±5^{o}C; the period is denoted as the reaction time. The peak heights for both chromium(III) and vanadium(V) were measured as a function of the reaction time, and are shown in Figure 5. The peak-heights for the Cr(III) speciation were not affected by the variation in the reaction time and temperature. On the other hand, the peak-height for the V(V) species with the reaction time at a room temperature (25±5^{o}C), and attained a constant value at a reaction time of 20 min. At a temperature of 25^{o}C, however, the peak height was independent of the reaction time. The temperature of the capacity system was set at 25°C, because reproducible results were obtained even when the test solution was introduced immediately after preparation. The reaction is rapid. A constant maximum absorbance was obtained just after 20 min of dilution to volume and remained strictly unaltered for 24 h Figure 5.

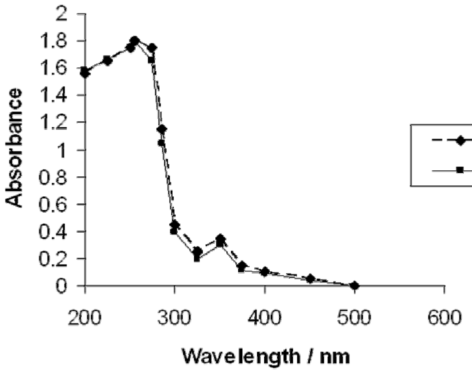

Figure 3. **UV-visible spectra for a 5 ×10^{-3} M of Mo(VI) - 5 ×10^{-4} M of P(V) system containing, 10 mgL^{-1} (a) Cr^{III} and (b) V^{V} in an aqueous solution of pH 2.0, path length 1.0 cm**

In order to optimized the Mo(VI) concentration in a sample solution to be determined, test solutions were prepared by varying the Mo(VI) concentration (1×10^{-3} - 1×10^{-2} M) while keeping [Cr(III)=V(V)]= 10mgL^{-1} in a 0.1M acetate buffer (pH 2.0). The test solutions were introduced into the capillary and electropherograms were recorded. In a series of electrophoretic measurements, a 0.1M acetate buffer (pH 2.0) was also used as a migration buffer. The optimum concentration of Mo(VI) was found to be 5×10^{-3} M. Similarly the optimum concentration of P(V) was found to be 5×10^{-4}M (0.5×10^{-3}M). A length 40 × 47 cm×50 μm i.d. fused silica capillary for the separation, 3.44KPa pressure for the sample injection; 10 to-25kV (preferably 10sec) for sample injection time, 7 – 7.8 min (preferably 7.4 min) for Cr and 9.0 – 9.9 min (preferably 9.5) for V were selected, these being a compromise between the sampling rate and the height of the peak Figure 2.

A well-known equation for photometric analysis in a very dilute solution was derived from Beer's law. The effect of the metal concentration was studied over 0.01 – 100 mg L^{-1} for both Cr(III) and V(V) distributed in two different sets (0.01 – 10.0 and 10 – 100 mg L^{-1}) for convenience of measurement.

