Kinetic Spectrophotometric Determination of Traces of Molybdenum(VI) by Its Inhibitory Effect on the Oxidation of 4-Hydroxycoumarin by Potassium Permanganate

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The present paper describes a simple, selective and sensitive kinetic method for the determination of trace amounts of molybdenum(VI) based on its inhibitory effect on the reaction oxidation of 4-hydroxycoumarin by KMnO_4 in the presence of hydrochloric acid, at pH 1.75 at 25°C. The rate of the indicator reaction was followed spectrophotometrically by measuring the decrease in the absorbance of KMnO_4 at 525 nm. The development method includes optimization of the reagent concentration and temperature. The calibration graph was linear in the range of concentrations from 20 to 200 ng/cm^3 of molybdenum(VI). The probable relative error was in the interval 3.10 – 10.52% for the concentration range of 200 – 20 ng/cm^3 molybdenum(VI), respectively. The interference effects of the foreign ions were determined to assess the selectivity of the method. The developed method was found to have relatively good selectivity, sensitivity, simplicity and rapidity. The proposed method was applied to the determination of molybdenum(VI) in a particular type of steel and alloy (hastelloy).

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Introduction

Molybdenum is a bio-essential element, and its occurrence in water samples is of interest from both environmental and chemical points of view. Molybdenum has an extremely important role in the metabolism of plants.¹ Molybdenum is added in trace amounts to fertilizers to stimulate plant growth. On the other hand, excess exposure can result in toxicity to animals and humans.² Molybdenum poisoning causes severe gastrointestinal irritation with diarrhea, coma ruminants and death from cardiac failure.² From an analytical point of view, it is important to find a selective and sensitive method for determination of molybdenum(VI). This can be carried out by atomic absorption spectrometry at the 313.3 nm molybdenum resonance line, using either flame (nitrogen oxide-acetylene) or electrothermal atomization as well as plasma emission. Both methods are disadvantageous in terms of cost and the instruments used in routine analysis.^{3–6}

Sensitive techniques for the determination of trace amounts of molybdenum include inductively coupled plasma-atomic emission spectrometry (ICP/AES)^{7–9} and neutron activation analysis (NAA).^{10,11} The high instrumental costs and need for preconcentration and/or separation are common disadvantages.

Spectrophotometric methods in which a number of reagents have been proposed in aqueous solutions are most commonly used for the determination of molybdenum. Most of them show poor selectivity or sensitivity, or the conditions of the color reaction, such as the pH, must be strictly controlled in order to obtain reliable results.^{12–14}

On the other hand, kinetic methods of analysis are very

simple, and inexpensive alternatives for molybdenum determination.^{15–20} The aim of this study was to develop a simple kinetic-spectrophotometric method for the determination of traces of molybdenum(VI). An indicator reaction (oxidation of 4-hydroxycoumarin by KMnO_4) has not previously been used for the kinetic determination of traces of molybdenum(VI). This paper reports on its use in a simple, sensitive, selective and inexpensive kinetic method for the determination of trace amounts of molybdenum(VI) based on its inhibitory effect on the reaction oxidation of 4-hydroxycoumarin by KMnO_4 in the solution at pH 1.75, at 25°C. The reaction is carried out by spectrophotometric measurements of the dependence of the absorbance (A) at 525 nm on time (s). The rate of the reaction decreases proportionally with increasing concentration of molybdenum(VI).

Experimental

Apparatus

A UV-VIS Perkin-Elmer Lambda 15 spectrophotometer with thermostated cylindrical cells (length of 10 cm) was used for absorbance measurements.

The pH was measured by means of a radiometer (PHM 29Bb pH-meter) and a combined glass-calomel electrode (GK2311C). Sigma buffers, pH 7 $\pm$ 0.01 and pH 4 $\pm$ 0.01, were used to calibrate the pH meter. All solutions were kept in a thermostatic water-bath at 25°C before beginning the reaction. Spectrophotometric measurements were done at a wavelength of 525 nm.

