

## A New Kinetic Method for Photometric Determination of Trace Zr(IV) in Industrial Al-Li Alloys

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A simple and fast kinetic method for determination of trace Zr(IV) has been described. Zr(IV) exerted a catalytic effect on the oxidation of 4-hydroxycoumarin by potassium permanganate in acetate buffer. Experimental parameters were appropriately adjusted in order to optimize the reaction conditions. Absorbance of potassium permanganate was measured at 525 nm. The Beer's law was obeyed in the analyte concentration range of 0.10–1.25 ppm. Sensitivity of the method was 0.1 ppm. The probable relative error ranged from –4.16 to 10.00 % within Zr(IV) concentration range 0.1–1.25 ppm. Tolerance limits for the interfering ions were also established. Kinetic equations of the studied reactions were derived. The proposed method was successfully applied to the determination of Zr(IV) content in industrial Al-Li alloys.

Opracowano prostą i szybką, kinetyczną metodę oznaczania śladowych ilości cyrkonu. W metodzie wykorzystano katalityczne działanie Zr(IV) zachodzące podczas reakcji utleniania 4-hydroksykumaryny za pomocą nadmanganianu potasu w środowisku buforu octanowego. Warunki reakcji zostały zoptymalizowane przez odpowiedni dobór parametrów doświadczalnych. Absorbancję roztworu nadmanganianu potasu mierzono przy długości fali 525 nm. Prawo Beera było spełnione w zakresie stężeń analitu: 0,10–1,25 ppm. Granica wykrywalności wynosiła 0,1 ppm. Możliwy błąd względny we wspomnianym wyżej zakresie stężeń analitu był w granicach od 4,16 do 10,0%. Ustalono granice tolerancji jonów przeszkadzających. Metodę zastosowano do oznaczania zawartości Zr(IV) w przemysłowych stopach Al-Li.

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Zirconium is used mainly in nuclear reactors due to its resistance to corrosion and low neutron cross-section. Moreover, it is used in glass and ceramic industries as refractory material, also as an alloying agent in steel and various light alloys [1, 2]. Up till now, zirconium has been regarded as neither essential nor toxic element, however the opposite has been reported recently [3, 4]. Exposure to this element has increased due to its increasing use in new materials and the increasing radioactive fallout. Consequently, the effects of zirconium on living organisms attract the increasing attention and there is a need for new sensitive and selective methods for determination of this element.

The number of methods for trace analysis of zirconium is limited. Several studies describe the use of organic solvents for extraction of zirconium [5–7]. Since some Zr complexes are strongly colored, they can be determined spectrophotometrically [8–10], however sensitivity of these determinations is insufficient. ICP methods, including ICP–IDMS [11], ICP–MS [12], ICP–AES [13, 14] have also some limitations in terms of high instrumentation cost in routine analysis and large matrix effects. These limitations have encouraged us to develop a sensitive and easily available analytical method for routine determination of trace Zr.

Kinetic analytical methods have some advantages, including high sensitivity, extremely low detection limit, good selectivity, short analysis time, and inexpensive instrumentation [15]. Catalytic-kinetic methods for Zr(IV) determination are extremely rare. Highly sensitive method has been developed by He *et al.* [16]. The achieved detection limit was  $0.4 \text{ ng mL}^{-1}$ ; interferences from  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ , and Cr(VI) were eliminated by using masking and reductive agents.

In this work we have proposed a simple, fast, and inexpensive analytical procedure for the determination of trace amounts of Zr(IV). The procedure is based on the catalytic effect of Zr(IV) on the oxidation of 4-hydroxycoumarin by potassium permanganate in acetate buffer solution. The proposed method has been successfully applied to the determination of trace Zr(IV) in industrial Al–Li alloys. Availability of spectrophotometric instrumentation and simplicity of analytical procedure make the proposed method widely applicable to the samples with low content of Zr(IV).