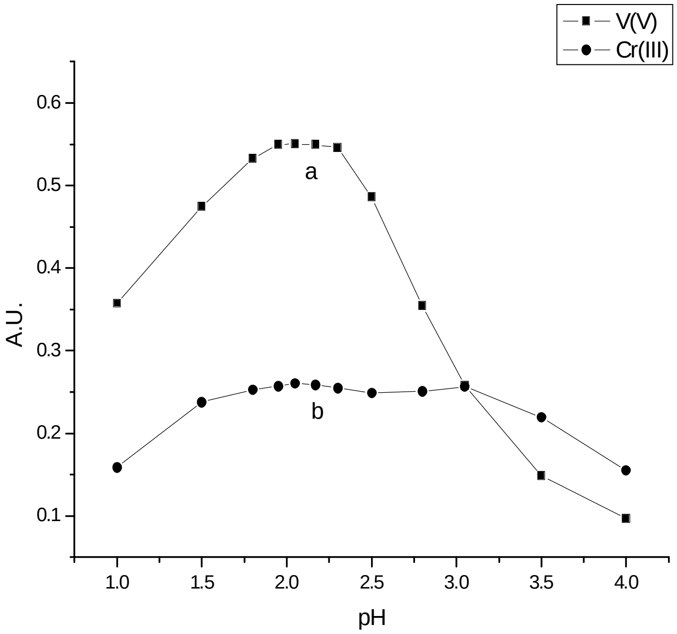

Figure 4. **Relationship between the sample pH and the peak-heights for (a) V(V) and (b) Cr(III). The test solution: 5.0 × 10^{-3}M of Mo(VI) – 5.0 × 10^{-4} M P(V) – 0.1 M acetate buffer containing 10 mg L^{-1} of V(V) and Cr(III). The running buffer, 0.1M acetate buffer (pH was adjusted to be the same as the sample buffer).**

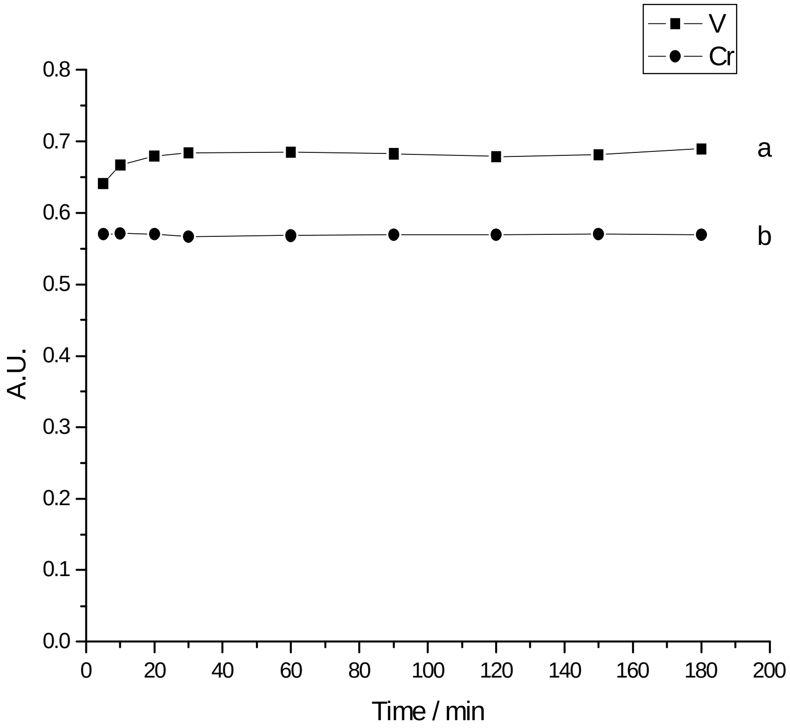

Figure 5. **Peak - height as a function of time for a 5.0 × 10^{-3} M Mo(VI) – 5.0 × 10^{-4} M P(V) – 0.1M acetate buffer (pH 2.0) system at room temperature(25±5) ^{0}C containing 20 mg L^{-1} (a) V(V) and (b) Cr(III) in an aqueous solution at 254 nm**

