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Flow injection kinetic spectrofluorimetric determination of trace amounts of osmium

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Abstract

A flow injection (FI) kinetic spectrofluorimetric method is described for the determination of osmium(IV) and the possible mechanism of catalytic reaction is discussed. The method is based on the fluorescence enhancing reaction of *o*-vanillin furfuralhydrazone (OVFH) with potassium bromate, which is catalyzed by Os(IV) in water medium at pH 6.10 and 45 °C. OVFH is newly synthesized and its ionization, IR and elemental analysis are established. Under these experimental conditions, the oxidized product of OVFH has excitation and emission maxima at 337 and 490 nm, respectively. The linear range of this method is 0–600 ng ml^{-1} with the R.S.D. of 1.2%. The detection limit is 1.0 ng ml^{-1} of Os(IV). A high analysis rate of 24 samples h^{-1} is obtained by the FI method. The proposed method is applied successfully to determine Os(IV) in synthetic mixture and mineral samples, and the results are well consistent with the standard values.

Keywords: Osmium(IV) determination; Flow injection; Catalytic kinetics; Spectrofluorimetric analysis; *o*-Vanillin furfuralhydrazone (OVFH)

1. Introduction

As a very valuable and precious metal element, osmium is widely used. Recently, osmium has been used in analysis field [1–5]. Osmium usually coexists with other platinum group metals in ores, rocks, soils, minerals and alloys. In order to obtain accurate values of trace osmium in these samples, it is necessary to find highly sensitive and selective method for determining this element.

In recent years, many new methods for osmium analysis have been proposed such as radiochemical neutron activation analysis (RNAA), inductively coupled plasma mass spectrometry (ICPMS), inductively coupled plasma atomic emission spectrometry (ICPAES) [6], electroanalytical method [7] and catalytic spectrophotometry [8,9]. The catalytic kinetic spectrofluorimetric method has many advantages, for example, it has high sensitivity and good selectivity and experimental operation and equipment are simple. In our work, trace amounts of osmium has been successfully determined by the catalytic kinetic spectrofluorimetry [10].

The flow injection (FI) method is a very useful technique for the rapid determination of many samples, because it can accomplish high sampling automatism with good precision. Moreover, FI technique can make reproducible timing analysis, eliminate sample pretreatment and minimize solvent and reagent consumption [11,12]. The determination of osmium with some new methods as follows: trace analysis of osmium using flow injection kinetic catalytic spectrophotometric methods were reported, such as γ-acid–O_2 system [13], bromphenol red–H_2O_2 system [14] and *m*-acetylchlorophosphonazo–osmium system [15]. The flow injection catalytic kinetic fluorescence method combines the advantages of the flow injection method with those of catalytic kinetic fluorescence method, so it is a kind of more perfect determination method. But so far, the flow injection catalytic kinetic fluorescence analysis for osmium has not been reported.

In this work, a new fluorescent reagent OVFH is synthesized and a novel flow injection spectrofluorimetry is developed to determine osmium. As osmium is determined

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in a positive catalyst to the fluorescence enhancing system of OVFH–$KBrO_3$, the linear range of this method is 0–600 ng ml^{-1} with a detection limit of 1.0 ng ml^{-1}. No coexisting ion interferes with the determination of the same level of Os(IV). The method has been successfully applied to determine osmium in synthetic mixtures and mineral samples.

2. Experiment

2.1. Apparatus

All fluorescent measurements were carried out on a CARY-Eclipse (Varian, Australia) spectrofluorimeter, with a xenon lamp and an 18 μl flow quartz cell. A FIA-3100 flow injection analysis device (Wantuo Experiment Device Works, Beijing, China) was used. The UV spectrum was recorded on the UV-265 recording spectrophotometer (Shimadzu, Kyoto, Japan). All pH measurements were made with a pHS-3c digital pH-meter (Shanghai Leici Device Works, Shanghai, China) with a combined glass–calomel electrode. Perkin–Elmer 983 infrared spectrophotometer (KBr discs, Norwalk, CT, USA) and Perkin–Elmer 2400 elementary analysis apparatus (Norwalk, CT, USA) were used. Constant temperature container CS50 (Chongqing Experiment Device Works, Chongqing, China) was also used.