Reagents

Analytical-grade reagents, deionized water and polyethylene vessels were used throughout this study. A solution of KMnO_4 of $2 \times 10^{-2} \text{ mol/dm}^3$ was prepared from an ampoule produced by

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Fig. 1 Effect of time on the determination of Mo(VI). Experimental conditions: 3.6×10^{-5} mol/dm³ of KMnO₄; 3×10^{-5} mol/dm³ of 4-hydroxycoumarine; pH, 1.75; 25°C. Mo(VI) concentration: 0, 0; 1, 20; 2, 50; 3, 100; 4, 150; 5, 200; 6, 300; 7, 400 ng/ml.

“Merck” by dissolving in a calibrated volumetric flask. The solution of KMnO₄ was saved in a dark reagent flask. Before the experiment, the concentration of the solution was checked spectrophotometrically at 525 nm. Further dilutions were made using this stock solution when needed (dilution was done with deionized water). A 1×10^{-3} mol/dm³ solution of 4-hydroxycoumarine was prepared by dissolving 0.16414 g of the solid in 10 cm³ of 0.1 M NaOH to improve the solubility of 4-hydroxycoumarine and diluting with deionized water to 1 dm³ in a calibrated volumetric flask. The solution of HCl (0.2 mol/dm³) was prepared from a 37% concentrated HCl solution. A standard solution of molybdenum(VI) 1000 µg/cm³ was prepared by dissolving 2.0425 g (NH₄)₂MoO₄ in 1 dm³ deionized water, with conductivity less than 0.5 µS. The exact concentration was determined volumetrically.

Procedure

The initial concentration of each of the reactants was in turn systematically varied, while the initial concentrations of the reactants were kept constant. Selected volumes of the reactants were put into a 20 cm³ standard flask in the order 4-hydroxycoumarine, 0.2 M solution of HCl, standard solution of molybdenum(VI) and deionized water to make up exactly to the predetermined volume. The flasks were kept in a thermostat for 10 min at a temperature of $25 \pm 0.1^\circ\text{C}$ before beginning the reaction. The solution was then made up to the mark with KMnO₄, and vigorously shaken, and a chronometer was simultaneously turned on. The cell of the photometer was rinsed well and filled with the prepared solution. During the reaction, the color of the solution disappeared and a colorless reaction product was formed. The absorbance (A) at 525 nm was measured after adding a solution of KMnO₄, starting from 30 s every 15 s over a period of 5 min of the reaction. The initial concentrations of the reagent solutions after dilution to 20 cm³ were: 1×10^{-5} – 4×10^{-5} mol/dm³ of 4-hydroxycoumarine; 1.5×10^{-5} – 4.5×10^{-5} mol/dm³ KMnO₄; 1.0×10^{-2} – 5.62×10^{-2} mol/dm³ H₃O⁺ ions; 20 – 200 ng/cm³ molybdenum(VI).

The dependence absorbance (A) vs. time (t) is presented in Fig. 1. The rate of the reaction decreases proportionally with increasing concentration of molybdenum(VI). The variation in the absorbance of KMnO₄ vs. time was started to be measured 30 s after the addition of KMnO₄ in the solution. The differential variant of the fixed time method was used for processing the obtained kinetic data.^{21,22} The measured kinetic

Fig. 2 Dependence of the reaction rate on the pH. Initial conditions: 3.6×10^{-5} mol/dm³ of KMnO₄; 3×10^{-5} mol/dm³ of 4-hydroxycoumarine. Mo(VI) concentration: curve 1, 400 ng/cm³; curve 2, 0 ng/cm³; $25 \pm 0.1^\circ\text{C}$.

parameter was ΔA vs. time (s), the difference between the absorbance of the indicating and inhibiting reactions corresponding to the same reading times (195 s). From Fig. 1, it follows that the maximum difference in the absorbance between the indicating (curve 0) and inhibiting reactions for different concentration of molybdenum(VI) (curves 1 – 7) occurred at 195 s.