## EXPERIMENTAL

### Reagents

$1 \times 10^{-3} \text{ mol L}^{-1}$  solution of 4-hydroxycoumarin was prepared by dissolving the appropriate amount of the solid compound. To improve its solubility, an equivalent amount of NaOH was added.

1000 ppm stock solution of Zr(IV) was prepared by dissolving 3.5330 g of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  in 50 mL of  $2 \text{ mol L}^{-1}$  HCl, and further dilution to 1 L with deionized water.

Acetate buffer was prepared from  $\text{CH}_3\text{COOH}$  and  $1 \text{ mol L}^{-1}$  NaOH solutions.

$\text{KMnO}_4$  solution was prepared by diluting Merck solution of the compound purchased in ampoules.

Analytical grade reagents, deionized water, and polyethylene vessels were used throughout.

### Apparatus

Spectrophotometric measurements were performed at the wavelength of 525 nm using a SPECOL 221 MA 9524 spectrophotometer. In these studies, a cuvette with an optical path length of 1 cm was used. A Radimeter PHM 29b pH-meter equipped with a GK 2311 C combined electrode served for pH measurements. Water thermostating bath „Sutjeska”, type 10, was used to keep the temperature at  $298.0 \pm 0.1 \text{ K}$ .

### General procedure

Initial concentrations of some of the reactants were varied, while of some others were kept constant.

Appropriate volumes of the reactants were placed in a 20 mL-in-volume standard flasks in the following order: 4-hydroxycoumarin, acetate buffer, catalyst, and water, up till the predetermined volume was reached. The content of the flask was thermostated for 15 min, and then the solution volume was made up to the mark with  $\text{KMnO}_4$  and water. The content of the flask was mixed well. The cell of the photometer was rinsed and filled with the prepared solution. Time changes of the absorbance,  $dA/dt$ , were measured every 15 s over a period of 5–6 min after addition of .  $dA/dt$  was proportional to the reaction rate ( $dc/dt$ ) and was expressed as:

$$\frac{dA}{dt} = \varepsilon \times l \times \frac{dc}{dt}$$

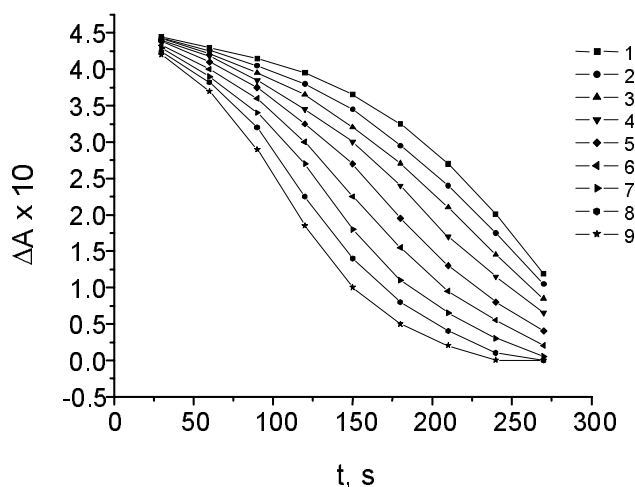
where  $\varepsilon$  is molar absorptivity,  $l$  denotes the optical path length in the cell, and  $c$  stands for the concentration of the  $\text{KMnO}_4$ .

### Procedure for the determination of Zr(IV) in Al-Li alloys

First, aluminum and iron were removed from the sample solution [17]. 20 mL of  $1 \times 10^{-3} \text{ mol L}^{-1}$  4-hydroxycoumarin solution were mixed with 12 mL of acetate buffer solution ( $\text{pH} = 3.8$ ) prepared from  $0.2 \text{ mol L}^{-1}$   $\text{CH}_3\text{COOH}$  and  $1 \text{ mol L}^{-1}$  NaOH. 6.4 mL of the obtained mixture were placed in each of three polyethylene vessels (20–30 mL-in-volume). 10 mL of deionized water and 10 mL of the sample solution for Zr(IV) analysis were added to the first and the second vessel, respectively. These vessels were thermostated at 298 K and to both of them 3.6 mL of  $1 \times 10^{-3} \text{ mol L}^{-1}$   $\text{KMnO}_4$  solution were added. Afterwards, the vessels were thermostated and  $\Delta A$  was measured for 150 s. The unknown concentration of Zr(IV) was calculated from equation (1). To the third vessel, 5 mL of the sample solution for Zr(IV) analysis and 5 mL of Zr(IV) standard solution were added, so that the final concentration of Zr(IV) was the same as in the second vessel. Reaction was started by adding 3.6 mL of  $\text{KMnO}_4$  and  $A$  was recorded for 150 s. The unknown concentration of Zr(IV) in the sample was calculated applying standard addition method. In the calculations, dilution of the sample was considered.