2.2. Reagents

All chemicals were of analytical reagents grade or the highest purity available. De-ionized water was used throughout. A stock solution of osmium(IV) (100 ng ml^{-1}) was prepared by dissolving 0.02308 g of spectrographically pure $(NH_4)_2OsCl_6$ in 20 ml of 2 mol l^{-1} HCl and diluting to 100 ml with water. OVFH solution (5.00×10^{-4} mol l^{-1}) was prepared by dissolving 0.0130 g of the reagent in 100 ml of absolute ethanol. The working solutions were prepared by stepwise dilution as required. Potassium bromate solution (0.040 mol l^{-1}) was prepared by dissolving 1.6700 g of the reagent in 250 ml of de-ionized water. A HAc–NaAc buffer (0.16 mol l^{-1}, pH 6.10) was used.

2.3. Synthesis and properties of OVFH

Synthesis route:

2.3.1. Synthetic route of *o*-vanillin furfuralhydrazone (OVFH)

2.70 ml of methyl-furoate (about 0.025 mol) and 3.00 ml of 85% hydrationhydrazine (about 0.025 mol) were put into a 50 ml flask, and then 25.0 ml of 95% ethanol was added. The mixture was refluxed for 5 h in a water bath at 80–90 °C, then it was distilled by decompression to eliminate ethanol. After the red-brown and ropy liquid was cooled, white and wax solid was obtained with a yield of 75%. The melting point of the solid was 75–76 °C.

1.26 g (0.010 mol) of formacylhydrazine was added into 40.0 ml of 95% ethanol, and the mixture was heated until it was dissolved completely, 1.52 g (0.010 mol) of *o*-vanillin was added into 20.0 ml of 95% ethanol, then it was heated to be dissolved. The solution of *o*-vanillin was added into the formacylhydrazine solution, then the mixture was refluxed for 2 h in a water bath at 90–100 °C, cooled and pumped out. The precipitation was washed with 10.0 ml of 95% ethanol for three times. 2.10 g of yellowish powder were obtained with a yield of 81%. The melting point of the powder was 147–148 °C.

2.3.2. Structure and ionization constants of OVFH

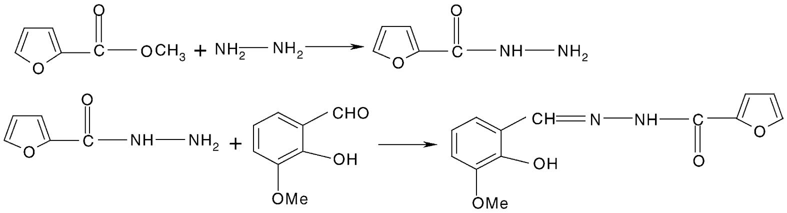
Elemental analysis gave a composition of: C 59.92%, H 4.61% and N 10.81%, which was in good agreement with the theoretical composition of OVFH: C 59.97%, H 4.65%, and N 10.77%.

The infrared spectrum of OVFH (KBr discs cm^{-1}) was obtained and the bands were assigned as follows: $\upsilon_{O–H}$ (3300), $\upsilon_{C=O}$ (1660), $\upsilon_{N–H}$ and $\upsilon_{C–N}$ (1555), $\upsilon_{C=N}$ (1608), $\upsilon_{C–N}$ (1250), $\upsilon_{Ar–O}$ (1238). The appearance of $\upsilon_{C–N}$ showed that the target compound of Scheme 1 synthetic reaction was formed.

Determination of ionization constants of OVFH:OVFH was insoluble in water but solved in ethanol more easily. The ultraviolet spectra of a water–ethanol solution of the reagent in media of various pH showed different absorbance maxima (Fig. 1). OVFH behaved as a bibasic substance with de-protonation of the hydroxy groups. Determined by a spectrophotometric method [16] (Fig. 2), the corresponding ionization constants were $pK_{a_1} = 3.82$, $pK_{a_2} = 8.10$, (in 0.10 mol l^{-1} KCl, at 20 ± 1 °C).

2.4. Procedure

The experimental flow injection diagram is given in Fig. 3. The positive and reversed phase flow injection systems were



Scheme 1.

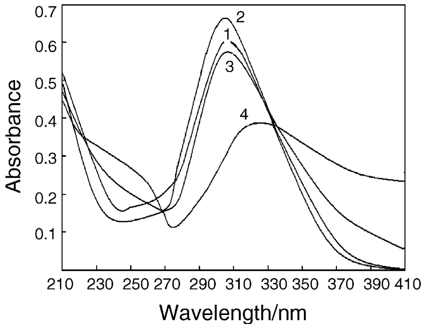


Fig. 1. Ultraviolet absorption of OVFH reagent (2.00×10^{-5} mol l^{-1}): (1) pH 2.80; (2) pH 6.10; (3) pH 9.30 and (4) pH 12.00.