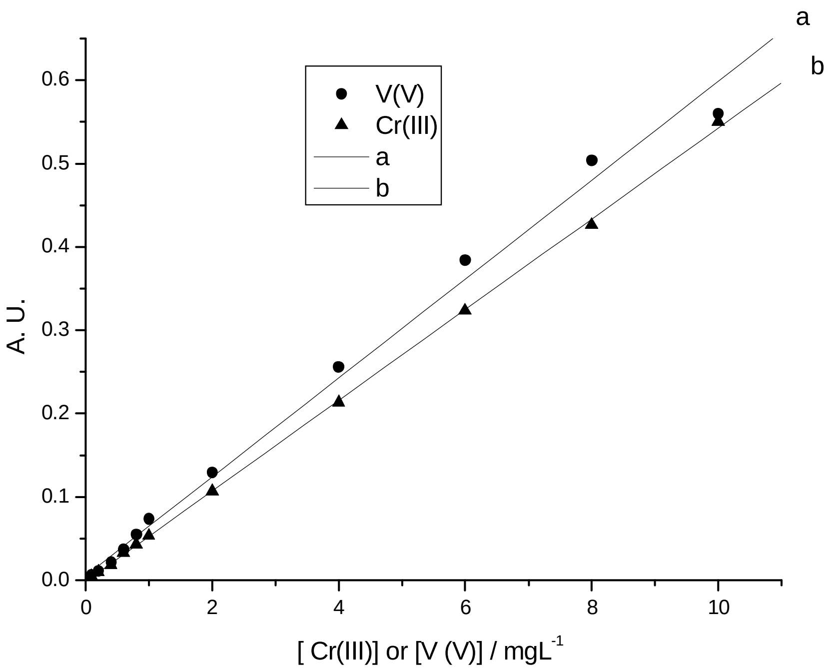

Figure 6. **Calibration graphs : (a) 0.05 – 10 mgL^{-1} of V(V) and (b) 0.06 - 10 mgL^{-1} Cr(III).**

The peak heights showed Figure 6 & 7 a linear dependence on the concentration of Cr(III) or V(V) in range of 0.06 – 60 mgL^{-1} or 0.05 – 80 mg L^{-1}, respectively. The correlation coefficients are 0.9998 and 0.997 for Cr(III) and V(V), respectively.

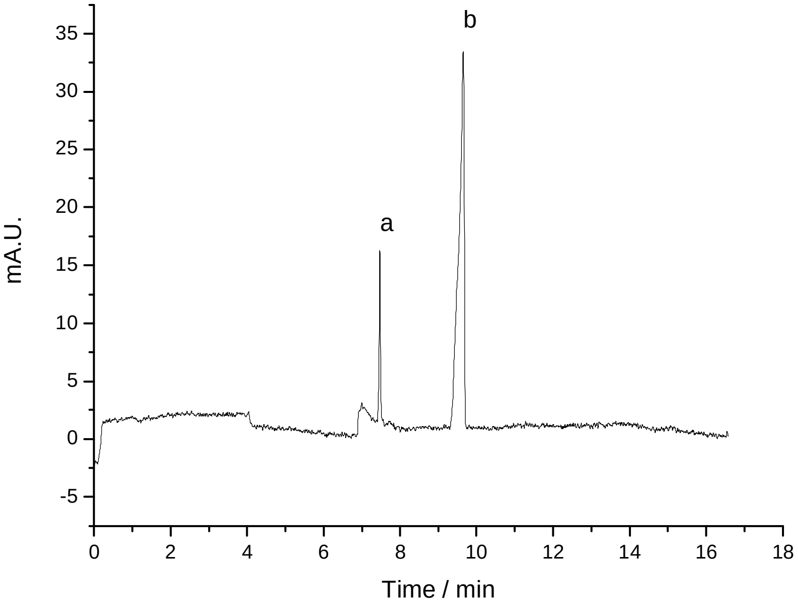

Figure 7. **Calibration graphs: (a) 10 – 80 mgL^{-1} of V(V) and (b) 10 - 60 mgL^{-1} Cr(III)**

