

Extended Abstract

## A Simple High Performance Capillary 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 ( $25 \pm 5$  °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<sup>-1</sup> and 0.05 - 80 mgL<sup>-1</sup> of Cr(III) and V(V), respectively; the detection limits were 6.0 g L<sup>-1</sup> and 5.0 g L<sup>-1</sup> for Cr(III) and V(V), respectively. The influence of several experimental parameters on both sensitivity and efficiency was investigated. The interference from over 60 cations, anions and complexing agents has been studied at 1 mgL<sup>-1</sup> 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 ( $s = \pm 0.02$  for 0.5 mg L<sup>-1</sup>).

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. Capillary Electrophoresis (CE) is being increasingly applied for the determination of metal ions, primarily because of its great flexibility and easy implementation [13]. Separations of metal

ions that exist in a free, uncompleted 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 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 mobility's. 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 m 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 °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.

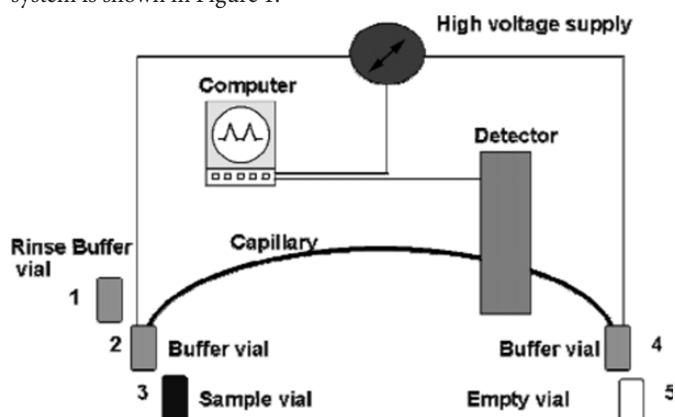


Fig. 1. Typical HPCE separation system

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### 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. Solutions of a large number of inorganic ions and complexing agents were prepared from their AnalR 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 0.1-1.0 mL of an aqueous solution containing 0.5 - 800 mg of vanadium(V) and 0.6 - 600 mg 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 °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 isotachopheresis 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.

### 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 1). The method was also successfully applied to the simultaneous determination of chromium (III) and vanadium (V) content in a synthetic sea water.

### 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 [14]. The beaker with the testing material and a mixture 10-mL of HF 2-mL HClO<sub>4</sub> and 10 mL HNO<sub>3</sub> were warmed slowly on a hot plate until complete dissolution was achieved. Then the temperature was increased to about 200°C to evaporate the excess acid. The sample was cooled and dissolved the salt in 10-mL of 10% H<sub>2</sub>SO<sub>4</sub> by warming. One mL of the working As<sup>III</sup> solution was added to the resulting solution and boiled gently for 5 min to reduce Cr<sup>VI</sup> to Cr<sup>III</sup> completely which has no reducing effect for V<sup>V</sup> [15, 16]. The pH of the resulting solution was adjusted to 2.0 – 0.1 using the dilute NH<sub>4</sub>OH 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 de-ionized 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 tartrate 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 1.

Certified reference material <sup>a</sup> (composition,%)	Chromium,	%	Recovery± sb (%)	Vanadium,	%	Recovery± sb, (%)
	Certified value	Foundc (n=5)		Certified value	Foundc (n=5)	
GSBH-40101-1996, Cr12Mo1VDie-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-Hightensile-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

- This CRMs were obtained from Beijing NCS Analytical Instruments Co. Ltd., P.R. China.
- The measure of precision is ±s.
- Average of five determinations

Table 1. Recoveries of total chromium and vanadium from certified reference materials.

### 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 [15,16]. 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<sup>-1</sup> levels in aqueous medium at room temperature (25 ± 5) °C.

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### References

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