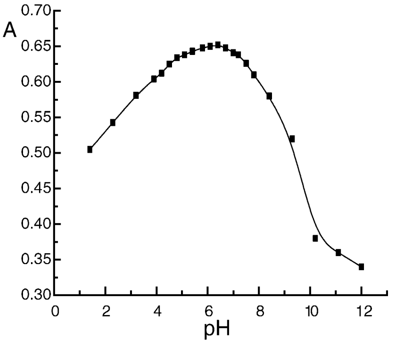


Fig. 2. Effect of pH on UV absorbance of OVFH reagent (2.00×10^{-5} mol l^{-1}) at 305.6 nm.

studied respectively. Positive phase FI was sample solution (osmium solution) being injected and OVFH solution as carrier, but reversed phase FI was reagent solution (OVFH solution) being injected and sample solution as carrier. It was found that fluorescence curve of positive phase FI was not stable, changed with time and had poor peak shape, but that of reversed phase FI was very stable and had good peak shape. So we chose reversed phase FI method, in which OVFH solution was injected, buffer and osmium solution were as carrier. All parameters were set up as following: $\lambda_{ex/em}$ = 337/490 nm, sampling volume 100 μl, reaction pipe length 200 cm, sampling time 38 s, injection time 22 s, peristaltic pump rotate speed of 30 rpm, the flow rate of OVFH was 1.38 ml min^{-1}, the flow rates of $KBrO_3$ and sample solutions were both 2.60 ml min^{-1}.

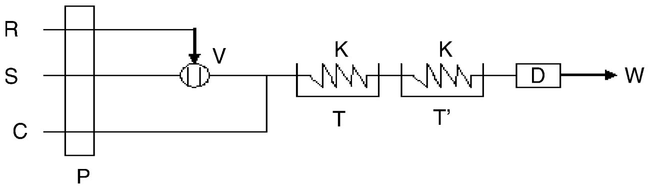


Fig. 3. Experimental flow injection diagram. R: reagent solution (OVFH + ethanol–water (v/v = 3:7) solution, 1.50×10^{-4} mol l^{-1}); S: buffer and osmium solution (pH 6.10, 0.16 mol l^{-1} HAc–NaAc); C: $KBrO_3$ (0.040 mol l^{-1}); P: peristaltic pump; V: sampling valve; K: reaction coil; T: constant temperature container (45 °C water bath); T': cooling device (cold water, room temperature 20 °C); D: spectrofluorimeter and W: waste.

The procedure was as follows: after peristaltic pump was started up, some OVFH solution was injected into reaction pipe, the carrier (buffer and osmium solutions) carried the injection zone flow through the reaction coil, in which they met the $KBrO_3$ solution. So the mixture produced enhancing fluorescence substance by catalytic oxidation reaction. Then flow injection system stopped for 90 s in 45 °C water bath. After flowing through the cold water bath to be cooled down to the room temperature, the solution flowed into flowing cell, in which the fluorescence intensity was measured at $\lambda_{ex/em}$ = 337/490 nm. Then the blank experiment was done with only buffer solution as carrier.

3. Results and discussion

3.1. Excitation and emission spectra

The fluorescence maxima of OVFH ($\lambda_{ex/em}$ = 344/494 nm) showed a hypsochromic change ($\lambda_{ex/em}$ = 337/490 nm) when potassium bromate was present in the solution. In the presence of trace amounts of Os(IV) the oxidation rate of OVFH increased owing to the catalytic effect of this ion (Fig. 4).

3.2. Influence of experimental variables

The pH of the medium had a great effect on the fluorescent intensity of the oxidized reagent (Fig. 5). In order to obtain the lower fluorescent intensity of the reagent blank and the higher signal-to-noise (the following optimum experimental variables were chosen, according to this principle also), a pH of 6.10 was fixed with acetate buffer. As the buffer injected (from 0.12 to 0.20 mol l^{-1}) had little effect on the fluorescent intensity, 0.16 mol l^{-1} acetate buffer was used in subsequent experiment.