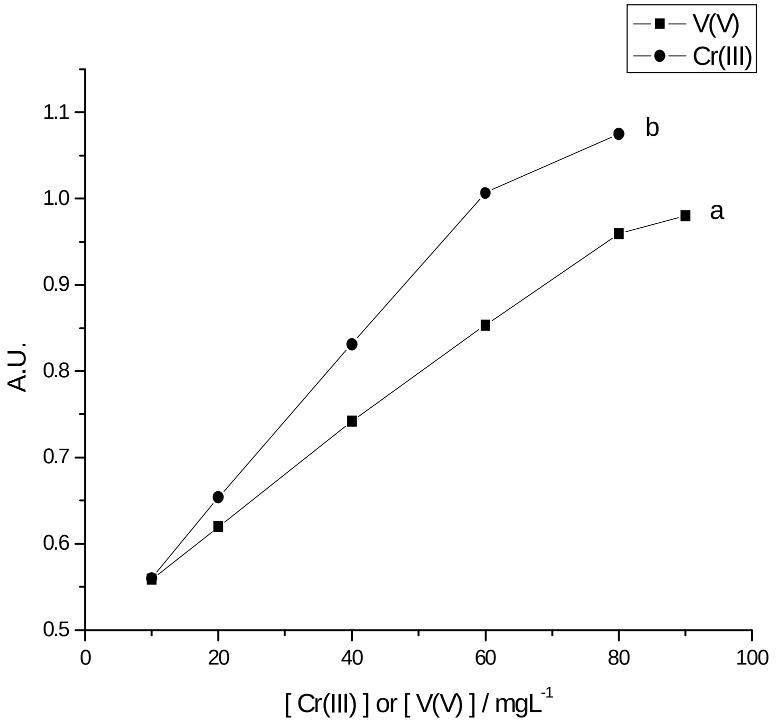

Figure 8. **An electropherogram for a Die steel sample solution containing of (a) 11.6 mgL^{-1} of Cr(III) and 0.41 mgL^{-1} V(V). The running buffer; 0.1M acetate buffer (pH 2.0)) at 254 nm. Electrophoretic conditions are identical to those shown in Fig. 2.**

Effect of foreign ions

The interference of several ions which may occur in environmental samples was studied by using a solution containing a mixture of Cr^{III} and V^{V} at concentration of 1 mg L^{-1}, adding where the relative error reached a value of about 5%. The errors were calculated by comparing the peak height to that obtained after injection of an aqueous solution of Cr^{III} and V^{V} containing no interfering ions, as reference. The results are summarized in Table 2. As can be seen, a large number of ions had no significant effect on the determination of Cr^{III} and V^{V}. The most serious interference was from V(IV) and Fe(III) ions. There is a possibility that these metal ions can also react with Mo(VI) in a migration buffer of pH 2. Their presence causes no serious errors because the mobility of the V(IV) and Fe(III) complexes are different from those of the Cr(III) and V(V). However, a greater tolerance limits for these ions can be achieved by using several masking methods. In order to eliminate the interference of V(IV) and Fe(III) ions, tartaric acid, EDTA or chloride can be used as masking agents.

Table 2. **Analytical features of the proposed method**

Parameter	Selected value for Chromium (III)	Selected value for Vanadium (V)
pH / Acidity (M)	2.0 / 0.1 M	2.0 / 0.1 M
Time	5 min – 24 h (preferably 25 min)	25 min – 24 h (preferably 25 min)
Temperature / ^{0}C (Temperature of capillary)	25 ± 5	25 ± 5
Separation time / min	7.0 – 7.8 (preferably 7.4)	9.0 – 9.9 (preferably 9.5)
Reagent [molar ratio, P(V) : Mo (VI)]	1 : 10	1 : 10
Linear range / mg L^{-1}	0.06 – 60	0.05 – 80
Detection limit / µg L^{-1} Quantization / µg L^{-1}	6.0 22.0	5.0 20.0
Reproducibility(% RDS)	0.2 – 2	0.1 – 2.5
Correlation coefficient (R^2)	0.9998	0.997

Evaluation of the Method

The reproducibility of the proposed procedure and sample throughput were determined by repeated injection of sample containing 1 mg L^{-1} Cr^{III} and V^{V}. The RSD (n=5) was 2-0.1% for 0.06-60.0 mg L^{-1} of Cr^{III} and 0.05-80.0 mg L^{-1} of V^{V} indicating that this method is highly precise and reproducible. The calibration graphs obtained from the peak heights were rectilinear for 60 µg L^{-1} to 60.0 mg L^{-1} of Cr^{III} and 50 µg L^{-1} to 80.0 mg L^{-1} of V^{V}, respectively. The correlation coefficients are 0.9998 and 0.997 for Cr^{III} and V^{V}, respectively. The limit of detection of 6.0 µg L^{-1} for Cr^{III} or 5.0 µg L^{-1} for V^{V}, for the photometric detection was calculated as the amount of metal ion, which produced a peak-height response equal to three times the detector baseline peak-to-peak noise. Important features of the proposed method for simultaneous determination of Cr^{III} and V^{V} are summarized in Table 3.

