



Janus Green Dye as a New Reagent for Catalytic Kinetic Determination of Zirconium in Ceramic Materials

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ABSTRACT

A new catalytic kinetic spectrophotometric procedure for determination of trace quantities of zirconium was proposed. Janus Green was oxidized by potassium bromate and zirconium catalyst which then converted to a colorless product in acidic media. Reaction rate was monitored spectrophotometrically at 606 nm. It relies on the linear relationship between the absorbance difference (ΔA) and Zr(IV) amounts in the range of 0.1-250 $\mu\text{g ml}^{-1}$. Under optimum conditions, the sensitivity of the proposed method, i.e. the detection limit corresponding to 3 min is about 0.08 $\mu\text{g ml}^{-1}$. The method is featured with good accuracy and reproducibility for zirconium(IV) determination in real samples. The method is simple, highly sensitive, selective and very stable. Prog. Color Colorants Coat. 3(2010), 58-65. © Institute for Color Science and Technology.

1. Introduction

Zirconium (Zr) is a strategic element and its identification and determination are very important. Zr is used for removing sulfur, nitrogen and oxygen from steel and in the copper manufacturing. Its alloys are employed in the production of optical glasses with high refractive index and in the ceramic industry to produce enamels. Also, its transparency to thermal neutrons has made Zr a good structural material in nuclear reactors and chemical plants [1]. The direct determination of Zr^{4+} ion in alloys and other samples is of great importance from an analytical point of view. In order to determine Zr,

different spectroanalytical techniques such as [2]: Laser ablation inductively coupled plasma optical emission spectrometry LAICP-OES [3], inductively coupled plasma mass spectrometry ICP-MS [4], X-ray fluorescence [5], as well as one-step procedures such as reversed phase liquid chromatographic separation (RP-LC) [6] or chelating ion exchange followed by spectrophotometric detection [7] have been reported. The detection limit of the above methods for determination of Zr varies in the range of 0.1-3 mg l^{-1} . Zirconium is chemically stable and has a high melting point and hence the atomic absorption method has not sufficient

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sensitivity to zirconium concentrations less than 8 ppm [8]. The ICP-MS which requires high temperatures has also limitation for trace determination of zirconium [9]. However, this deficiency can be overcome by pre-concentration by liquid-liquid extraction technique. The main reason for the wide use of extraction technique in combination with ICP-AES is the improvement in the sensitivity arising partly from higher element concentration and also, because, nebulization of organic solvent can produce a more finely dispersed aerosol [10].

The catalytic kinetic methods have shown some very promising features for determination of metal ions in ultra-trace levels. These methods have many advantages such as high sensitivity, good selectivity, needing only expediency operation and simple equipments for trace determinations [11]. Catalytic-kinetic procedures are most attractive for achieving trace level elements determination, but those for zirconium had rarely been reported so far. Some recently reported procedures have been proposed based on the indicator reactions of zirconium(IV) catalyzed oxidation of Eriochrome Blue Black R [12] and/or Coomassie Brilliant Blue G [13] by hydrogen peroxide and/or bromate, respectively, and catalytic potentiometric methods based on iodide oxidation by bromate [14] and hydrogen peroxide [15]. A more recent kinetic spectrophotometric method for the determination of zirconium is based on oxidation of Gallocyanine by hydrogen peroxide in the presence of Zr(IV) (Table 1) [16].

Unfortunately, the catalytic spectrophotometry methods that mentioned here must be carried out at elevated temperature (100°C) in order to obtain satisfactory sensitivity and must terminate the reaction by dropping the temperature of the system abruptly and this will be difficult to control in most cases. In addition, the

linear ranges of the method are very narrow. Furthermore, the sensitivity of catalytic potentiometric methods is poor, i.e. it can only be used to micromolar concentration level of zirconium. From this point of view, novel catalytic/kinetic procedures for zirconium with higher sensitivity and easier control (especially procedures which could be carried out at room temperature) are still urgently needed.