The effect of temperature on both catalyzed and uncatalyzed reaction was studied over the range from 15 to 70 °C. The fluorescent intensity of both systems increased smoothly in the range of 15–50 °C, increased greatly in the range of

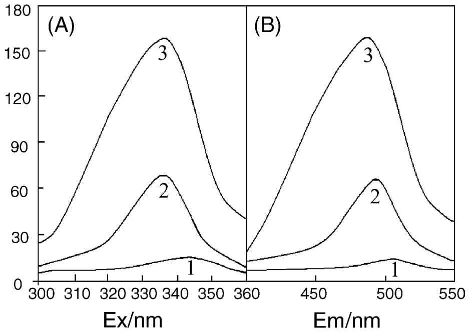


Fig. 4. Excitation (A) and emission (B) spectra. (1): OVFH; (2): OVFH + $KBrO_3$; (3): OVFH + Os(IV) + $KBrO_3$. [OVFH]: 1.50×10^{-4} mol l^{-1}; [Os(IV)]: 100 ng ml^{-1}; [$KBrO_3$]: 4.00×10^{-2} mol l^{-1}; pH 6.10, 0.16 mol l^{-1} HAc–NaAc.

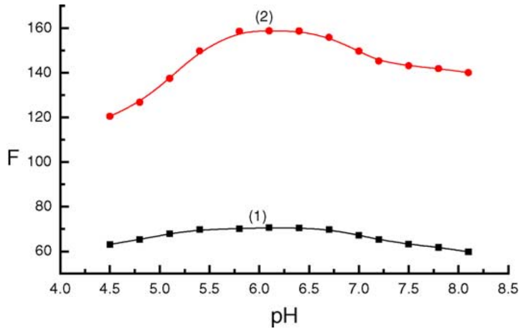


Fig. 5. Effect of pH on fluorescence intensity. (1): Uncatalyzed reaction; (2): catalyzed reaction. [OVFH]: 1.50×10^{-4} mol l^{-1}; [Os(IV)]: 100 ng ml^{-1}; [$KBrO_3$]: 4.00×10^{-2} mol l^{-1}.

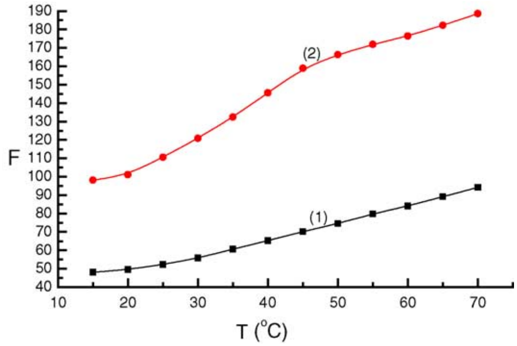


Fig. 6. Effect of temperature on fluorescence intensity. (1) Uncatalyzed reaction; (2): catalyzed reaction. [OVFH]: 1.50×10^{-4} mol l^{-1}; [Os(IV)]: 100 ng ml^{-1}; [$KBrO_3$]: 4.00×10^{-2} mol l^{-1}; pH = 6.10, 0.16 mol l^{-1} HAc–NaAc.

50–70 °C, so 45 °C was chosen as the optimum reaction temperature (Fig. 6).

When the temperature was fixed at 45 °C, the fluorescent intensity of the catalyzed reaction had linear relationship with the stopped-flow time, whereas the uncatalyzed reaction rate increased smoothly. So the catalyzed reaction could be regarded as pseudo-zero reaction within the time range of 30–210 s (Fig. 7). Hence, the stopped-flow time was chosen as 90 s at a 45 °C water bath. The sampling time and injection time were fixed at 38 and 22 s, respectively. Under these conditions, the analysis rate was 24 samples h^{-1}.

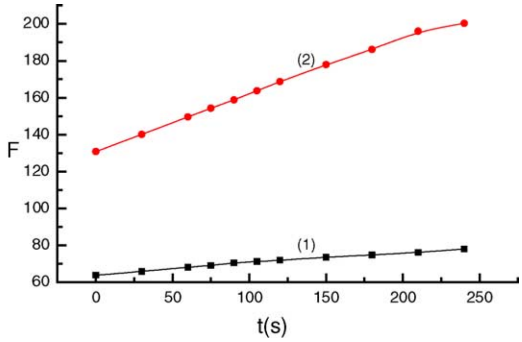


Fig. 7. Effect of stopped-flow time on fluorescence intensity. (1) Uncatalyzed reaction; (2): catalyzed reaction. [OVFH]: 1.50×10^{-4} mol l^{-1}; [Os(IV)]: 100 ng ml^{-1}; [$KBrO_3$]: 4.00×10^{-2} mol l^{-1}; pH 6.10, 0.16 mol l^{-1} HAc–NaAc.