## RESULTS AND DISCUSSION

Kinetic results were obtained by spectrophotometric monitoring of the color of permanganate, which deteriorated as the reaction advanced. The results were processed applying differential variant of the fixed time method [18].



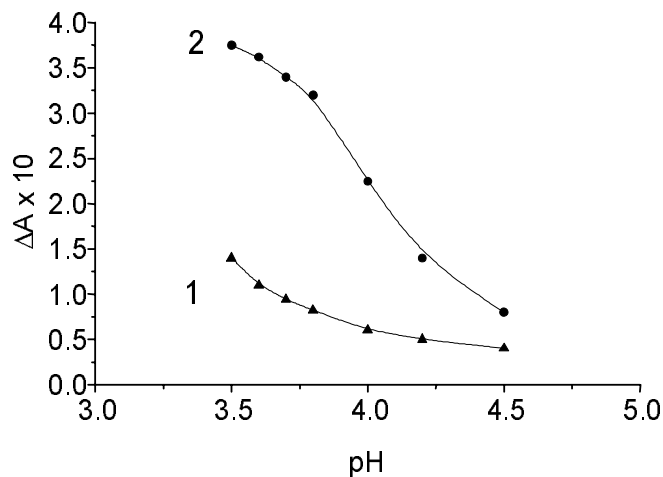
**Figure 1.** Change of absorbance ( $\Delta A$ ) at different concentrations of Zr(IV) (ppm): 1 – 0.00; 2 – 0.10; 3 – 0.20; 4 – 0.30; 5 – 0.50; 6 – 0.75; 7 – 1.00; 8 – 1.25; 9 – 1.50; T = 298 K

It can be seen in Figure 1 that the differences in the measured  $\Delta A$  values for non-catalytic (curve 1) and catalytic reactions (curves 2–9) became more pronounced as the concentration of Zr(IV) in the sample was increased, and reached maximum after 150 s. Slight induction period reflected in the shapes of the curves is characteristic of the autocatalytic effect of  $Mn^{2+}$  ions being the product of reduction of  $KMnO_4$  [19].

#### Effect of experimental conditions

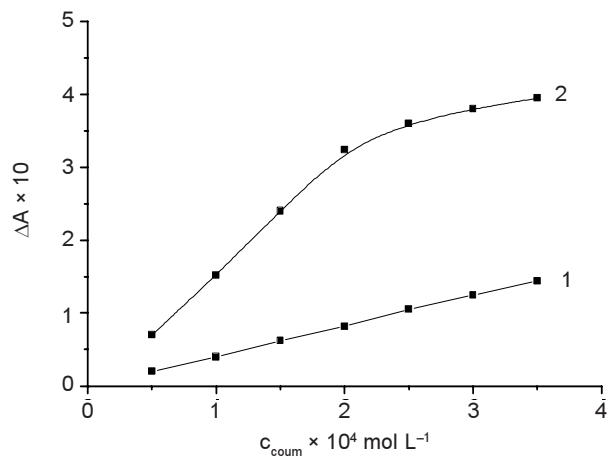
Optimum conditions were established by changing the concentrations of some components and keeping concentrations of the other constant.