Many commercially available dyes are known and approximately one million tons of these dyes are produced annually worldwide. Also, the synthetic dyes (e. g. Janus Green) represent a relatively large group of organic chemicals that are met in practically all spheres of our daily life. The cationic dye such as Janus Green (JG) is an important group of organic compounds which have a variety of scientific and industrial applications [21,22]. Under the experimental conditions, this dye is highly stable under light and washing conditions. It is also resistant to microbial attack. Therefore, it is not readily degradable and can be used as a suitable chromogenic agent in spectrophotometric determination. The method is suitable for the selective and rapid determination of Zr(IV) concentrations as low as 0.08 µg ml⁻¹. In addition, advantages of the proposed method include performing the reaction at room temperature and using lower reaction time.

In continuation of our research works on spectrophotometric determination of some chemical species [17-19], in this paper, a new kinetic spectrophotometric method based on the catalytic effect of Zr(IV) on the oxidation of an azo dye, Janus Green (JG), by potassium bromate at room temperature (25 °C) is proposed. The term azo dye is applied to synthetic organic colorants that are characterized by a nitrogen-nitrogen double bond [20].

Table 1: Comparison of proposed method for the determination of zirconium(IV) with the recently published catalytic kinetic methods.

No.	Indicator reactions	Temperature (°C)	Linear range (µg ml ⁻¹)	Ref.
1	Eriochrome Blue Black R + H ₂ O ₂	100	0 ~ 0.044	12
2	Coomassie Brilliant Blue G + BrO ₃ ⁻	100	0 ~ 0.0104	13
3	Gallocyanine + H ₂ O ₂	R.T *	0 ~ 0.11	16
4	Janus Green + BrO ₃ ⁻	25 °C	0.1 ~ 250	This paper

* R.T Room Temperature.

2. Experimental

2.1. Reagents

All chemicals were of analytical reagent grade or the highest purity available from Merck (Merck, Darmstadt, Germany) and double-distilled water (DDW) was used throughout the study. In addition, all glassware were soaked in dilute nitric acid for 12 h and finally rinsed for three times with DDW prior to use. Some of the important physicochemical properties of the investigated dye (Merck) are given in Table 2.

6.0×10^{-4} M Janus Green (JG) solution was prepared by dissolving 0.0307 g of its powder in 100 ml of water. Zirconium(IV) standard solution of 100 mg ml^{-1} was prepared by dissolving 0.0883 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in 5 ml water and 5 ml of 0.5 mol L^{-1} HCl, and then diluted to 250 ml. Working solutions were obtained by appropriate dilution. Potassium bromate stock solution of 2.0×10^{-2} M was prepared by dissolving 0.8350 g of KBrO_3 (Merck) in appropriate amount of water and diluting to 250 ml.

1.84 M Sulfuric acid solution was prepared by directly dissolving 25 ml of concentrated sulfuric acid ($a=98\%$, $d=1.84 \text{ gml}^{-1}$) in an appropriate amount of water and this mixture was diluted to 250 ml after cooling.

2.2. Apparatus

A Shimadzu spectrophotometer (160-A, Japan) with a glass cell of 1 cm path length was used for obtaining the absorption spectra and the absorbance measurements. A Rikakika thermostated water bath (UA-1, Japan) was used to keep the temperature of all solutions at the working temperature ($25 \pm 0.1^\circ\text{C}$). A stop-watch was used for recording the reaction time. In addition, all

glassware were soaked in dilute nitric acid for 12 h and finally rinsed for three times with deionized water prior to use.

2.3. Recommended procedure

0.9 ml of 1.84 M sulfuric acid solution, 0.6 ml of 6.0×10^{-4} M JG and 1 ml of Zr^{4+} (80.00 ppm) were added to a series of 10 ml volumetric flask. The solution was diluted to ca. 8 ml with water. Then 0.7 ml of bromated solution was added to the reaction mixture, followed by dilution to 10 ml with water. Time measurement started just after the addition of the oxidant solution. After thorough mixing for 3.0 minutes, a portion of this solution was transferred to a cuvette and the absorbance was measured against pure water reference at 606 nm and 25°C for fixed times of 15.0 and 180.0 s. The measurement was repeated in the absence of Zr(IV) to obtain the value for the uncatalyzed reaction and this blank value was subtracted from the catalyzed reaction absorbance.