Because sampling volume had a great effect on sensitivity and sampling frequency, with different sampling volume (50, 100, 200 and 300 μl) was examined. When the sampling volume increased the fluorescence intensity increased but the sampling frequency decreased. Hence, 100 μl of sampling volume was optimum. The effect of different peristaltic pump rotate speed on ΔF was also examined. The pumping rotate speed 30 rpm was chosen. Under these conditions, the flow rate of 1.50×10^{-4} mol l^{-1} OVFH was 1.38 ml min^{-1}, the flow rates of 4.0×10^{-2} mol l^{-1} $KBrO_3$ and sample solution were both 2.60 ml min^{-1}.

3.3. Determination of Os(IV)

3.3.1. Analytical characteristics

Under the optimum experimental conditions, there was a linear relationship between the fluorescent intensity and Os(IV) concentration in the range of 0–600 ng ml^{-1} with a correlation coefficient (r) of 0.9994. The regression equation was $\Delta F = 0.3280[\mathrm{Os(IV)}] + 6.400$, [Os(IV)]: ng ml^{-1}, 45 °C. The standard deviation of the fluorescence measurements was 0.1123 obtained from a series of 11 blank solutions. The detection limit was determined to be 1.0 ng ml^{-1}, according to IUPAC definition [17]. The relative standard deviation was 1.2% obtained from a series of 11 standards each containing 100 ng ml^{-1} of osmium.

3.3.2. Effect of interferences

Over thirty cations and anions and some complexing agents were studied individually to find their effects on the determination of 100 ng ml^{-1} Os(IV) by the procedure. An error of ±5% in the intensity values was considered tolerable. No interference was encountered from (tolerance ratio in mass): K^+, Na^+, Mg^{2+}, Cl^-, Br^-, $SO_4{}^{2-}$, tartrate (1000); Ba^{2+}, Ca^{2+}, Cr^{3+}, I^-, SCN^- (500); Pb^{2+}, Ni^{2+}, Mn^{2+} (200); Fe^{2+}, Be^{2+}, Cd^{2+}, Co^{2+}, Pd^{2+}, Sr^{2+}, Fe^{3+}, As(III), As(V) (100); Hg^{2+}, Sn^{2+}, Zn^{2+}, Sb^{3+}, F^-, EDTA (50); Ag^+, Pt(IV), Au^{3+},Cr(IV), $MnO_4{}^-$ (20); Cu^{2+}, Ru^{3+}, Rh^{3+}, Ir(IV) (10); Al^{3+} (2). Al^{3+} interfered with determination of Os(IV), but they were avoided by separating osmium through distillation [18].

3.3.3. Mechanism of reaction

The oxidation reaction of OVFH catalyzed by Os(IV) had Michaelis kinetic character: catalyzer and $KBrO_3$ could form 1:1 complex [19], which was the center of the oxidation reaction. The electrons transferred from OVFH to the lack of electrons center of osmium, which made OVFH oxidized and Os (IV) was oxidized to Os(IV) by $KBrO_3$. Reaction equation was as follows:

$$2BrO_3{}^- + OsCl_6{}^{2-} + 2H_2O$$
$$= (OsO_2(OH)_2)^{2+} + 2BrO_2{}^- + 6Cl^- + 2H^+$$

Table 1
Determination of osmium in synthetic mixtures

Sample	Composition of solution (ng ml^{-1})	Added (ng ml^{-1})	Found (ng ml^{-1})	Average (ng ml^{-1})	Average recovery (%)	R.S.D. (%)
A	Os(IV) (100) + Pd^{2+} (1000) + Ag^{+} (400) + Au^{3+} (400) + Pt(IV) (400)	100.0	100.6, 101.0, 100.1, 99.60, 99.80	100.2 ± 0.6	100	0.60
B	Os(IV) (100) + Rh^{3+} (200) + Ir(IV) (100)	100.0	98.50, 100.3, 99.40, 100.2, 99.90	99.66 ± 0.7	99.7	0.70
C	Os(IV) (100) + Ir(IV) (100) + Ru^{3+} (100) + Al^{3+} (60)	100.0	99.80, 100.5, 99.90, 100.2, 100.9	100.3 ± 0.5	100	0.50

$$(OsO_2(OH)_2)^{2+} + 2BrO_3^{-} = OsO_2(OH)_2(BrO_3^{-})_2$$

$$\begin{aligned}&4(OVFH)_{Red} + OsO_2(OH)_2(BrO_3^{-})_2 + 2H_2O\\&\quad \rightarrow 4(OVFH)_{Ox} + (OsO_2(OH)_2^{2+} + 2BrO_2^{-}\\&\quad + 4H^{+}(OVFH)_{Ox} : \text{oxide of OVFH}\end{aligned}$$

