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Determination of europium by using the chemical oscillating system of Ce(IV)-$KBrO_3$-acetone-oxalic acid-H_2SO_4

Research Article

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Abstract: A sensitive and convenient method for the determination of trace europium ions using an oscillating chemical reaction involving Ce(IV) - $KBrO_3$ - acetone - oxalic acid - H_2SO_4 was proposed. The results indicated that the changes in oscillating period (T) was linearly proportional to the negative logarithmic concentration of Eu^{3+} (-log C) in the range of $1.41 \times 10^{-8} \sim 1.41 \times 10^{-4}$ mol L^{-1} ($r = 0.9982$) with a detection limit of 1.04×10^{-9} mol L^{-1}. The recoveries were limited to the range of 99.5% to 100.8%. Under the same conditions, other rare earth ions did not interfere with the determination of Eu^{3+}. In addition, a perturbation mechanism was

Keywords: *Europium • oscillating chemical reaction • determination*

1. Introduction

As an analytical method, the Belousov-Zhabotinsky (B-Z) oscillating chemical reaction has been widely used. The essential principle is based on the perturbation of an analyte in a regular oscillating chemical reaction, causing a change in the amplitude and/or period as well as the induction period. These changes are directly related to the amount of analyte added. With the aid of this relationship between the change of signal and the amount of analyte added, various analytical methods will be investigated [1,2]. The classical B-Z reaction was designed as a redox system consisting of malonic acid (reductant) and potassium bromate (oxidant) in an acidic solution (sulfuric acid). This reaction also requires a catalyst (cerium ion Ce^{4+}) to speed up the rate of reaction. During this process an autocatalytic species, $HBrO_2$, was formed to alter the intermediate reaction pathway. The oxidized cerium ion, Ce^{4+}, is pale yellow in color and the reduced state, Ce^{3+}, is clear. The oscillation for this reaction can be clearly observed due to the change of the cerium ion from yellow to clear and back to yellow again. This oscillation can be also recorded using an electrochemical instrumental based on the change of potential or current versus the reaction time [3-5]. This reaction is a regular oscillating chemical profile similar to the baseline found in instrumental analysis. Because different oscillators (*i.e.*, different composite of system) have the different sensitivity to the analytes, some researchers have moved their focus on the improved B-Z oscillating system. In this paper, we proposed a B-Z oscillating system containing Ce(IV), $KBrO_3$, acetone, oxalic acid and H_2SO_4 [6-13]. It was found that this system was very sensitive and highly selective towards Eu^{3+}.

The determination of europium is generally established using spectrofluorimetry, flow injection spectrophotometry, laser-induced breakdown spectroscopy, or voltammetry [14-23] and sometimes a pre-separation and a lot of solvent are required for these methods. Relative to these techniques, the proposed method has many benefits, such as simple set-up with ease of operation, and a wide linear range with lower detection limit. These qualities satisfy the requirements of most fields.

2. Experimental procedure

2.1. Reagents

All chemicals used to establish the B-Z oscillating system such as $KBrO_3$, acetone, oxalic acid, H_2SO_4, and $Ce(SO_4)_2 \cdot H_2O$ were of analytical grade. Doubly distilled water was used for solution preparation. Solutions

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of $KBrO_3$, $Ce(SO_4)_2$, acetone, and oxalic acid were prepared in 1.00 mol L^{-1} sulfuric acid. Stock solutions of various rare earth ions (RE^{3+} ions) were prepared by dissolving their oxides in 1.00 mol L^{-1} sulfuric acid and their concentration were determined by EDTA titration using xylenol orange as an indicator. Solutions of lower concentration were temporarily diluted with 1.00 mol L^{-1} sulfuric acid just prior to use.

2.2. Apparatus

The experiment was performed in a closed thermostat-regulated glass container (*ca.* 50 mL) equipped with a magnetic stirrer for homogenization. A CHI832 electrochemical analytical instrument (Chenhua Instrumental Company, Shanghai, China) was connected to a reactor through two Pt electrodes (Rex, 213, China), one electrode is functioning as the working electrode and the other as the counter electrode, and an $Hg/Hg_2SO_4/K_2SO_4$ is employed as the reference electrode (Rex, 217, China) to record the potential changes. A Type 302 bromide selective electrode was used to measure the change of bromide ion concentration. A micro-injector was used to inject sample solution.

