Available online at www.sciencedirect.com
ScienceDirect
J China Univ Mining & Technol 18 (2008) 0613–0617
JOURNAL OF CHINA UNIVERSITY OF MINING & TECHNOLOGY
www.elsevier.com/locate/jcumt

Catalytic effects of trace ruthenium on oxidation of dimethyl yellow with bromate and its application

ZHOU Zhi-rong[1], WANG Qun[2], ZHANG Shu-yuan[2]

[1]*College of Public Health, Guangdong Pharmaceutical University, Guangzhou 5102400, China*
[2]*Hospital of East China University of Technology, Fuzhou, Fujian 344000, China*

Abstract: A spectrophotometric method for the determination of ruthenium(III) is described, based on its catalytic effect on the oxidation reaction of dimethyl yellow (DMY) with potassium bromate in an acid solution medium and in the presence of an OP emulsifier (*p*-*iso*-octyl phenoxy polyethoxy ethanol) at 100 °C. This reaction was followed spectrophotometrically by measuring the decrease in the absorbance at 530 nm of the catalytic reaction of DMY. The calibration curve for the recommended method was linear in the concentration range over 0.0–1.0 μg/L and the detection limit of the method for Ru(III) was 0.01 μg/L. The method is highly sensitive, selective and very stable and has been successfully applied for the determination of trace amounts of ruthenium in some ores and metallurgy products with the relative standard deviations (RSD) over 1.6%–2.8% and a recovery over 98.7%–104.0%.

Key words: analytical chemistry; ruthenium; catalytic spectrophotometry; dimethyl yellow; potassium bromate

1 Introduction

Due to its relatively high sensitivity, simple instrumentation and simplicity, kinetic methods attract the interest of scientists in the field of analytical chemistry of platinum metals where it is frequently necessary to analyze samples of very small amounts of these metals. Ruthenium and its chloro-complexes, particularly in their tervalent oxidation state, have attracted attention in recent years because of their use in homogeneous and heterogeneous catalyses of the oxidation of a wide range of organic substrates.

Recently, some methods for the determination of ruthenium have been reported in the literature, including analytical techniques such as proton activation analysis, fluorescent quenching, inductively coupled plasma mass spectrometry and atomic absorption spectroscopy[1–4]. Many of these methods suffer from more or less time consuming procedures, complicated and expensive instrumentation, toxicity and unavailability of the required reagents. The catalytic-kinetic spectrophotometric method has received considerable attention because of its significant advantages in the determination of many components at trace levels. Various catalytic kinetic methods for the determination of ruthenium have been reported, especially on the oxidation reactions of organic reagents by IO_4^- and H_2O_2[5–6]. The catalytic effects of ruthenium on a number of redox reactions like H_2O_2-arsenazo III (AsA III), IO_4^--azure I (AzU I), IO_4^--pyronine GS (PGS), IO_4^--pyronine B (PB), $Fe(CN)_6^{3-}$-benzylamine (BA), IO_4^--Cotton blue (CB), BrO_3^--aniline blue (AB), BrO_3^--Arsenazo M (AsA M), IO_4^--acridine red (AR), IO_4^--orange G (OG), IO_4^--arsenazo-DBM (AsA DBM) and IO_4^--chromotrope 2R (CMT 2R) have been used for the determination of ruthenium[7–18].

DMY(dimethyl yellow) is an important acid-base indicator, which has been extensively applied in titration and is also an important redox indicator in catalytic kinetic spectrophotometry where it has been used for the highly sensitive determination of Se(IV), Pd(II), Ti(IV) and other elements by kinetic methods[19–21]. Empirically, it was found that ruthenium could catalyze the oxidation of DMY by $KBrO_3$ in an acidic medium and in the presence of an OP emulsifier at 100 °C, where it has been used for the kinetic determination of ruthenium by measuring the decrease in absorbance. The method is highly sensitive, selective and very stable and has been tested for the determination of trace amounts of ruthenium in some ores and metallurgy samples with satisfactory results.

Received 16 March 2008; accepted 11 June 2008
Project 2007GGW03 supported by the Science Research Foundation of Guangdong Pharmaceutical University
Corresponding author. Tel: +86-13265359863; E-mail address: zhouzhirong1965@sina.com

2 Experimental

2.1 Reagents and equipment

Absorption spectra were recorded on a Shimadzu Model UV-260 Spectrophotometer with a 1-cm glass cell. Another Model, A 721-A Spectrophotometer with a 1-cm glass cell was used for absorbance measurements at a fixed wave length. A water bath with a Model 501 thermostat was used to control the reaction temperature. A stopwatch was used for recording the reaction time.

Analytical reagent grade chemicals and doubly distilled water were used throughout for the preparation of solutions.

