CROATICA CHEMICA ACTA CCACAA **64** (4) 679–687 (1991)

ISSN-0011-1643
UDC 543
CCA-2035

Original Scientific Paper

Kinetic-Potentiometric Determination of Fe(III) using a Fluoride Ion-Selective Electrode*

Njegomir Radić and Josipa Komljenović

Laboratory for Analytical Chemistry, Faculty of Technology, University of Split, 58000 Split, Croatia

Received October 14, 1991

A kinetic-potentiometric method is described for the determination of Fe(III), based on monitoring of the formation of FeF^{2+} in acid solution, using a fluoride ion-selective electrode. The influence of pH and fluoride concentration in cell solution on the kinetics of iron – fluoride reaction was studied. The initial rate of the complex formation reaction, or change in potential during fixed time interval (1 minute), was used to construct calibration graphs. There is a linear relationship between the calculated initial rate or $(\Delta E)_{1\mathrm{min}}$ and the concentration of iron in the cell solution. Good linearity (r = 0.9979) was achieved in the range of iron concentration from 3.5 x 10^{-5} M to 1.4 x 10^{-3} M.

INTRODUCTION

The fluoride ion-selective electrode (FISE) with LaF_3 membrane has proved to be one of the most successful ion-selective electrodes. Combination of the simplicity of the kinetic method with the advantages of this sensor (low detection limit, high selectivity) produces an excellent analytical technique for determination of metal ions that form complexes with fluoride.

Suitability of the FISE for monitoring a reasonably fast reaction of the formation of FeF^{2+} in acid solution has been previously established.[1] Oehme and Dolezalova reported[2] the possibility of direct potentiometric determination of Fe^{3+} based on iron-fluoride complex formation but no detailed information was given.

The ion-doped chalcogenide glasses electrode responds to iron(III) ion concentration over a wide concentration range, with an average slope close to the electrode with the characteristics for monovalent ions. Studies were carried out in acid media (pH = 1 – 2), because decreased acidity causes a sharp potential fall.[3]

---

*Presented in part at the *12th Meeting of Chemists of Croatia, Zagreb, February 1991.*

The phenomenon of interference of iron(III) on solid state CuISE which contains a mixed sulphide has been used for the determination of iron(III) in aqueous solution.[4] The linear change in the potential of the electrode, which was sub-Nernstian, is caused by the Fe^{3+} oxidation of sulphide ion around the electrode surface. For this reason, the electrode's surfaces should be restored frequently by polishing, and the method is not recommended for measurements of high Fe(III) concentrations.

Previously we reported,[5] using CuISE and Cu^{2+}-EDTA buffered (pH = 4) cell solution, a kinetic determination of Fe(III) based on a Cu^{2+} displacement reaction. The relationship between the average rate of displacement reaction and the concentration of iron(III) was found to be linear for different concentrations of the Cu-EDTA complex.

In this work, the kinetics of the FeF^{2+} formation reaction were studied in acidic solution (pH = 1.8; 2.5). The initial rates of iron-fluoride complex formation in the solution, calculated from the non-steady-state potential values recorded after addition of Fe(III), were shown to be proportional to the analytical concentration of this ion in cell solution. The described procedure can be usefully applied for the determination of free Fe(III) or labile Fe(III), as the fluoride may displace weaker ligands.

EXPERIMENTAL

Potentiometric rate measurements were carried out with an Orion Model EA 940 Expandable ion Analyzer using a double-walled thermostated reaction vessel, maintained at 25±0.1 °C. Cell potentials were measured with an Orion 94-09 FISE *versus* an Orion 90-02 single-junction Ag/AgCl (3 M KCl) reference electrode. The pH values were checked with an Orion 91-02 glass electrode and 701 pH/mV-meter. During measurements, the solution was stirred by means of a Teflon-coated magnetic bar. Stirring speed and electrode distance were both kept constant.

Reagents

All chemicals were of analytical-reagent grade and were used without further purification. All solutions were prepared with water doubly distilled in glass.

Sodium fluoride solutions. Standard sodium fluoride solution, 0.1 M, was prepared in a polypropylene calibrated flask from dried (0.1 MPa, 110 °C) sodium fluoride. Dilute standard fluoride solution was prepared from the stock solution by dilution, using a propylene flask and a pipette.

Iron(III) standard solution. A stock solution of approximately 0.1 M was prepared by weighing and dissolving an appropriate amount of iron(III) nitrate in 1 M perchloric acid. Other solutions of iron were prepared from the standard solution by dilution with 0.1 M perchloric acid. Concentration of the ferric ion in the solution was estimated by titration with a standard solution of EDTA, using sulfosalicylic acid as indicator.