The absorbance changes of the catalyzed and uncatalyzed reactions were labeled ΔA_o and ΔA_u , respectively. The calibration graph was constructed by plotting analytical signal ($\Delta A = \Delta A_o - \Delta A_u$) versus the zirconium concentration.

3. Results and discussion

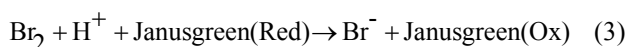
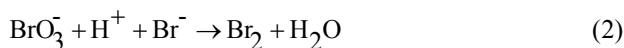
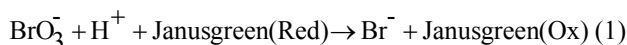
Janus Green is an azo dye that can be oxidized by oxidizing agents such as peroxodisulphate to produce a colorless oxidized product[23]. In the presence of trace amounts of Zr(IV) , JG is oxidized by bromate in acidic media and increase the rate of the reaction.

Table 2: Some important physicochemical properties of the Janus Green dye.

Dye	Chemical formula	Molecular structure	M.W.(g mol ⁻¹)	C. I. Number
Janus Green (JG)	$\text{C}_{30}\text{H}_{31}\text{ClN}_6$		511.07	11050

This reaction proceeds slowly in the absence of zirconium as a catalyst. The decrease in absorbance, i.e. decrease in the concentration of JG, was measured at 606 nm (Figure 1).

The possible mechanism of the Janus Green reaction may be contributed to the following reactions in its simplest form (equation 1-3).



where "Red" and "Ox" are reduction and oxidation reactions, respectively. Because reaction (1) is very slow, in the absence of zirconium, BrO_3^- oxidized Janus Green to produce weak reduction in absorbance of dye. By adding zirconium to the system, the velocity of reactions (2) and (3) undergoes a significant increase, because the in situ-generated Br_2 in this system is a nascent oxidant.

3.1. Optimization of reaction variables

In order to find the optimum conditions, the influence of reagents concentration, temperature and time on the reaction rate was studied based on fixed time method. The optimum conditions used for the final working procedure were chosen as a compromise in order to ensure low blank values, extended linearity and short measuring time.

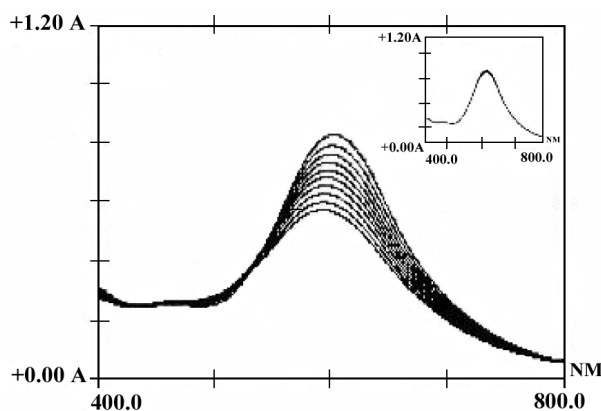


Figure 1: Catalytic effect of Zr (IV) on reaction rate. (a) Catalyzed reaction, sample conditions: H_2SO_4 ; 0.9 ml (1.84 M), JG; 0.6 ml (6×10^{-4} M), Zr(IV); 1.0 ml ($100.0 \mu\text{g ml}^{-1}$), KBrO_3 ; 0.7 ml (0.02 M), 25 °C, 180 s. (b) Uncatalyzed reaction.

3.2. Effects of reagents concentrations

The effect of acid volume on the reaction rate of 3.0×10^{-5} M JG in the presence of 2.0×10^{-3} M BrO_3^- and 1.0 ml of $80.0 \mu\text{g ml}^{-1}$ Zr(IV) was studied in the volume range of 0.1-1.3 ml. The absorbance measured at maximum wavelength of JG and at the corresponding acid concentration was recorded as a function of time. The results are shown in Figure 2 and 0.9 ml of sulfuric acid was selected as optimum. The influence of JG concentration on the reaction rate was studied in the range of 1.2×10^{-5} to 4.2×10^{-5} M. Decrease in absorbance augments linearly with increasing JG concentration, but the uncatalyzed reaction shows a smaller increase (Figure 3). From an analytical point of view, JG concentration can provide an absorbance peak in the range of minimum photometric error. Therefore, 3.6×10^{-5} M of JG was chosen as the most suitable concentration.