The analytical results must be evaluated with regard to the validity of the analytical method. Poor analytical quality may lead to false conclusions [20]. Keeping this in our mind the validity of our method was tested by analyzing several Standard Reference Materials, recovery studies and also comparing the results with conventional analysis (spectrophotometry). The performance and reproducibility of the proposed method are also shown in Table 4-5. The reliability of the proposed procedure was also assessed by Certified Reference Materials. The results for total Cr^{III} or V^{V} were in good agreement with certified values (Table 3). The method was also tested by analyzing synthetic seawater containing standard Cr^{III} and V^{V} (Table 4). The reliability of the proposed Procedure was also tested by performing recovery studies. The average percentage recovery obtained for the addition of Cr^{III} and V^{V} spike to some environmental water and synthetic sea water samples were quantitative as shown in Table 5. The results of tap and lake water and synthetic sea water analyses by the present method were in excellent agreement with those obtained by spectrophotometry (Table 5). The precision and accuracy of the method are satisfactory.

Table 3. **Tolerance limits of foreign ions**[a]

Species x	Tolerance ratio x/Cr^{III}(w/w)	Tolerance ratio x/V^V(w/w)
Ascorbic Acid	100	100
Ammonium(I)	500	500
Arsenic (III)	50^b	50^b
Arsenic (V)	50	50
Aluminum	100	100
Azide	50	50
Barium	100	100
Bismuth (III)	50b	50b
Bromide	100	100
Citrate	100	100
Chloride	100	100
Tartrate	1000	1000
EDTA	100	100
Fluoride	100	100
Chromium (VI)	10^{b+c}	10^{b+c}
Cobalt (II)	50	50
Cobalt (III)	100	100
Cadmium	100	100
Calcium	100	100
Cesium	100	100
Copper (II)	100	100
Iodide	100	100
Oxalate	100	100
Nitrate	50	50
Iron (II)	10^{b+c}	10^{b+c}
Iron (III)	50	50
Lead (II)	100	100
Manganese (II)	50^b	50^b
Mercury (II)	50^c	50^c
Nickel (II)	50	50
Potassium	100	100
Sodium	100	100
Tin (II)	50	50
Thiocyanide	100	100
Thallium(I)	50	50
Selenium(IV)	50	50
Tungsten(VI)	100	100
Vanadium (IV)	20^{b+c}	20^{b+c}
Zinc	100	100

[a] ***Tolerance limit defined as ratio that causes less than 5% interference***
[b] ***With 10mg L-1 EDTA***
[c] ***With 10mg L-1 Chloride***
[d] ***With 10mg L-1 Tartrate***

Applications

The proposed method was used to determine the total chromium and vanadium contents in a number of certified reference materials (alloys and steels) (Table 4). The method was also successfully applied to the simultaneous determination of chromium(III) and vanadium(V) content in a synthetic sea water (Table 5). The method also extended to the simultaneous determination Cr^{III} and V^V in a number of environmental waters. The samples were spiked with the concentration of Cr^{III} and V^V and recoveries determined (Table 5). The results of analyses of environmental waters by our procedure were in excellent agreement with those obtained by spectrophotometry (Table 5).

Determination of total chromium and vanadium in certified reference material

A 0.1g amount of an alloy or steel sample was accurately weighed into a 150 mL Teflon beaker and digested following a method recommended by Van Loon et al [21]. the beaker with the testing material and a mixture 10 mL of HF 2 mL $HClO_4$ and 10 mL HNO_3 were warmed slowly on a hot plate until complete dissolution was achieved. Then the temperature was increased to about 200^oC to evaporate the excess acid. The sample was cooled and dissolved the salt in 10 mL of 10% H_2SO_4 by warming. One mL of the working As^{III} solution was added to the resulting solution and boiled gently for 5 min to reduce Cr^{VI} to Cr^{III} completely which has no reducing effect for V^V [22]. The pH of the resulting solution was adjusted to 2.0 ± 0.1 using the dilute NH_4OH solution. The content of the beaker was filtered through a Whatman no.40 filter paper into a 25-mL calibration flask and made up the mark with deionized water. A suitable aliquot of the above-mentioned solution was taken into a 10-mL calibrated flask and chromium(III) and vanadium(V) content was determined, as described under procedure using tatrate or EDTA as masking agent. Based on five replicate analyses, the average chromium and vanadium concentration determined by the CE method was in close agreement with the certified values. The results are given in Table 4. The electropherograms for sample 1 and sample 2 are shown in Figure 8 & 9.