2.3. Procedure

The reaction was carried out in a glass vessel (*ca.* 50 mL) fitted with a Model 501 thermostat and a Model ML-902 magnetic stirrer. A mixed solution containing 6.10 mL of 4.67×10^{-1} mol L^{-1} acetone, 2.60 mL of 1.5×10^{-1} mol L^{-1} oxalic acid, 5.00 mL of 1.00 mol L^{-1} sulfuric acid, 5.40 mL of 6.67×10^{-2} mol L^{-1} of potassium bromate and 0.90 mL of 1.00×10^{-2} mol L^{-1} of $Ce(SO_4)_2$ was loaded into a water-jacket reactor to with a total volume of 20.00 mL. The solution was mixed well by stirring and maintained at 28 ± 0.1°C. Meanwhile, the indicator, counter and reference electrodes were immersed into the mixture solution and the data acquisition was initiated. After 400 s, the amplitude and period of oscillation were stabilized, and then 0.20 mL of various amounts of RE^{3+} sample solutions were injected while the platinum electrode potential was dropped to a minimum. The lowest position of the regular oscillating profile is the optimal injection point because this is where the system will respond to the most to changes with both period and amplitude.

3. Results and Discussion

For convenience, we defined the change of oscillating period ($\Delta T = T - T_o$) as the detection criterion before and after adding the analyte into the oscillating reaction system, where T_o and T represent the period before and after introducing the analyte into the system. As shown in Fig. 1, the perturbed profile would be restored in a shorter time, and this feature offers the opportunity for continuing analyte injection. The pre-examination showed that the injection position was generally selected at the bottom of the profile in order to obtain the largest response. Before the determination, each injection point must be rechecked to ensure good repeatability. All results indicated that the changes of period (ΔT) were proportional to the negative logarithm of the concentration of the analytes. When the Eu^{3+} was injected into the system, the oscillating period of system was clearly reduced as shown in Fig. 1.

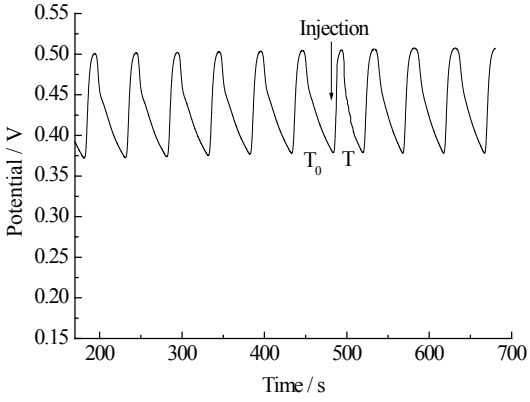

Figure 1. The perturbation of Eu^{3+} to the regular B-Z oscillating chemical system.
Experimental conditions: [acetone] = 1.42×10^{-2} mol L^{-1}, [$(COOH)_2$] = 1.95×10^{-2} mol L^{-1}, [H_2SO_4] = 1.00 mol L^{-1}, [$KBrO_3$] = 1.80×10^{-2} mol L^{-1}, [$Ce(SO_4)_2$] = 4.50×10^{-4} mol L^{-1}, [Eu^{3+}] = 1.41×10^{-3} mol L^{-1}, T = 28 °C

3.1. Optimization of experimental conditions for the determination

To gain the maximum sensitivity and accuracy possible in the determination of Eu^{3+}, the following parameters were examined in detail. In all experiments, only one parameter was changed within a limited range while the other parameters were kept constant, and the total volume was always maintained at 20.00 mL.

Based on the experimental results, the chemical oscillating described in this paper could appear to be periodic with oscillating behavior only when the concentrations of its components and temperature are limited to narrow ranges, otherwise, the regular oscillating profile would be destroyed. For example, when the concentration of acetone is too low (see Fig. 2a) or too high (see Fig. 2c), the regular oscillating profiles disappeared for a while and were unstable. In other words, the best regular oscillating behavior for this solution only exists with an acetone concentration of 1.42×10^{-2} mol L^{-1} (shown in Fig. 2b). Therefore, 1.42×10^{-2} mol L^{-1} acetone was chosen for the determination. A similar analysis were used to establish the following optimal experimental

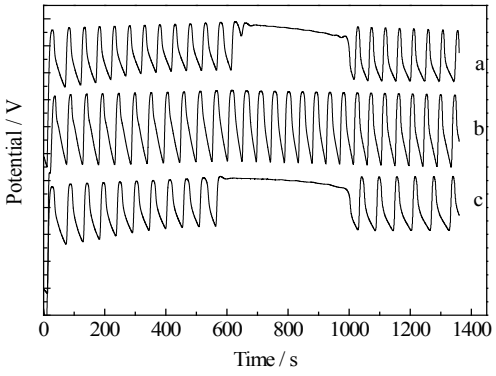

Figure 2. Potential-time profile of B-Z oscillating system at different experimental conditions.
Conditions: (a) [acetone] = 1.28×10^{-2} mol L^{-1}; (b) [acetone] = 1.42×10^{-2} mol L^{-1}, (c) [acetone] = 1.51×10^{-2} mol L^{-1}. Other conditions are the same as which in Fig. 1

parameters for obtaining the regular oscillating profiles for the determination of Eu^{3+}; 4.50×10^{-4} mol L^{-1} Ce^{4+}, 1.95×10^{-2} mol L^{-1} oxalic acid, 1.00 mol L^{-1} H_2SO_4, 1.80×10^{-2} mol L^{-1} $KBrO_3$ and a temperature of 28°C.

