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Spectrochimica Acta Part A 69 (2008) 911–916
SPECTROCHIMICA ACTA PART A
www.elsevier.com/locate/saa

Kinetic-spectrophotometric determination of trace amounts of vanadium(V) based on its catalytic effect on the reaction of DBM-arsenazo and potassium bromate

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Received 20 August 2006; accepted 18 May 2007

Abstract

A simple and sensitive kinetic-spectrophotometric method is developed for the determination of trace vanadium(V), based on the catalytic effect of vanadium(V) on the oxidation of DBM-arsenazo by potassium bromate in 0.0138 mol l^{-1} phosphoric acid medium and at 100 °C in the presence of citric acid as activator. The absorbance is measured at 528 nm with the fixed-time method. The optimization of the operating conditions regarding concentrations of the reagents, temperature and interferences are also investigated. The working curve is linear over the concentration range 0–20 ng ml^{-1} of vanadium(V) with good precision and accuracy and the detection limit was down to 3.44 ng l^{-1}. The relative standard deviation for a standard solution of 14 ng ml^{-1} is 0.28% ($n = 11$). The apparent activity energies of the catalytic reaction and the non-catalytic reaction are 73.48, 113.5 kJ/mol, respectively. The proposed method proved highly sensitive, selective and relatively rapid for the assay of vanadium at low-level range of 0–20 ng ml^{-1} without any pre-concentration step. Thw method was applied to the determination of vanadium(V) in steels, rice, flour, cabbage, potato, fish, shrimp and tea samples with satisfactory results. The obtained results for the steel samples were excellent agreement with the standard reference values. The analytical results of the rice, flour, cabbage, potato, fish, shrimp and tea samples were excellent agreement with those of atomic absorption spectrometry. The recovery experiments have been made for the rice, flour, cabbage, potato, fish, shrimp and tea samples except the steels; excellent results were obtained. The relative standard deviations were over the range of 0.18–2.60% and the recoveries were over the range of 98.00–102.4%, respectively. The analytical results obtained were satisfactory.

Keywords: Vanadium(V); Kinetic-spectrophotometry; DBM-arsenazo; Potassium bromate; Citric acid

1. Introduction

Vanadium exists in the +2 to +5 oxidation states with vanadium(V) being the most stable in solution, followed by vanadium(IV). Vanadium is a trace element of highly critical role in biochemical processes and of interest in environmental, biological and industrial analysis due to its toxicity. Owing to the toxic and essential nature of vanadium in biological and other systems, there has been considerable interest in the determination of its content in different kinds of samples. Instrumental techniques, such as inductively coupled plasma atomic emission spectrometry and mass spectrometry and atomic absorption spectrometry have been used for the determination of total vanadium, but for the determination of nanogram level or lower amounts, these techniques can be applied only after preliminary isolation and pre-concentration procedures and they need costly instruments. Especially for vanadium, the technique of atomic absorption has some drawbacks as [1]: (a) the line spectrum of vanadium is not excited in an oxygen–hydrogen or an oxygen–acetylene flame and nitrous oxide–acetylene flame is necessary, (b) at wavelength less than 3053.7 Å, all the vanadium lines suffer from inadequate emission intensity from hollow-cathode lamps. Lines between 3828.6 and 3855.8 Å lie in a region of very intense cyanogen bands and are too noisy even for atomic absorption, (c) the detection limit of the method depending on the applied flame and wavelength is ranging from 0.4 to 90 μg ml^{-1}, (d) increase of sensitivity can be obtained by using an electrothermal atomic absorption, unfortunately high signal instability causes a relative standard deviation of approximately 10%. Among several analytical techniques for the determination of vanadium, spectrophotometric methods are

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doi:10.1016/j.saa.2007.05.054

very popular due to their simplicity and low-cost instrumentation [2]. Kinetic methods afforded with spectrophotometric detection and based on the catalytic action of vanadium are more sensitive and due to their selectivity no preconcentration steps are necessary. Furthermore, these methods are relatively simple and easy to perform. The most of the methods are based on the catalytic effect of vanadium(V) on oxidation of organic compounds such as gallocyanine [3], 1,4-dihydroxyphthalimide dioxime [4], 3,5-diaminbenzoic acid dihydrochloride [5], perphenazine [6], *o*-phenylenediamine [7], metol [8,9], 1-naphthyl red [10], 5-Cl-PADAT [11], acid chrome blue K [12], beryllon III [13], etc., by an inorganic oxidant. All the above methods have their own characteristics as well as their drawbacks. Many of them lack either sensitivity or satisfactory selectivity or they have a limited dynamic range. Therefore, developing new kinetic spectrophotometric method for the determination of vanadium is still of interest. *p*-Methyldibromoarsenazo (DBM-ASA) is an azo dye reagent that has been used for the spectrophotometric determination of rare earths [14]. In this paper it is found that DBM-ASA can be oxidated by potassium bromate in a dilute phosphoric acid medium and trace amount vanadium(V) can catalyse this reaction. Citric acid was found to have a highly activating effect on the vanadium-catalyzed oxidation of DBM-ASA with bromate at the same time. An extremely sensitive, selective and simple method was developed for the determination of vanadium. The present method was successfully applied to the analysis of real samples of steels, rice, flour, cabbage, potato, fish, shrimp and tea samples with satisfactory results. In addition, the elementary discussion on the reaction mechanism is proposed.