Table 4. **Recoveries of total chromium and vanadium for certified reference materials.**

Certified reference materiala[a] (composition,%)	Chromium,%		Recovery ± s[b], (%)	Vanadium,%		Recovery ± s[b], (%)
	Certified value	Found[c] (*n*=5)		Certified value	Found[c] (*n*=5)	
GSBH 40101-1996, Cr12Mo1V-Die steel C=1.50, Mn=0.155, P=0.0188, S=0.0089, Si=0.235, Cr=11.63, Ni=0.095, Cu=0.082, Mo=0.96, V=0.411, Co=0.02, Sn=0.0118	11.63	11.51	99 ± 1.0	0.411	0.405	98.5± 1.5
BH 1013-1, 9Cr17MoVCo-High-tensile steels. C=0.90, Cr=16.30, Si=0.44, Mo=0.52, Mn=0.81, P=0.042, V=0.24, S=0.046	16.30	16.15	99 ± 0.9	0.24	0.235	98 ± 2.0

[a] *This CRMs were obtained from Beijing NCS Analytical Instruments Co. LTD., P.R. China.*
[b] *The measure of precision is ± s.*
[c] *Average of five determination.*

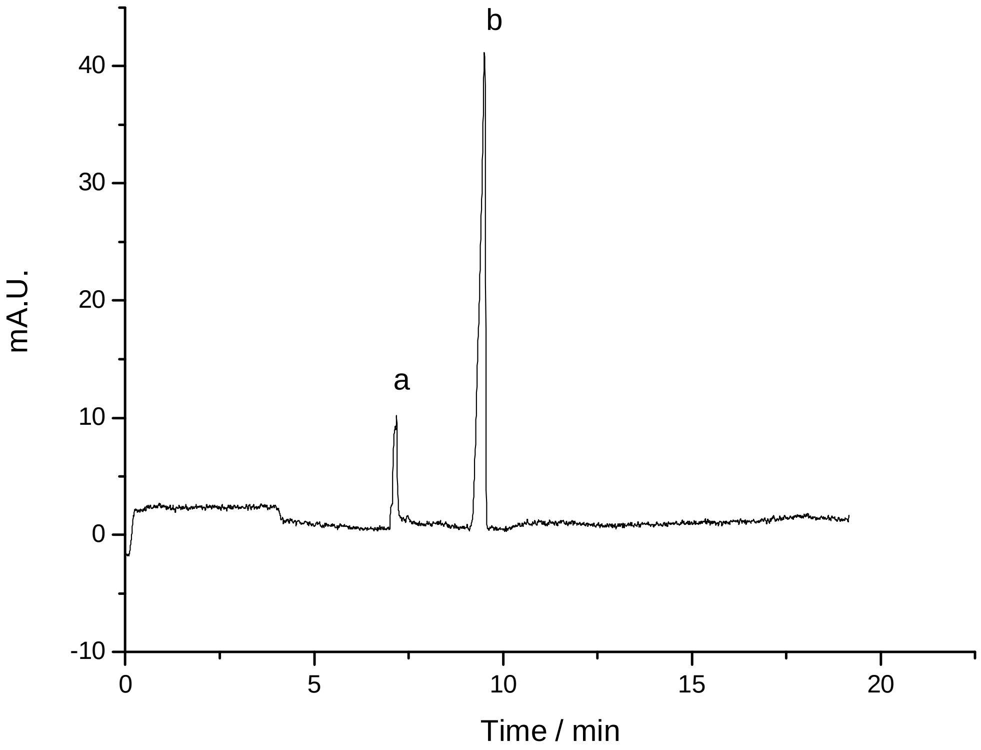

Figure 9. **An electropherogram for a High tensile steel sample solution containing of (a) 16.3 mgL^{-1} Cr(III) and (b) 0.24 mgL^{-1} of V(V). The running buffer; 0.1M acetate buffer (pH 2.0)) at 254 nm. Electrophoretic conditions are identical to those shown in Fig. 2.**