A standard stock ruthenium(III) solution (1.00 mg/mL, containing 1.2 mol/L hydrochloric acid) was prepared by the chlorization in a sealed tube following the protocol by Liu et al[9], with 0.1000 g of pure ruthenium power (99.9%). Working solutions were obtained by appropriate dilution of the stock standard with a 0.01 mol/L hydrochloric acid solution.

A solution of DMY (2.5×10^{-4} mol/L) in ethanol, a 1.0% solution of OP emulsifier, an aqueous solution of 0.05 mol/L potassium bromate and a solution of 0.1 mol/L sulfuric acid were used.

2.2 Experimental method

An appropriate amount of standard Ru(III) solution was placed in a 50-mL test tube for the catalyzed reaction, and then the tube was diluted to 10 mL. A drop solution of 2, 4-dinitrophenol was added to the tube. The solution in the tube was adjusted to a yellow appearance with a 7.0 mol/L $NH_3{\cdot}H_2O$ solution, adjusted until the yellow colour had disappeared, with a 0.1 mol/L H_2SO_4 solution. A 2.0 mL DMY solution, a 1.5 mL OP emulsifier solution, a 1.5 mL sulfuric acid solution and 2.0 mL of potassium bromate were added into the tube successively. The solution in the tube was diluted to 25.0 mL with water, then shaken well using semi-closed plugs and was then heated for 10 minutes at 100 °C in the water bath with the thermostat. The solution was then cooled to room temperature by placing it under running tap water for 5 min. An uncatalyzed system was prepared in the same manner, replacing the Ru(III) solution with double distilled water. After this, the absorbance A of the catalyzed solution and the absorbance A_0 of the uncatalyzed solution were measured at room temperature in a 1-cm cell at 530 nm against a distilled water reference and ΔA ($=A_0-A$) was calculated.

3 Results and discussion

3.1 Absorption spectra

The absorption spectra of the catalytic and noncatalytic systems against water in the range of 450–610 nm were recorded. Fig. 1 shows the absorption spectra of solutions according to the general procedure. The results suggest that the absorbance values of different systems reach their maximum at 530 nm. The decolorizing oxidation of DMY with $KBrO_3$ in this acid medium is very slow. Fig. 1 indicates that the oxidation of DMY by $KBrO_3$ is catalyzed in the presence of trace amounts of Ru(III). The acceleration effect was greater when Ru(III) was present in the system. The difference in absorbance (ΔA) has a quantitative relationship with Ru(III) concentration within a prescribed range. Therefore, trace amounts of Ru(III) can be determined at 530 nm by using spectrophotometry. The determination was therefore carried out at 530 nm throughout our experiment.

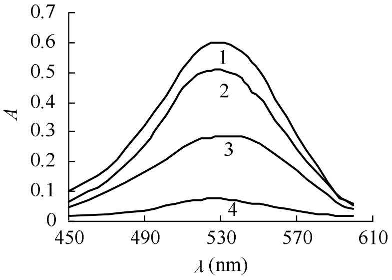

Fig. 1 Absorption spectra: 0.08 mol/L sulfuric acid; 2.0×10^{-5} mol/L dimethyl yellow; 0.06% OP emulsifier, 0.004 mol/L potassium bromate; 100 °C

1. H_2SO_4 + DMY + OP; 2. H_2SO_4 + DMY + $KBrO_3$+ OP;
3. H_2SO_4 + DMY + $KBrO_3$ + OP + 0.01 μg Ru (III);
4. H_2SO_4 + DMY + $KBrO_3$ + OP + 0.02 μg Ru (III)

3.2 Effects of medium and acidity

Under the same conditions, several mineral acids including H_2SO_4, HCl, H_3PO_4, HNO_3 and HOAc were tested according to our experimental method. The experimental results show that the oxidation of DMY by $KBrO_3$ catalyzed by Ru(III) should preferably be carried out in a weak, acidic medium. We established that the determinations should be carried out in a H_2SO_4 solution because the use of a H_2SO_4 solution gave the highest values of ΔA.

In order to achieve better sensitivity, various dosages of H_2SO_4 solution were applied to study their effect on the absorbance signal. The absorbance difference (ΔA) was found to reach a maximum and remained unchanged when using dosages of H_2SO_4 in the range of 1.0–2.0 mL. Whole heartedly, we accepted therefore a reagent dosage of 1.5 mL and used this throughout all our determinations.

3.3 Effects of reagent dosage

The concentrations of dimethyl yellow exhibited profound effects on the measurements of the amounts of Ru(III). At high concentrations, the rates of the uncatalyzed reactions increased, which decreased the values of ΔA. In addition, the background absorbance A_0 was so great that the error of the instrument reading increased. When the concentrations of DMY were