A Kinetic Spectrophotometric Method for Simultaneous Determination of Uranium, Iron and Vanadium with a Stopped-Flow Technique

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A kinetic spectrophotometric method for simultaneous determination of components of a ternary mixture is proposed. A procedure for simultaneous determination of uranium(IV), iron(II) and vanadium(IV) is established, based on the inductive effect of them on chromium(VI)–iodide reaction in weak acidic medium. The reaction was monitored with the stopped-flow spectrophotometric technique by using I$_3$–starch complex as indicator. The calibration graphs are linear for 0–3.6 μg ml$^{-1}$ U(IV), 0–2.8 μg ml$^{-1}$ Fe(II) and 0–2.5 μg ml$^{-1}$ V(IV). Most foreign ions, except antimony(III) and titanium(III), do not interfere with the determination. Uranium, iron and vanadium contents in a phosphate ore were determined with the proposed method, and the results are satisfactory.

The determination of uranium is more and more important in environmental analytical chemistry, owing to the increasing application of nuclear materials. Among the routine techniques, spectrophotometric procedures had taken an important part...
in practice [1–3]. Kinetic procedures had successfully been used for determination of trace elements in various samples, but only few procedures for determination of uranium are available [4, 5]. Uranium content in phosphate ore had been determined in our laboratory using uranium(IV) induced chromium(VI)–iodide indicator reaction [6], but iron(II) and vanadium(IV) seriously interfere with the determination. The suitable separation procedures must be introduced.

In the present paper a method for simultaneous determination of ternary mixture is proposed, based on the principle of induced reactions. The kinetics of uranium(IV), iron(II) and vanadium(IV) induced chromium(VI)–iodide reaction was investigated with stopped-flow technique by using I$_3^-$–starch complex as indicator, and a kinetic procedure for simultaneous determination of uranium, iron and vanadium without separation is proposed. The content of uranium, iron and vanadium in a phosphate ore and in a synthetic sample had been determined and the results are satisfactory.

EXPERIMENTAL

Reagents

All solutions were prepared using analytical grade chemicals and redistilled water.

Uranium stock solution (120 μg ml$^{-1}$): Dissolve 0.0212 g of UO$_2$SO$_4$·3H$_2$O in 5 ml of water, and reduce U(VI) to U(IV) with Jones Reductor prepared according to literature [7]. Adjust the solution to pH 2.0, and dilute it to 100 ml. This solution must be prepared weekly.

Iron(II) stock solution (25 μg ml$^{-1}$): Dissolve 0.0438 g of (NH$_4$)$_2$Fe(SO$_4$)$_2$·6H$_2$O in water, adjust the solution to pH 2.0 with diluted HCl, and dilute it to 250 ml.

Vanadium(IV) stock solution (50 μg ml$^{-1}$): Dissolve 0.0178 g of V$_2$O$_5$ in 5 ml of 2 mol l$^{-1}$ HCl, reduce V(V) to V(IV) with Jones Reductor, adjust the solution to pH 2.0, and dilute it to 200 ml. This solution is stable for a fortnight.

Chromium(VI) solution: 1.6x10$^{-3}$ mol l$^{-1}$, prepared using standard K$_2$Cr$_2$O$_7$, pH 2.0.

Potassium iodide solution: 1.8x10$^{-2}$ mol l$^{-1}$, pH 2.0, prepared daily.

The carrier solution is redistilled water of pH 2.0, and containing 0.1 % of starch.

Apparatus and procedure

The reaction rate was followed on a 721 type spectrophotometer at 590 nm, which is equipped with a 10 μl flow cell, connected to a Syntone FIA-2400 analyzer with two peristaltic pumps of 10 channels and controlled by a computer. The sample solutions were introduced via a 16-ways injection valve with the sample loop of 20 μl.

The flow manifold is showed in Fig. 1. The inner diameter of the used Teflon tube was 0.5 mm, and the length of the mixing coil was L$_1$ = 300 mm, L$_2$ = 150 mm. The flow rate of carrier solution was 3.2 ml min$^{-1}$, and those of chromium(VI) and iodide solutions were both 3.0 ml min$^{-1}$.