Determination of total chromium and vanadium in environmental water sample

Each filtered (with 0.22µm membrane filter) environmental water sample (500 ml) was evaporated nearly to dryness with a mixture of 5 mL of concentration H_2SO_4 and 10 mL of concentrated HNO_3 in a fume cupboard, following a method recommended by Mitra [23] and was then cooled to room temperature (25±5°C). The residue was then heated with 10 mL of deionized water in order to dissolve the salts. One mL of the working As^{III} solution and 5 mL of 0.1M acetic acid were added to the resulting solution and boiled gently for 5 min to reduce Cr^{VI}. The pH of the final solution was adjusted to 2.0±0.1 using dilute NH_4OH solution in presence of 1-2 mL of 0.01% (w/v) EDTA or tartrate solution. The resulting solution was filtered and quantitatively transferred into a 25-mL calibrated flask and made up to the mark with deionized water. A aliquot (1-2 mL) of this preconcentrated water sample was pipetted into a 10-ml calibrated flask and chromium and vanadium contents was determined as describe under procedure using EDTA or chloride as a masking agent. The proposed procedure for the simultaneous electrophoretic determination of chromium and vanadium was applied to the analysis of synthetic sea water. Synthetic sea water was prepared according to the procedure recommended by [24]. A typical electropherogram for V^v and Cr^{III} in spiked synthetic sea water is shown in Figure 10. The results of environmental analyses by the capillary electrophoretic method were found to be in excellent agreement with those obtained by spectrophotometry. The analyses of environmental water samples from various sources for total chromium and vanadium are given in Table 5.

Table 5. **Determination of chromium and vanadium in some environmental water samples.**

Sample	**Concentration of chromium / μgL^{-1}**					**Concentration of vanadium / μgL^{-1}**				
	Proposed CE method (*n*=5)			**Spectrophotometry (*n*=5)**		**Proposed CE method (*n*=5)**			**Spectrophotometry (*n*=5)**	
	Added	**Found[a]± s**	**Recovery %**	**Found[a]±s**	**Recovery %**	**Added**	**Found[a] ±s**	**Recovery %**	**Found[a]±s**	**Recovery %**
Tap Water	0	2.5		1.5		0	3.5		2.0	
	100	103 ± 0.5	100.5	102 ± 0.6	100.5	100	104 ± 0.7	100.5	101.5± 0.5	99.5
	500	504 ± 0.6	100.8	503 ± 0.8	100.3	500	508 ± 1.0	101.6	505 ± 1.0	100.6
Well Water	0	6.5		7.0		0	5.5		6.5	
	100	102 ± 0.8	99.5	106 ± 0.6	99.0	100	107 ± 0.7	101.4	106 ± 1.2	99.5
	500	509 ± 0.5	100.5	503 ± 0.8	100	500	508 ± 1.0	100.5	507 ± 1.5	100
Lake Watera[b]	0	12.8		15.0		0	16.5		17.0	
	100	115 ± 0.9	102	114 ± 1.5	99.1	100	118 ± 1.2	101.3	119 ± 1.2	101.7
	500	510 ± 1.0	99	513 ± 1.3	99.6	500	520 ± 1.5	100.7	507 ± 1.5	100.6
Synthetic Sea water[c]	0	0.0		0.0		0	0.0		0.0	
	100	102 ± 0.5	102	101 ± 0.5	101	100	103 ± 1.0	103	102 ± 0.4	102
	500	503 ± 0.8	100.6	500 ± 0.0	100	500	504 ± 0.6	100.8	502 ± 0.6	100.4

[a] ***Average of five replicate determinations***

[b] ***Weiming Lake, Peking University Campus, Beijing.***

[c] ***Composition of synthetic sea water[24] : $NaCl=24.72\ gL^{-1}$, $KCl=0.67\ gL^{-1}$, $CaCl_2,2H_2O=1.36\ gL^{-1}$, $MgCl_2,6H_2O=4.66\ gL^{-1}$, $MgSO_4.7H_2O=6.29\ gL^{-1}$, $NaHCO_3=0.18\ gL^{-1}$, Tris HCl(pH 8.2)=0.005M, H_2O= made up to 1L.***