Recommended procedure for measurements

First, 3 cm³ of a 1×10^{-3} M prepared solution of 4-hydroxycoumarine, 9 cm³ of a 0.2 M solution of HCl, and 20 cm³ of deionized water were placed in a reagent flask. From that mixture, 6.4 cm³ was taken and put in three polyethylene vessels (I, II, and III). To the first vessel (I) was added 10 cm³ deionized water, and to the second vessel (II) was added 10 cm³ of the solution sample of molybdenum(VI). The solutions were thermostated at $25 \pm 0.1^\circ\text{C}$ before the reaction began. A solution of KMnO₄ (2×10^{-4} M) was prepared by diluting a standard solution of KMnO₄ (2×10^{-2} M), and was also thermostated for 10 min before the reaction began at $25 \pm 0.1^\circ\text{C}$; then, to the first vessel (I) and to the second vessel (II) were added 3.6 cm³ of a 2×10^{-4} M solution of KMnO₄, and ΔA was measured for 195 s after the reaction began. An unknown concentration of Mo(VI) was calculated by Eq. (1). Then, 5 cm³ of the sample solution of molybdenum(VI) and 5 cm³ of the standard solution of molybdenum(VI) in equal concentrations were placed in vessel (III); after adding KMnO₄, ΔA was measured for 195 s, after beginning of reaction. All procedures mentioned above were carried out at a temperature of $25 \pm 0.1^\circ\text{C}$. The absorbance of the colored solution was measured at 525 nm. Finally, the unknown concentration of molybdenum(VI) was calculated by the method of standard addition.

Results and Discussion

Effect of the reaction parameters

In order to establish the optimum conditions for the determination of molybdenum(VI), the influence of the pH as well as the KMnO₄ and 4-hydroxycoumarine concentrations were studied on the indicating and inhibiting reactions by the fixed-time method.

Keeping all other experimental parameter constant, we studied the influence of the pH on the system in the range 1.2 – 2.0 (Fig. 2). It can be seen that the greatest difference between the rates of the indicating and inhibiting reactions occurred at pH 1.75, when molybdenum(VI) maximally decreased the reaction rate.

Fig. 3 Dependence of the reaction rate on the 4-hydroxycoumarine concentration. Initial conditions: 3.6×10^{-5} mol/dm³ of KMnO₄; pH, 1.75. Mo(VI) concentration: curve 1, 400 ng/cm³; curve 2, 0 ng/cm³; $25 \pm 0.1^\circ\text{C}$.

Fig. 4 Dependence of the reaction rate on the KMnO₄ concentration. Initial conditions: 3×10^{-5} mol/dm³ of 4-hydroxycoumarine; pH, 1.75. Mo(VI) concentration: curve 1, 400 ng/cm³; curve 2, 0 ng/cm³; $25 \pm 0.1^\circ\text{C}$.

Fig. 5 Dependence of the reaction rate on the Mo(VI) concentration. Initial conditions, 3.6×10^{-5} mol/dm³ of KMnO₄; 3.0×10^{-5} mol/dm³ of 4-hydroxycoumarine; pH, 1.75; 1, temperature $20 \pm 0.1^\circ\text{C}$; 2, temperature $25 \pm 0.1^\circ\text{C}$.

For further work, a pH of 1.75 was chosen.

The dependence of ΔA on the 4-hydroxycoumarine concentration is shown in Fig. 3. The maximum difference between the rates of the inhibited and the indicated reactions occurred for concentrations of 3×10^{-5} mol/dm³ of 4-hydroxycoumarine. For further work, a concentration of 4-hydroxycoumarine of 3×10^{-5} mol/dm³ was selected as the optimal value.

The dependence of ΔA on the concentration of KMnO₄ is

Table 1 Accuracy and precision of molybdenum(VI) determination

Taken (μ) (ng/cm ³)	Found (x) (ng/cm ³)	n	$\frac{100ts}{\bar{x}\sqrt{n}}$, %	$\frac{\bar{x}-\mu}{\mu}$, %
20	23	5	10.52	15.0
50	54	5	6.44	8.0
100	94	5	3.84	-6.0
200	190	5	3.10	-5.0

$\bar{x}$, Mean value; μ , true value; s , standard deviation; t , Student's test for 95% confidence; $100ts/\bar{x}\sqrt{n}$, precision; $(x - \mu)/\mu$, accuracy.

shown in Fig. 4. The maximum difference between the rates of the inhibited and indicated reactions occurred for concentrations of 3.6×10^{-5} mol/dm³ of KMnO₄. For further work, a concentration of KMnO₄ of 3.6×10^{-5} mol/dm³ was selected as the optimal value.