The temperature was controlled with a Syntone FIA-T01 thermostat and pH measurements were performed on a PX5-5 type pH meter.

The sample solution was carried with starch containing redistilled water and mixed first with the potassium iodide solution inside the coil L$_1$, and then mixed with chromium(VI) solution inside the coil L$_2$, and was driven into the flow cell for stop. The rate of the coloured product formation was measured at 590 nm with respect to a reagent blank which has been predetermined and stored in the computer, and was deducted automatically during the determination. The absorption of I$_3^-$–starch complex was measured after 10 s, 20 s and 30 s from the stop of the flow.
Simultaneous determination of $U(IV)$, $Fe(II)$ and $V(IV)$

**Figure 1.** The manifold used in the determinations: $P_1$, $P_2$ - peristaltic pumps, $V$ - injection valve, $L_1$, $L_2$ - mixing coils, $R$ - recorder, $CR$ - data processing system controlled by a computer, $C$ - carrier, $R_1$ - KI solution, $R_2$ - chromium(VI) solution, $S$ - sample solution, $W$ - waste

**Principles of the determination**

Suppose that $I_1, I_2, \ldots, I_l$ are the inductors for the kinetically inhibited reaction: $Ox + Red \rightarrow P$, and that there are no interactions between the inductors or between intermediates of these induced reactions. The concentration of product $P$, arising from each induced reaction after a given time $t$, should, under fixed conditions and provided that neither reagent is exhausted (i.e. $t < \tau_o$), be proportional to the concentration of the corresponding inductor, i.e. $[P_i] = k_i[I_i]$, where each factor $k_i$ is a function of the inductive rate constant, the concentration of reagent, Ox or Red, and the temperature, etc.; $[I_i]$ is the analytical concentration of an inductor which remains unchanged along the reaction. Suppose that the product $P$ will form a complex with a colour reaction product, the absorbance of the complex at a certain wavelength will be

$$A = \sum k_i[I_i] = \sum K_i[I_i]$$

and at a certain time $t_j$ the total absorbance should be

$$A_{ij} = \sum K_{ij}[I_i]$$

The parameters $K_{ij}$ are determined in the reaction systems induced by a single inductor $I_i$ only, with the aid of the graph of absorbance versus inductor concentration at time $t_j$. The concentrations of inductors in the samples can then be calculated by solving the above equations with a computer.

In the present paper, the stopped time was chosen as $t = 30$ s, the absorbances were measured 10 s, 20 s and 30 s after the stop of the flow, and the absorbance was represented by the relative peak height.

**RESULTS AND DISCUSSION**

**The influence of acidity**

The determinations have been made in different acidic media, such as $\text{HNO}_3$, $\text{H}_2\text{SO}_4$, $\text{HCl}$, $\text{HClO}_4$ and $\text{H}_3\text{PO}_4$. The results indicated that the highest sensitivity was obtained in HCl medium. It was also showed that the acidity had a significant effect on the chromium(VI)–iodide reaction (Fig. 2). It is obvious that the relative peak height of induced–uninduced reaction systems reached maximum at pH range of
1.8–2.4, 1.7–2.2 and 1.6–2.0 for U(IV), Fe(II) and V(IV) induced reactions, respectively. The results also indicated that the reproducibility was worse at the acidity of pH<1.8, and the reaction was rather slow at pH>2.4. The acidity of pH 2.0 was therefore chosen for the procedure of determination.

![Figure 2](image)

**Figure 2.** The influence of pH on the relative peak height; [Cr(VI)] = 1.6×10^{-3} mol l^{-1}, [I^-] = 1.8×10^{-2} mol l^{-1}, t = 30 s; A – [U] = 0.6 μg ml^{-1}, B – [Fe] = 0.6 μg ml^{-1}, C – [V] = 0.6 μg ml^{-1}

**The influence of chromium(VI) and iodide concentrations**

Figures 3 and 4 show the effect of chromium(VI) and iodide concentrations on the relative peak height. It can be seen the remarkable influence of them on the determination. The increase of chromium(VI) concentration results in a significant increase of the relative peak height at a certain range, and the sensitivity is improved.