3.2. Determination of Eu^{3+}

When a certain amount of Eu^{3+} is added into the Ce(IV) - $KBrO_3$ - acetone - oxalic acid - H_2SO_4 chemical oscillating system, the oscillating period decreases (as shown in Fig. 1), and the changes in oscillating period are linearly proportional to the negative logarithm concentration of Eu^{3+} (-logC) in the range of 1.41×10^{-8}~1.41×10^{-4} mol L^{-1} (r=0.9982) with a detection limit of 1.04×10^{-9} mol L^{-1}, as shown in Fig. 3. The linear relationship can be expressed by the following regression equation:

ΔT (s) = -2.307-0.268×(-logC)

(r = 0.9982, SD = 2.36%)

Under the optimal conditions described above, the perturbations of 13 RE^{3+} (expect for Eu^{3+}) were investigated. If we take the size of ΔT (ΔT = -0.2s) caused by 1.41×10^{-8} mol L^{-1} Eu^{3+} as a reference, the concentrations of the other RE^{3+} ions need to be higher, that is, the sensitivities could be lower. In Table 1, the concentrations of other RE^{3+} ions are more than 1.41×10^{-8} mol L^{-1}. Table 2 showed the tolerance level which was defined as the maximum amount of foreign species causing an error being limited less than ±5% (R.S.D.) for determination of Eu^{3+} of 1.41×10^{-8} mol L^{-1}. It can be seen from Table 1 and Table 2 that the other rare earth ions did not interfere with the determination of Eu^{3+}. However, Cl^- and I^- ions slightly affect the determination of Eu^{3+} (see Table 3), since they can perturb the regular profile [24].

3.3. Comparison with other methods

In order to ensure the sensitivity responsible of the proposed method, Eu^{3+} was also measured using other

Table 1. The determination of the concentration of RE^{3+} (C_{RE}^{3+}/ mol L^{-1}) when ΔT = -0.2 s

RE^{3+}	**Y^{3+}**	**La^{3+}**	**Pr^{3+}**	**Nd^{3+}**	**Sm^{3+}**	**Eu^{3+}**	**Gd^{3+}**
C_{RE}^{3+} (mol L^{-1})	1.25×10^{-7}	1.09×10^{-5}	8.12×10^{-7}	1.47×10^{-7}	1.47×10^{-7}	1.41×10^{-8}	1.41×10^{-7}
RE^{3+}	**Tb^{3+}**	**Dy^{3+}**	**Ho^{3+}**	**Er^{3+}**	**Tm^{3+}**	**Yb^{3+}**	**Lu^{3+}**
C_{RE}^{3+} (mol L^{-1})	2.63×10^{-7}	1.05×10^{-6}	6.17×10^{-6}	1.66×10^{-4}	1.70×10^{-5}	1.51×10^{-6}	1.62×10^{-6}

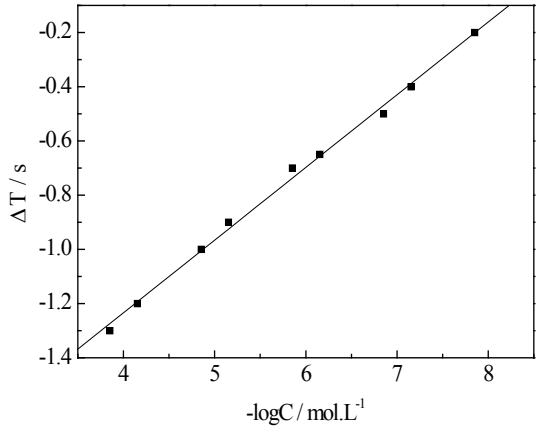

Figure 3. Calibration curve for the ΔT versus -logC_{Eu}^{3+}

Table 2. The effect of other RE^{3+} ions on the determination of Eu^{3+} of 1.41×10^{-8} mol L^{-1}

Foreign species	**Tolerated ratio (Foreign/ Eu^{3+})**
Er^{3+}	12000
Tm^{3+}	1200
La^{3+}	800
Ho^{3+}	450
Lu^{3+}, Yb^{3+}	100
Dy^{3+}	70
Pr^{3+}	60
Tb^{3+}	20
Nd^{3+}, Sm^{3+}, Gd^{3+}, Y^{3+}	10