Calibration graph

For the optimal conditions described above, a calibration graph was prepared at 2 different temperatures of $20 \pm 0.1^\circ\text{C}$ (Fig. 5, line 1) and $25 \pm 0.1^\circ\text{C}$ (line 2). There is a linear relationship between ΔA and the molybdenum(VI) concentration from 20 to 200 ng/cm³ at 525 nm. Line 2 at $25 \pm 0.1^\circ\text{C}$ is steeper, which makes it more sensitive for the molybdenum(VI) determination. Rigorous control of the temperature is necessary to attain the good precision and accuracy of the results.

Based on calibration graph (2), for $25 \pm 0.1^\circ\text{C}$, an unknown concentration of molybdenum(VI) can be determined by the following equation, which was obtained by the least-squares method:

$$C_{\text{Mo(VI)}} = \frac{0.8 - \Delta A}{0.0018} \text{ (ng/cm}^3\text{)} \quad (1)$$

where ΔA is the change in the absorbance of the indicator substance (KMnO₄) after 195 s from beginning the reaction.^{20,21}

Accuracy and precision

In order to assess the precision and accuracy of the proposed method, the reaction rates were determined for five replicate determinations²³ (Student's criteria) at each of four different molybdenum(VI) concentrations in the range of the calibration graph (20.00, 50.00, 100.00, 200.00 ng/cm³).

The probable relative error ranged from 10.52% to 3.10% for concentrations of molybdenum(VI) from 20 to 200 ng/cm³. The results are presented in Table 1.

Interference study

To access the selectivity of the method, the influence of some foreign ions on the inhibited reaction rates was studied, under the optimal conditions mentioned above, at a constant molybdenum(VI) concentration of 200 ng/cm³. The results are summarized in Table 2. This table shows that the Au³⁺ ion seriously interferes with the determination of Mo(VI).

Application

The method was applied to the determination of molybdenum(VI) in steel and an alloy (hastelloy), which is resistant in corrosion gases. The obtained amount of molybdenum(VI) in the analyzed sample of steel was 1.61%. The obtained amount of molybdenum(VI) in the analyzed sample of alloy (hastelloy) was 17.70%. The results obtained

Table 2 Effect of foreign ions on the determination of 200 ng/cm³ of Mo(VI)

Tolerance limit Foreign ion/Mo(VI)	Ion added
104	Cl ⁻ , Na ⁺ , K ⁺ , NH ₄ ⁺ , Mg ²⁺ , Sr ²⁺ , Ba ²⁺ , Ca ²⁺ , NO ₃ ⁻ , SO ₄ ²⁻ , Cl ⁻ , CH ₃ COO ⁻ ,
400	Sn ²⁺ , Pb ²⁺ , Hg ²⁺ , Cd ²⁺ , Ni ²⁺ , Co ²⁺
> 250	Pd ²⁺ , Pt ²⁺ , Cu ²⁺ , Zn ²⁺ , Ti ⁴⁺ , Zr ⁴⁺
200	Al ³⁺ , Cr ⁶⁺
200	Fe ³⁺
100	Bi ³⁺ , Sb ³⁺ , As ⁵⁺
50	PO ₄ ³⁻ , SCN ⁻ , C ₄ O ₄ ²⁻ , citrates
40	Ag ⁺
10	V ⁵⁺
5	WO ₄ ²⁻
1	Au ³⁺

for both samples are summarized in Table 3. When the results from the proposed method are compared with the results from the AAS measurements for the same samples, it can be concluded that the proposed method is in a good agreement with AAS method.^{24,25} For determining an unknown amount of molybdenum(VI) in samples, the method of standard addition was used.

Conclusion

This work describes a relatively inexpensive, rapid, simple and sensitive kinetic method for the determination of trace amounts of molybdenum(VI) based on the its inhibitory effect on the reaction oxidation 4-hydroxycoumarine by KMnO₄ at pH 1.75. The method was applied to the determination of molybdenum(VI) in steel and an alloy (hastelloy), with a satisfactory sensitivity and selectivity.

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Table 3 Determination of molybdenum(VI) in samples (%)

Sample	Proposed method ^a	AAS method ^a	RSD, % ^b
Steel 93.78% Fe, 1.56% Mo, 2.8% Cr, 0.92% V, 0.55% Mn, 0.39% C	1.61	1.56	2.70
Alloy (hastelloy) 14.14% Cr, 57.86% Ni, 16.85% Mo, 5.15% W, 6.00% Fe	17.70	16.85	3.92

a. Average values of 5 separate determinations.

b. RSD for the proposed method.

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