Concentration of  $H_3O^+$  was varied from  $3.16 \times 10^{-5}$  to  $3.16 \times 10^{-4}$  mol L<sup>-1</sup>. Figure 2 shows the influence of pH on the rates of catalytic and non-catalytic reactions. The relationship between the pH and the reaction rate was complex. The reaction order varied depending on  $H_3O^+$  concentration within the studied pH range. Finally, pH of 3.80 was selected for further investigations.



**Figure 2.** pH dependence of the reaction rate; initial concentrations:  $C_{\text{MnO}_4^-} = 1.8 \times 10^{-4} \text{ mol L}^{-1}$ ,  $C_{4\text{-OHcoum}} = 2 \times 10^{-4} \text{ mol L}^{-1}$ ,  $C_{\text{Zr(IV)}} = 1.2 \text{ ppm}$ ,  $T = 298 \text{ K}$ ; 1 – non-catalytic reaction, 2 – catalytic reaction

The dependence of the reaction rate on the concentration of 4-hydroxycoumarin is presented in Figure 3.

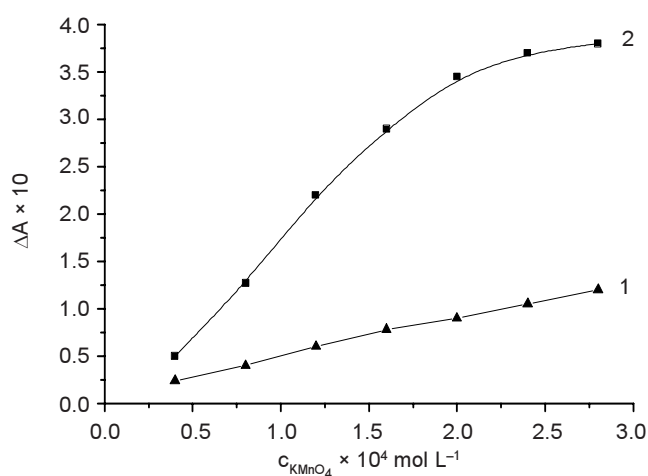


**Figure 3.** Dependence of the reaction rate on the concentration of 4-hydroxycoumarin; initial concentrations:  $C_{\text{MnO}_4^-} = 1.8 \times 10^{-4} \text{ mol L}^{-1}$ ,  $\text{pH} = 3.80$ ,  $C_{\text{Zr(IV)}} = 1.2 \text{ ppm}$ ,  $T = 298 \text{ K}$ ; 1 – non-catalytic reaction, 2 – catalytic reaction

Concentration of the reducing agent was changed in the range  $5 \times 10^{-5}$ – $3.5 \times 10^{-4} \text{ mol L}^{-1}$ . The non-catalytic reaction was of the first order with respect to the concentration of

4-hydroxycoumarin. The catalytic reaction was the first order reaction to value of  $2 \times 10^{-4} \text{ mol L}^{-1}$  of 4-hydroxycoumarin, and its order varied for higher concentrations. Thus, the concentration of  $2 \times 10^{-4} \text{ mol L}^{-1}$  of 4-hydroxycoumarin was selected for further studies.

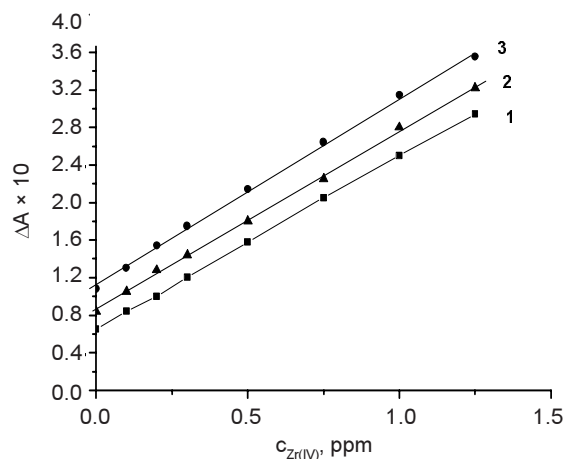
The rates of catalytic and non-catalytic reactions differed the most for  $\text{KMnO}_4$  concentration  $1.8 \times 10^{-4} \text{ mol L}^{-1}$  (Fig. 4). At this concentration, both reactions were of the first order.