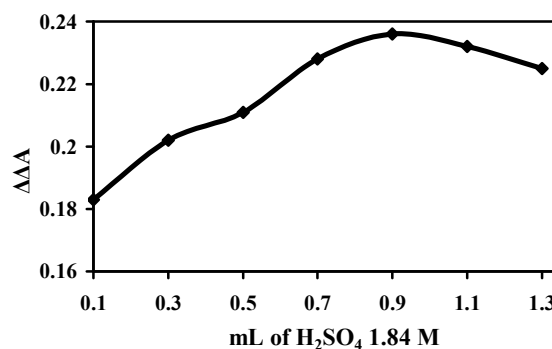


Figure 2: Effect of H_2SO_4 on reaction rate. JG; 0.5 ml (6×10^{-4} M); Zr(IV); 1.0 ml ($80.0 \mu\text{g ml}^{-1}$); KBrO_3 ; 1.0 ml (0.02 M), 25 °C, 180 s.

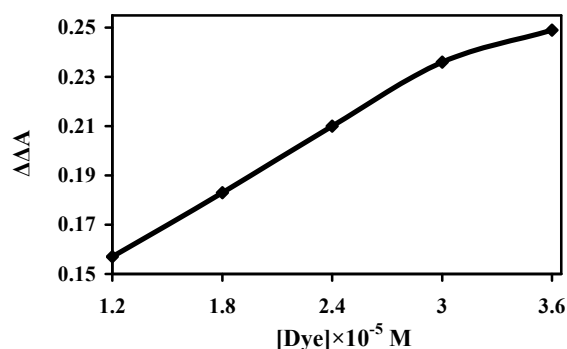


Figure 3: Effect of Janus Green concentration on reaction rate. H_2SO_4 ; 0.9 ml (1.84 M); Zr(IV); 1.0 ml ($80.0 \mu\text{g ml}^{-1}$); KBrO_3 ; 1.0 ml (0.02 M), temperature; 25 °C, time; 180 s.

As shown in Figure 4, the effect of bromate concentration on the catalyzed and uncatalyzed reactions was monitored in the range of 2.0×10^{-4} - 2.2×10^{-3} M of bromate. Based on the results, 1.4×10^{-3} M of bromate was chosen as the optimum concentration of oxidizing agent.

3.3. Effects of temperature and time on reaction rate

The effect of temperature on reaction rate was studied in the range of 15-45 °C at optimum reagents concentration. Increasing temperature up to 25 °C caused an increase in absorbance variations, whereas at higher temperatures, the change in absorbance decreases (Figure 5) due to partial dissociation of JG at these temperatures. Thus, 25 °C was selected as an optimum temperature.

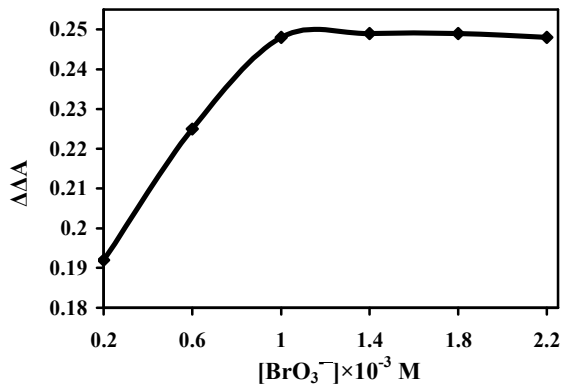


Figure 4: Effect of bromate concentration on reaction rate. H₂SO₄; 0.9 ml (1.84 M); JG; 0.6 ml (6×10^{-4} M) Zr(IV); 1.0 ml ($80.0 \mu\text{g ml}^{-1}$); temperature; 25°C, time; 180 s.