![Figure 3](image)

**Figure 3.** The influence of chromium(VI) concentration on the relative peak height; [I^-] = 1.8×10^{-2} mol l^{-1}, pH 2.0, t = 30 s; A – [U] = 0.6 μg ml^{-1}, B – [Fe] = 0.6 μg ml^{-1}, C – [V] = 0.6 μg ml^{-1}
Simultaneous determination of \( \text{U(IV)}, \text{Fe(II)} \) and \( \text{V(IV)} \)

\[ \text{[Cr(VI)]} \times 10^{-3}, \text{ mol l}^{-1} \]

**Figure 4.** The influence of iodide concentration on the relative peak height; \([\text{Cr(VI)}] = 1.6 \times 10^{-3} \text{ mol l}^{-1}\), pH 2.0, \( t = 30 \text{ s} \); A - [U] = 0.6 \( \mu \text{g ml}^{-1} \), B - [Fe] = 0.6 \( \mu \text{g ml}^{-1} \), C - [V] = 0.6 \( \mu \text{g ml}^{-1} \)

The relative peak heights remain unchanged or slightly increase as Cr(VI) concentration becomes greater than \( 2.0 \times 10^{-3} \text{ mol l}^{-1}, 1.5 \times 10^{-3} \), and \( 1.0 \times 10^{-3} \text{ mol l}^{-1} \), for U(IV), Fe(II) and V(IV) induced reactions respectively. On the other hand, the relative peak heights increase all along with the iodide concentration within the range of \([\Gamma^{-}] < 4.0 \times 10^{-2} \text{ mol l}^{-1} \). The results also indicated that the recalling effect of the tube increased remarkably and the reproducibilities deteriorated as \([\text{Cr(VI)}]\) was greater than \( 2.0 \times 10^{-3} \text{ mol l}^{-1}\) or \([\Gamma^{-}] > 2.4 \times 10^{-2} \text{ mol l}^{-1} \). So the concentrations \([\text{Cr(VI)}] = 1.6 \times 10^{-3} \text{ mol l}^{-1}, [\Gamma^{-}] = 1.8 \times 10^{-2} \text{ mol l}^{-1} \) were chosen for the procedure of determination.

The influence of stopped time and temperature

It is known that the sensitivity of I\(_3\)-starch complex reaction depends on the temperature [8]. The results indicated that higher sensitivity could be obtained with the increase of temperature within 15–50°C, but the complex tended to be unstable at higher temperature, which results in worse reproducibility. The determination was carried out at 25°C. The relative peak heights increased with stopped time within 0–300 s and 0–50 s for U(IV) or Fe(II) and V(IV) induced reactions, and the sensitivity of determination was improved. The stopped time \( t = 30 \text{ s} \) was chosen to increase only the sampling rate. The sensitivity of the determination was high enough under the conditions established above, and the sampling rate was 90 h\(^{-1}\).

Calibration and interferences

Different amount of uranium(IV), Fe(II) and V(IV) standard solutions were introduced into the reaction systems under the optimal conditions previously established, relative peak heights were measured 10 s, 20 s and 30 s after the stop of the flow. The following linear relationships were obtained between relative peak heights and uranium(IV), iron(II) and vanadium(IV) concentrations:
where \( r \) is the regression coefficient for several determinations.

The linear calibration graphs were obtained for 0–3.6 \( \mu g \) ml\(^{-1}\) U(IV), 0–2.8 \( \mu g \) ml\(^{-1}\) Fe(II) and 0–2.5 \( \mu g \) ml\(^{-1}\) V(IV). The working equations were derived as:

\[
\]

\[
\]

\[
H(30) = 38.768[U] + 55.345[Fe] + 52.646[V] - 5.125
\]

It is obvious that there is a surplus item in the working equation owing to the deviation of calibration graphs from origin of coordinates. This item must be considered into the working equations, otherwise it will cause a great error in the determinations.