**Figure 4.** Dependence of the reaction rate on the concentration of  $\text{KMnO}_4$ ; initial concentrations:  $C_{4\text{-OH coum}} = 2 \times 10^{-4} \text{ mol L}^{-1}$ ,  $C_{\text{Zr(IV)}} = 1.2 \times 10^{-6} \text{ ppm}$ ,  $\text{pH} = 3.80$ ,  $T = 298 \text{ K}$ ; 1 – non-catalytic reaction, 2 – catalytic reaction

### Calibration plot

Under the optimized experimental conditions ( $\text{pH} = 3.8$ ,  $C_{4\text{-OH coum}} = 2 \times 10^{-4} \text{ mol L}^{-1}$ ,  $C_{\text{KMnO}_4} = 1.8 \times 10^{-4} \text{ mol L}^{-1}$ ), concentration of  $\text{Zr(IV)}$  was varied in the range 0.1–1.25 ppm at three different temperatures. Figure 5 shows the corresponding calibration plots, which were used for determination of  $\text{Zr(IV)}$  concentration in the investigated range. The slopes of the obtained calibration lines No 1 –  $293 \pm 0.1 \text{ K}$ , 2 –  $298 \text{ K}$ , and 3 –  $303 \pm 0.1 \text{ K}$  were very similar, however the temperature of  $298 \text{ K}$  is recommended.



**Figure 5.** Dependence of the reaction rate on the concentration of Zr(IV); initial concentrations:  $C_{4-OH_{coun}} = 2 \times 10^{-4} \text{ mol L}^{-1}$ ,  $C_{KMnO_4} = 1.8 \times 10^{-4} \text{ mol L}^{-1}$ , pH = 3.80, T = 293 ± 0.1 K (1); 298 ± 0.1 K (2); 303 ± 0.1 K (3)

The unknown concentration of Zr(IV) was determined using the below equation:

$$C_{Zr(IV)} = \frac{\Delta A - 0.082}{0.196} (\text{ppm}) \quad (1)$$

where  $\Delta A$  is the absorbance change of  $KMnO_4$  after 150 s from the beginning of reaction; T = 298 K,  $\lambda = 525 \text{ nm}$ , thickness of absorption layer 1 cm.

### Kinetic and analytical parameters

For the investigated catalytic and non-catalytic reactions, the following kinetic equations have been deduced assuming constant pH and utilizing the obtained graphic correlations as a basis:

$$\text{for catalytic reaction: } -dc/dt = k_1 \cdot C_{MnO_4^-} \cdot C_{coun} \cdot C_{Zr(IV)} \quad (2)$$

where:  $C_{coun} \leq 2 \times 10^{-4} \text{ mol L}^{-1}$ ;  $C_{KMnO_4} \leq 1.8 \times 10^{-4} \text{ mol L}^{-1}$ ;  $0.1 \text{ ppm} \leq C_{Zr(IV)} \leq 1.25 \text{ ppm}$ ;  $k_1$  – catalytic reaction rate constant

$$\text{for non-catalytic reaction: } -dc/dt = k_0 \cdot C_{MnO_4^-} \cdot C_{coun} \quad (3)$$

where:  $C_{coun} \leq 3.5 \times 10^{-4} \text{ mol L}^{-1}$ ;  $C_{KMnO_4} \leq 2.8 \times 10^{-4} \text{ mol L}^{-1}$ ,  $k_0$  – non-catalytic reaction rate constant.

Accuracy and precision data are presented in Table 1. Reaction rates were estimated in five replicate determinations of three different concentrations of Zr(IV).