2. Experimental

2.1. Reagents and solutions

All chemicals were of analytical-reagent grade. Doubly deionized water was used throughout.

Vanadium(V) stock standard solution (1.000 mg ml^{-1}) was prepared by dissolving 0.2296 g of ammonium metavanadate (NH_4VO_3, Shanghai Sanpu Chemical Engineering Co., Ltd., China) in 100 ml water. Working solutions were subsequently prepared before use by appropriate dilution of the stock solution. A 0.50 g l^{-1} (2.81×10^{-3} mol l^{-1}) solution was made by dissolving 0.5000 g *p*-methyldibromoarsenazo (DBM-ASA, Shanghai Changke Research Institute for Reagents, China) in 100 ml water. Potassium bromate (0.10 mol l^{-1}) solution was prepared by dissolving 1.6700 g potassium bromate (Shanghai Second Reagent Plant) in 100 ml water; citric acid solution (20.00 g l^{-1}) was prepared by dissolving 2.000 g citric acid (Beijing Chemical Engineering Plant) in 100 ml water; phosphoric acid (1.724 mol l^{-1}) solution was made by mixing appropriate volumes of water and concentrated phosphoric acid in the volume ratio 1:10.

2.2. Appatatus

A 722S spectrophotometer (Shanghai Lingguang Technique Co. Ltd., China) equipped with 1-cm quartz or glass cells was used for all absorbance measurements. The HH-4 digital display constant temperature water-bath boiler (Jintan City Ronghua Instrumental Manufacture Co. Ltd., China) was used for the control of temperature; a stopwatch was used for recording the reaction time.

2.3. Procedures

2.3.1. Recommended procedure for vanadium

A solution of less than 0.50 μg of vanadium was placed into a 25-ml calibrated flask, then 0.20 ml of 1.724 mol l^{-1} phosphoric acid solution, 2.00 ml of 20.00 g l^{-1} citric acid solution, 2.00 ml of 0.10 mol l^{-1} potassium bromate solution and 2.00 ml of 0.50 g l^{-1} DBM-ASA solution were added. The mixture was diluted to the mark with water. Shaking well, the mixture was placed in a boiling water bath for heating for 15 min and was rapidly taken out and cooled for 10 min by running water. The absorbance A_t was measured against water at 528 nm.The measurement in the absence of added vanadium was repeated to obtain the values A_o for the uncatalyzed reaction. The values $\Delta A = A_o - A_t$ or $\log(A_o/A_t)$ were calculated. From the previous values of standard vanadium solution, a calibration graph of change of absorbance at a fixed time versus vanadium concentration was constructed.

2.3.2. Determination of vanadium in steels

0.1000 g of steel sample was accurately weighed and 30 ml of hydrochloric acid (1 + 1, volume ratio) solution and 3.0 ml of hydrofluoric acid (1 + 1, volume ratio) solution were added. They were heated and dissolved. One millilitre of concentrated nitric acid was added and continuously heated and the steel was completely dissolved. Three millilitre of sulfuric acid (1 + 1, volume ratio) solution was added to it and heated and white vapor showed up. It was taken out, cooled and dissolved by 0.5 mol l^{-1} sulfuric acid. It was transferred to a 250-ml calibrated flask and was diluted to the mark with water. One millilitre of the aliquots of the above resulting solution was taken out and determined using the recommended procedure.

2.3.3. Determination of vanadium in rice and flour

Twenty gram of rice or flour sample was accurately weighed and placed into quartz crucible. Ten millilitre of concentrated sulfuric acid was added to it and evaporated to near dryness; then 10 ml of nitric acid (1 + 1, volume ratio) was added and evaporated to dryness. Under heating condition concentrated hydrogen peroxide was added by drop till the solution clearness and evaporated. Water was added and continued to heat to remove hydrogen peroxide. The residue cooled and was transferred into a 50-ml calibrated flask and diluted to the mark with water. Volumes of 2.00 ml of each of the aliquots were taken for the determination of vanadium via the recommended procedure under the established optimum conditions.

2.3.4. Determination of vanadium in cabbage and potato

The cabbage and potato samples were washed and cut into bar. Then the samples were dried at 110 °C for 4 h. Ten grams of the dried samples were accurately weighed and placed into