The mixture of 1.0 \( \mu g \) ml\(^{-1}\) U(IV), 1.0 \( \mu g \) ml\(^{-1}\) Fe(II) and 1.0 \( \mu g \) ml\(^{-1}\) V(IV) was determined six times. The average recoveries for uranium, iron and vanadium were 95.1 %, 104.8 % and 96.7 %, respectively. The detection limits, calculated as three times the standard deviation of background, were 0.024 \( \mu g \) ml\(^{-1}\) U(IV), 0.008 \( \mu g \) ml\(^{-1}\) Fe(II) and 0.010 \( \mu g \) ml\(^{-1}\) V(IV). The results also did not show any interactions between uranium(IV), iron(II) and vanadium(IV) or between intermediates of the induced reactions.

The influence of foreign ions on the determination had also been studied, and the results are listed in Table 1. In each case, an appropriate amount of foreign ion was added to the standard U(IV), Fe(II) and V(IV) solutions and the recommended procedure was applied. The ions in Table 1 can be tolerated in the listed amounts within ±5 % error.
Simultaneous determination of U(IV), Fe(II) and V(IV)

Table 1. The influence of foreign ions on the determination of 1.0 μg ml⁻¹ U(IV), 1.0 μg ml⁻¹ Fe(II) and 1.0 μg ml⁻¹ V(IV)

<table>
<thead>
<tr>
<th>Ion</th>
<th>Tolerance ratio</th>
<th>Ion</th>
<th>Tolerance ratio</th>
<th>Ion</th>
<th>Tolerance ratio</th>
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</thead>
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<tr>
<td>Al(III)</td>
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<td>Mn(II)</td>
<td>200</td>
<td>Sn(II)</td>
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<tr>
<td>As(III)</td>
<td>10</td>
<td>Mo(VI)</td>
<td>50</td>
<td>Th(IV)</td>
<td>400</td>
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<tr>
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<td>Ni(II)</td>
<td>300</td>
<td>Ti(IV)</td>
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<tr>
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<td>Pb(II)</td>
<td>50</td>
<td>Ti(III)</td>
<td>1</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>100</td>
<td>RE(III)</td>
<td>300</td>
<td>W(VI)</td>
<td>300</td>
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<tr>
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<tr>
<td>Hg(II)</td>
<td>200</td>
<td>Se(IV)</td>
<td>20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Mean of six determinations.

Application of the method

2.0 g of phosphate ore were dissolved in 10 ml of 6 mol l⁻¹ HCl and appropriate amount of water, and heated to boil for several minutes. The solution was filtered, 0.5 g of zinc metal powder was then added to the solution and vigorously stirred for 15 min. The solution was filtered, adjusted to pH 2.0 with diluted NaOH solution, and diluted to 50 ml.

The synthetic sample solution was prepared in a similar way, and diluted to 100 ml.

The amount of uranium, iron and vanadium was then determined with the previously established procedure and using atomic absorption spectrometric method. The results are summarized in Table 2.

It is obvious that the results of the suggested method coincide well with those of atomic absorption spectrometric method.

Table 2. Determination of uranium, iron and vanadium content in phosphate ore and in a synthetic sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Uranium content* μg g⁻¹</th>
<th>Iron content* μg g⁻¹</th>
<th>Vanadium content* μg g⁻¹</th>
</tr>
</thead>
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<tr>
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<td>suggested method (RSD, %)</td>
<td>AAS method</td>
<td>suggested method (RSD, %)</td>
</tr>
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<td>Phosphate ore</td>
<td>32.78 (4.8)</td>
<td>34.48</td>
<td>78.64 (3.9)</td>
</tr>
<tr>
<td>Synthetic sample</td>
<td>60.78 (3.7)</td>
<td>63.18</td>
<td>37.54 (5.6)</td>
</tr>
</tbody>
</table>

*Mean of six determinations.
REFERENCES


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