3.3.4. *Catalytic kinetic reaction mechanism*

The reaction mechanism probably consisted of oxidation scission of the azomethine group and oxidation of the resulting compounds [20]. σ coordinate bond was formed between full load π2p molecular orbital of –C=N– double bond and empty $5d^{2}6s6p^{3}$ hybrid orbital of Os(IV) in the way of lateral group complexation. Meanwhile, π bond was formed between electron-packed 5d6p hybrid orbital of Os(IV) and empty π*2p orbital of –C=N– double bond. This kind of bond formed between –C=N– and Os(IV) was similar with μ bond described by Dewar–Chatt–Duncanson model, which made partial electrons of z π bond in azomethine group's excited to π* antibond orbital (π–π* transition). Thus, the π bond in azomethine group was weakened. That was to say π bond was activated by the complexation between azomethine group and Os(IV). Because the donicity of azomethine group was greater than its acceptability, unsaturated carbon atom partially became positive ions which facilitate the nucleophilic attack. Then, the azomethine group was scissioned by oxidation. The oxidation was as follows: Os(IV) was oxidized to Os(VIII) by potassium bromate, then Os(VIII) oxidized OVFH to a fluorescence product and itself reduced to Os(IV).

One of the oxidation products was considered to be *o*-vanillic acid or its acid group [21], whose (π–π*) singlet state energy was not higher than that of (*n*–π*). When it existed in high polar hydrogen bond solvent, the charge transfer between carbonyl group and benzene ring would be reinforced by the intermolecular hydrogen bond. As a result, the lowest excitation singlet state changed from (*n*–π*) to (π–π*) and the fluorescence quantum yield increased greatly [22].

The reaction was regarded as a pseudo-zero order reaction within 30–210 s. Under the conditions established above, the reaction rate equation was:

$$R = -\frac{d[OVFH]}{dt} = \frac{dF}{dt} = K[Os(IV)] \qquad (1)$$

the integrating equation of (1) is: $F = K[Os(IV)]t$.

Table 2
Determination of osmium in mineral sample ($n = 5$)

Sample	Standard value (g/T)	Found value (g/T)	R.S.D. (%)
Mineral sample of the geological system of China (No. 974)	0.05800	0.05620 ± 0.00180	3.2

The linear relationship between the fluorescent intensity of the oxidation product and the concentration of the catalyzer (Os(IV)) had been testified. Moreover, two working curves had been made at different temperature

$$\begin{aligned}\Delta F &= 0.3280[Os(IV)] + 6.4000,\\ r &= 0.9994([Os(IV)] : ng\,ml^{-1},\ 45\,^{\circ}C)\end{aligned} \qquad (2)$$

$$\begin{aligned}\Delta F &= 0.2056[Os\ (IV)] + 3.1200,\\ r &= 0.9994([Os(IV)] : ng\,ml^{-1},\ 35\,^{\circ}C)\end{aligned} \qquad (3)$$

Two different rate constants could be gained from Eqs. (2) and (3): $K_{45\,^{\circ}C} = 0.2187\ min^{-1}$, $K_{35\,^{\circ}C} = 0.1371\ min^{-1}$. So the Arrhenius equation was: $\ln K = -4122.1/T + 11.432$; apparent activation energy was $E_a = 34.271\ kJ\ mol^{-1}$, and frequency factor was: $A = 9.225 \times 10^{4}\ min^{-1} mol\ l$.

3.4. *Applications*

The developed method had been successfully applied to the determination of osmium in a series of synthetic mixtures (Table 1) and in mineral sample (Table 2).

It was necessary to separate the osmium from the interfering ions in synthetic mixture C [18].

The procedure of mineral sample analysis was as reference [10].

4. Conclusions

The method was found to be a perfect spectrofluorimetric determination method of osmium(IV) with good selectivity, high sensitivity and wide linear range. Distillation was used to separate osmium from interfering elements in the samples. The proposed method has been successfully applied to the determination of osmium in synthetic mixtures and mineral sample.

Acknowledgements

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