**Table 1.** Accuracy and precision of Zr(IV) determination;  $\bar{x}$  – mean value;  $\mu$  – true value;  $s$  – standard deviation;  $t$  – Student's test for 95% confidence;  $\frac{100 \cdot t \cdot s}{\bar{x} \sqrt{n}}$  – precision;  $\frac{\bar{x} - \mu}{\mu} \cdot 100$  – accuracy

Taken ( $\mu$ ) $\mu\text{g mL}^{-1}$	Found ( $\bar{x}$ ) $\mu\text{g mL}^{-1}$	n	$\frac{100 \cdot t \cdot s}{x \sqrt{n}}$ , %	$\frac{\bar{x} - \mu}{\mu} \cdot 100$ , %
0.10	0.11	5	7.90	10.00
0.50	0.54	5	7.65	8.00
1.20	1.15	5	5.23	-4.16

The probable relative error ranged from  $-4.16 \div 10.0\%$  for Zr(IV) concentration range 0.1–1.5 ppm.

The minimum determinable concentration of Zr(IV) was calculated applying the method proposed by Perez-Bendito and Silva [15]. Limit of detection (LD) and limit of quantitation (LQ) were found 0.0384 ppm and 0.1280 ppm, respectively.

### Interference study

To assess selectivity of the proposed method, the influence of the presence of several foreign ions on the catalytic reaction rate was investigated at the constant concentration of Zr(IV) (1.2 ppm). Since Hf(IV) and Ti(III) belong to the same group as Zr(IV) does, they had a similar effect on the studied system [20]. Th(IV) exhibited half of the zirconium activity. The results for other foreign ions are presented in Table 2.

**Table 2.** Tolerance limits for various interferents in kinetic determination of Zr(IV)

Tolerance limit foreign ion/Zr(IV), ppm	Ion added	Comment
$10^3$	$\text{CH}_3\text{COO}^-$ , $\text{K}^+$ , $\text{Na}^+$ , $\text{Cl}^-$	no influence
500	$\text{NO}_3^-$ , $\text{NH}_4^+$ , $\text{Mg}^{2+}$ , $\text{Ba}^{2+}$ , $\text{Ca}^{2+}$ , $\text{Sr}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Sn}^{2+}$ , $\text{SO}_4^{2-}$	no influence
100	$\text{Pb}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Cr}_2\text{O}_7^{2-}$ ,	no influence
50	$\text{Ni}^{2+}$ , $\text{Hg}^+$ , $\text{Sb}^{3+}$ , $\text{Bi}^{3+}$	small catalytic effect
20	$\text{Co}^{2+}$	small catalytic effect
5	$\text{PO}_4^{3-}$ , $\text{SCN}^-$ , citrate	inhibit the reaction
$10^{-1}$	$\text{Al}^{3+}$ , $\text{In}^{3+}$ , $\text{Y}^{3+}$ , $\text{La}^{3+}$	catalyze the reaction



### Application

In order to evaluate analytical applicability of the proposed method, it was applied to the determination of Zr(IV) concentration in the real samples of industrial Al-Li alloys. These alloys are used in aviation industry, especially for construction of fins. They combine advantageous properties, such as low density, high module of elasticity, good formability, and durability under high pressure. The presence of zirconium (0.01÷0.25%) gives to the alloy a fine, equiaxed grain structure. Al-Li alloys AA 8090 and AA 2090 were investigated. The results obtained for both samples applying the proposed method and the reference atomic absorption spectrophotometric method (AAS) are presented and compared in Table 3. Both sets of results are in good agreement.

**Table 3.** Results of determination of Zr(IV) in the real samples

Sample chemical composition, wt.% [balance-Al]	Proposed method*	AAS method*	RSD, %**
AA8090 Li (2.2–2.7), Cu (1.0–1.6), Mg (0.6–1.3), Zr (0.04–0.16), Si (0–0.20), Fe (0–0.3)	0.1142	0.1098	3.45
AA 2090 Li (1.9–2.6), Cu (2.4–3.0), Mg (0–0.25), Zr (0.08–0.15), Si (0–0.10), Fe (0–0.12)	0.1408	0.1351	4.05

\* Averaged from five separate determinations.

\*\* For the proposed method.

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