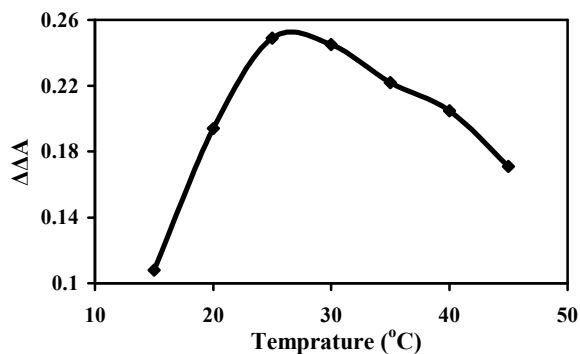


Figure 5: Effect of temperature on reaction rate. H₂SO₄; 0.9 ml (1.84 M); JG; 0.6 ml (6×10^{-4} M); Zr(IV); 1.0 ml ($80.0 \mu\text{g ml}^{-1}$); KBrO₃; 0.7 ml (0.02 M); time; 180 s.

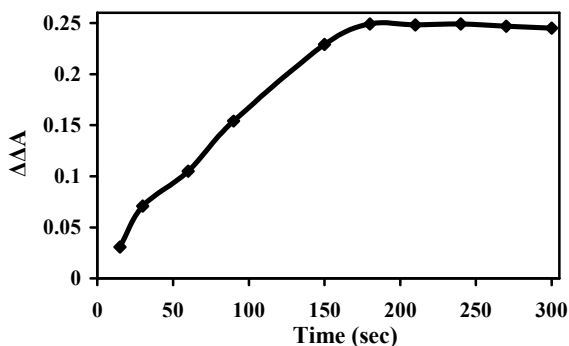


Figure 6: Effect of time on reaction rate. H₂SO₄; 0.9 ml (1.84 M); JG; 0.6 ml (6×10^{-4} M); Zr(IV); 1.0 ml ($80.0 \mu\text{g ml}^{-1}$); KBrO₃; 0.7 ml (0.02 M); temperature; 25 °C.

The optimum time was found by measuring the absorbance during 15-300 s. The decrease in absorbance occurred up to 180 s. At still higher time, the rate was almost constant, thus 180 s was selected as optimum time (Figure 6). All reagent concentrations in the reaction system are in great excess and so could be considered to be constant during the measurements, except that of zirconium(IV). The results show that ΔA at an exact time (the initial reaction rate) is proportional to zirconium concentration as a pseudo first order for Zr(IV). The kinetic equation for the oxidation of JG by bromate catalyzed by zirconium(IV) was thus formulated as equation 4.

$$d[\text{JG}]/dt = k_1 C_{\text{Zn(IV)}} \times k_2 \quad (4)$$

where k_1 and k_2 , determined by the original concentrations of JG and BrO_3^- and also by temperature, and all related variables involved in the measurements are constant under the conditions described above.

3.4. Calibration graph and detection limit

Calibration curve was obtained by applying the fixed time method under the optimum conditions. the plot of the absorbance versus Zr(IV) concentration in the reaction mixture which changes after 3.0 minutes was linear in the range of 0.1 - $250.0 \mu\text{g ml}^{-1}$ [Zr(IV)]. The linear regression equation is given in equation 5.

$$\Delta A = 0.0023[\text{Zr(IV)}] + 0.0681 \quad (5)$$

$$(R^2 = 0.999)$$

Experimental detection limit ($3S_b/m$) was $0.08 \mu\text{g ml}^{-1}$ Zr(IV).

3.5. Accuracy

We verified the accuracy of zirconium(IV) determination in the samples (tap water) by the standard addition method. Results shown in Table 3 indicate that the Zr(IV) recoveries from the samples are quantitative. Thus, zirconium can be determined in the specified concentration range in mixtures containing many ions in relatively high concentrations. The higher recovery in each case may be attributed to synergistic effect due to presence of other cations in samples, which is not uncommon.

3.6. Interference studies

In order to investigate the analytical applicability i.e. selectivity, the fixed method was used. A foreign ion was considered to interfere significantly when it gave a Zr(IV) measurement error of more than 5.25%. The influence of several cations and anions were tested using

the standard solution of zirconium ($5.0 \mu\text{g ml}^{-1}$). The results are given in Table 4. The results shown in Table 4 indicate that most common ions do not interfere with the catalytic determination except for Cr(VI) and Fe^{3+} which showed serious positive interferences. However, the interfering effect of Fe^{3+} could be eliminated by masking with 0.1 ml EDTA (0.04%) and that of Cr(VI) by reducing it to Cr(III) with ascorbic acid.