In order to evaluate the quantitative performance of the method, several real samples were analyzed by using CE and conventional spectrophotometric methods. For the determination of total chromium, 1,5-diphenylcarbazide[25] and for vanadium, 5,7-dibromo- 8-hydroxyquinoline methods [26] were used, respectively. The results obtained by both techniques are compared in Table 5. Finally, the recovery tests were performed for samples spiked with metal species at various concentration levels. The mean recoveries were in the range 97-105% for all analytes studied. These results illustrate that CE offers promise for the simultaneous determination of metal ions in real samples.

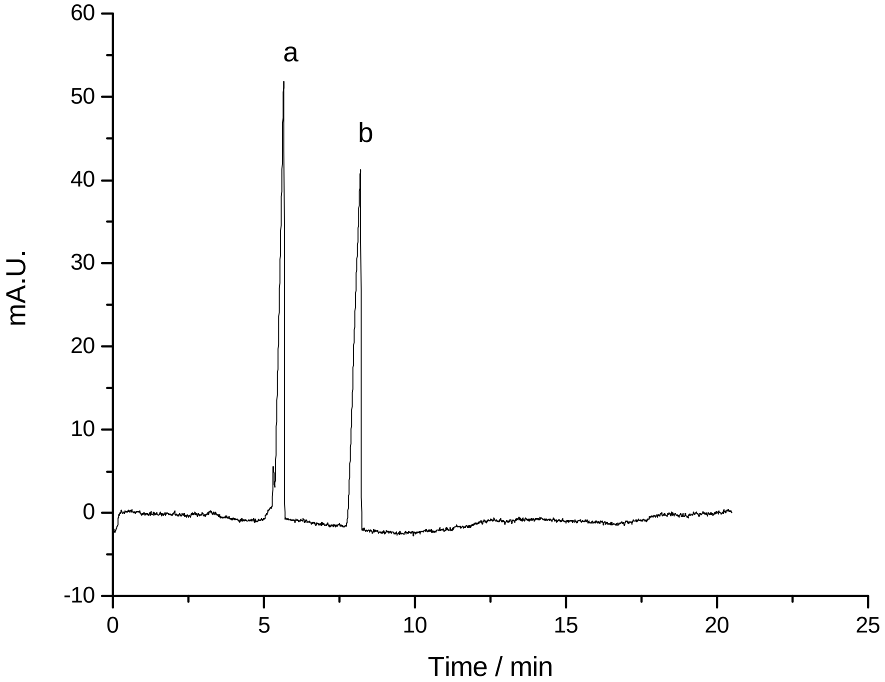

Figure 10. An electropherogram for a test solution consisting of synthetic sea water and a 5.0 × 10^{-3} M Mo(VI) – 5.0 × 10^{-4} M P(V) – 0.1M acetate buffer (pH 2.0) containing 10.0 mgL^{-1} V(V) and 10.0 mgL^{-1} Cr(III). The running buffer; 0.1M acetate buffer (pH 2.0) (a) V(V) and (b) Cr(III) at 254 nm (applied Voltage = - 15 kV) [Recovery = 110% for V(V) and 103% for Cr(III), n=3].

Conclusions

The results of this work demonstrate that Mo(VI)-P(V) reagent can be successfully used for simultaneous determination of metal ions by capillary electrophoresis. The pre-column complexation of both metal ions before the separation offers a possibility to determine both ions in a single run with a good determination using direct UV detection. The proposed method using Mo(VI)–P(V) reagent is not only one of the most sensitive and selective methods for the simultaneous determination of chromium and vanadium, but also excellent in terms of accuracy and simplicity. It is a new approach and could be an alternative to the rapid simultaneous determination of chromium and vanadium in the procedures reported earlier [22,27]. The sensitivity in terms of detection limits and precision in terms of relative standard deviation of the present method are very reliable for the determination of chromium and vanadium in real samples down to ng g^{-1} levels in aqueous medium at room temperature (25 ± 5°C).

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