Table 3. The effect of other foreign species on the determination of Eu^{3+} of 1.41×10^{-8} mol L^{-1}

Foreign species	**Tolerated ratio (Foreign/Eu^{3+})**
Na^+, K^+, Mg^{2+}, HPO_4^{2-}, NO_3^-, $H_2PO_4^-$	5000
Cu^{2+}, Ba^{2+}, Zn^{2+}, Al^{3+}, CN^-	2000
Fe^{2+}, Fe^{3+}	200
Cl^-, I^-	10

Table 4. A comparison of the proposed method with other methods for determining Eu^{3+}

Method	Linear range (mol L^{-1})	Detection limit (mol L^{-1})
Flow injection spectrophotometry [14]	6.58×10^{-7}~3.95×10^{-6}	6.58×10^{-8}
Flow injection chemiluminescence [15]	2.0×10^{-7}~1.0×10^{-5}	6.2×10^{-8}
Spectrofluorimetry [16]	5.0×10^{-9}~1.0×10^{-6}	1.0×10^{-10}
Laser-induced breakdown spectroscopy(LIBS) [17]	6.6×10^{-5}~2.0×10^{-2}	3.3×10^{-5}
luminescence spectrometry[21]	1.00×10^{-11}~1.00×10^{-6}	1.00×10^{-13}
Spectrofluorimetry [22]	5.0×10^{-11}~5.0×10^{-7}	1.0×10^{-13}
Cathodic stripping voltammetry [23]		1.0×10^{-11}
The present work	1.41×10^{-8}~1.41×10^{-4}	1.04×10^{-9}

Table 5. The determination results of Eu^{3+} of groundwater samples.

Samples (n=6)	1	2	3	4	5	6
Result (mol L^{-1})	5.50×10^{-6}	5.54×10^{-6}	5.50×10^{-6}	5.50×10^{-6}	5.53×10^{-6}	5.49×10^{-6}

Table 6. The results and recoveries for determining Eu^{3+} in artificial water samples.

Sample No. (n=4)	Original (mol L^{-1})	Added (mol L^{-1})	Found (mol L^{-1})	Recovery (%)
1	1.41×10^{-6}	7.03×10^{-9}	1.41×10^{-6}	99.5
2	1.41×10^{-6}	7.03×10^{-8}	1.49×10^{-6}	100.7
3	1.41×10^{-6}	7.03×10^{-6}	8.51×10^{-6}	100.8
4	1.41×10^{-6}	7.03×10^{-5}	7.21×10^{-5}	100.5

techniques. As seen in Table 4, the proposed method is fairly sensitive, and useful for the routine analysis of Eu^{3+}.

3.4. Detection of water samples

Fresh groundwater samples were boiled for 1 minute, then filtered through a 0.45 μm sand funnel to remove any suspended particulate matter and cleaned with tetrachloromethane to leach the organic substances. Six samples are collected in glass bottles and stored in the dark until analysis. The results show that this method has good reproducibility (see Table 5).

In addition, four artificial wastewater samples containing Eu^{3+} were analyzed using the proposed method, and satisfactory results were obtained in Table 6. The recoveries were limited to the range between 99.5% and 100.8%.

3.5. Possible mechanism

The system disturbances may have two reasons, one of them may give rise to redox reactions; another cause is that the analyte reacting with the substrate and/or intermediate in the oscillating system to form a complex. In this oscillating system, when certain amounts of RE^{3+} were added into the system, some of the redox reactions between RE^{3+} and Ce(IV) or Ce(III) ions appears more reasonable. This would change the ratio of Ce(IV)]/Ce(III) immediately after the injection of the RE^{3+} sample, causing a change in the period and/or amplitude for a short time until a full system of reactions is restored to its original dynamics state. As we know, in an acidic solution the alternation between Eu^{3+} and Eu^{2+} ions is easier than other rare earth ions, thus, this system would be very sensitive to Eu^{3+} ions. On the other hand, some RE^{3+} ions could also react with oxalic acid to form rare earth oxalate precipitation and causing the concentration of oxalic acid in the oscillating system decreased slightly, in which the solubility product of europium oxalate is smaller than other rare earth oxalate. The formation of a rare earth oxalate would change the optimal conditions for maintaining a regular oscillating profile for a time and because of these facts the proposed oscillator can be used to determine the europium.

4. Conclusions

In this paper, a sensitive and selective method for the determination of trace amount Eu^{3+} was proposed. Relative to the instrumental analysis, the equipment used in the proposed method is less expensive. Moreover, a larger linear range and lower detection limit could satisfy the need of common determination.

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