3.7. Applications to real samples

The present procedure was applied to the determination of zirconium in zirconium bronze and ceramic samples. For these applications, 0.2 g of zirconium bronze sample or 0.1 g of certified reference material (rocks, clays and minerals) were dissolved in a mixture of 20 ml HCl and 60 ml HNO_3 by gentle heating in a fume board, the solution was kept boiling till white fumes were formed. After the fumes disappeared, an appropriate amount of HCl (4 M) was added to the residue, the solution was then transferred into a 100 ml flask and made up to mark with redistilled water.

Table 3: Accuracy and precision of proposed method.

Sample no.	Added ($\mu\text{g ml}^{-1}$)	Found $\pm S_d^*$ ($\mu\text{g ml}^{-1}$)	RSD (%)	Recovery (%)
1	10.0	10.3 ± 0.18	1.75	103.0
2	100.0	99.5 ± 0.72	0.72	99.5
3	200.0	198.7 ± 1.05	0.53	99.4

* Mean \pm /standard deviation (n= 10).

Table 4: Tolerance limit of interfering species on the determination of $5.0 \mu\text{g ml}^{-1}$ Zr(IV).

Interfering species	Tolerated mass ratio, (ion: Zr(IV))
Na^+ , K^+ , Mg^{2+} , Ca^{2+} , NH_4^+	1200
NO_3^- , CO_3^{2-} , HCO_3^- , SO_4^{2-} , HSO_4^- , PO_4^{3-} , CH_3CO_2^- , BO_3^{3-} , Citrate	1000
Cl, Br, I, Pb^{2+} , Cd^{2+}	700
Zn^{2+} , Cu^{2+}	500
Cr^{3+} , Co^{2+}	400
Mn^{2+} , Ag^+ , Fe^{2+} , Ni^{2+}	350
Cr^{6+} , Fe^{3+}	50

Table 5: Determination of Zr(IV) in bronze sample.

Sample	Found±Sd ^a (g/T)	Standard value(g/T)	SD%	t Test ^b
Bronze sample of the geological system of China (No. 4655.9)	0.7532 ± 0.028	0.7500	3.72	0.26

^a Mean± standard deviation (n= 5).

^b Tabulated t-value for 4 degrees of freedom at P (0.95) is 2.776.

Table 6: Determination of Zr(IV) in ceramic samples.

Zr(IV) / (µg ml ⁻¹) Proposed method				
Sample no	Added	Found ^a	Recovery (%)	RSD (%)
1	-	5.2 ± 0.10	-	1.92
	10.0	15.7 ± 0.30	103.3	1.91
	20.0	25.8 ± 0.41	102.4	1.59
2	-	16.7 ± 0.41	-	2.46
	20.0	37.7 ± 0.51	102.7	1.35
	40.0	55.8 ± 0.63	98.4	1.13
3	-	100.8 ± 0.91	-	0.90
	100.0	199.8 ± 1.54	99.5	0.75
	120.0	222.8 ± 2.09	102.0	0.69

^a Mean± standard deviation (n= 5).

The zirconium contents in the above solution were determined by the recommended procedure and the results are listed in Table 5. In case of ceramic samples, a 0.2 g of sample was treated in a platinum dish in 10 ml of HF (49%) with 1 ml of HClO₄ (70%) and evaporated to dryness on a hot plate. The salts and residue were then covered with 2g of the fusion agent (4:3 NaKCO₃+H₃BO₃) and fused for 10 min in a propane-air burner. After cooling, the melt was dissolved in 50 ml of a mixture of 5% (v/v) HCl and 0.5% (v/v) HF by heating gently on the water bath. The solution was then transferred to a 100 ml PE volumetric flask and diluted to the mark using the acid mixture (Table 6).

4. Conclusions

This paper reports a very sensitive and highly specific spectrophotometric method for trace determination of zirconium using JG as a new reagent for the first time. The method possesses distinct advantages over existing methods in cost, simplicity, ease of operation and applicable to real samples. The determination can be carried out at room temperature.

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