Acetate buffer (pH = 3.4). Buffer was made by mixing 380 cm^3 0.2 M acetic acid with 20 cm^3 0.2 M sodium acetate. The appropriate pH was checked by using pH electrode.

Measurement Procedure

Pipette 15.0 cm^3 of the acetate buffer, 10.0 cm^3 of water and 2.0 cm^3 of fluoride standard solution into the thermostated (25 °C) reaction vessel. In one part of experiments, 25.0 cm^3 of 0.01 M HCl_4 was added instead of acetate buffer and water. Start the stirrer and record the potential of the cell at 1-minute intervals. Initiate the iron-fluoride complex formation reaction by adding 2.0 cm^3 of iron working standard solution (10^{-4}–10^{-2} M) and record the reaction curve for 2–3 minutes.

Evacuate the reaction vessel, wash the vessel and electrodes with water and proceed to the next run. Before the next run, the FISE was soaked 2 minutes in stirred unbuffered 2 x 10^{-3} M fluoride solution and washed twice with water.

Using the standard solutions of iron, record the change in potential ΔE (mV) for 1 minute time intervals. When the acidities of standards and sample are different, ΔE for the blank should be subtracted from every ΔE measured for the standards or the sample. Construct a calibration graph for the fixed time method ΔE *versus* $-\log c_{\mathrm{Fe(III)}}$.

RESULTS AND DISCUSSION

Optimization of Initial Conditions

It is well known that the rate of a metal-fluoride complex formation is generally dependent on the pH. The influence of pH on both the kinetics of iron-fluoride complex formation and on the potential response of FISE has been considered.

In acidic solution, the cell potential is given by the equation:

$$E = E' - S \log\left\{c_{\mathrm{F}} / (1 + K_{\mathrm{HF}}\,[\mathrm{H}^+])\right\} \tag{1}$$

where S, c_{F} and K_{HF} denote the Nernstian slope (59 mV), total or analytical concentration of fluoride and the formation constant of HF ($K_{\mathrm{HF}} = 7.93 \times 10^2$), respectively.

The analytical concentration of iron in aqueous acidic solution is given by

$$c_{\mathrm{Fe(III)}} = [\mathrm{Fe}^{3+}] + [\mathrm{FeOH}^{2+}] + [\mathrm{Fe(OH)}_2^+] \tag{2}$$

Also, a polycomplex $\mathrm{Fe_2(OH)_2}^{4+}$ can be formed, but at low concentration of iron ($< 10^{-3}$ M) the formation of this kind of complex is neglected. If the next reaction between Fe^{3+} ions and fluoride is assumed to be the main path for the initial consumption of the complex with fluoride:

$$\mathrm{Fe}^{3+} + \mathrm{F}^- \rightleftharpoons \mathrm{FeF}^{2+} \tag{3}$$

the concentration of fluoride in solution, where $c_{\mathrm{Fe(III)}} >> c_{\mathrm{F}}$ may be defined by:

$$[\mathrm{F}^-] = [\mathrm{FeF}^{2+}] / \left([\mathrm{Fe}^{3+}] \times \beta_1\right) \tag{4}$$

where β_1 denotes the stability constant of FeF^{2+}.

For the chosen pH interval, from 0 to 4, changes in potential values, corresponding to the concentration of H^+, were calculated by using equation (5):

$$\Delta E = \left\{-\log\,[\mathrm{F}^-]_t - (-\log\,[\mathrm{F}^-]_{\mathrm{initial}})\right\} \times S \tag{5}$$

$$[\mathrm{F}^-]_t = \frac{c_{\mathrm{F}}}{\left\{\left(c_{\mathrm{Fe(III)}} - c_{\mathrm{F}}\right) / \left(1 + \beta_1^* / [\mathrm{H}^+] + \beta_2^* / [\mathrm{H}^+]^2\right)\right\} \times \beta_1} \tag{6}$$

$$[\mathrm{F}^-]_{\mathrm{initial}} = c_{\mathrm{F}} / (1 + K_{\mathrm{HF}} \times [\mathrm{H}^+]) \tag{7}$$

where βi^* ($i = 1, 2$) denote the hydrolysis constants of Fe^{3+},

$$\beta_i^* = \left([\mathrm{Fe(OH)}_i] / [\mathrm{Fe}^{3+}]\right) \times [\mathrm{H}^+]^i .$$

The values of 1.62×10^5, 1.00×10^{-3} and 5.01×10^{-7} for β_1, $\beta_1{}^*$ and $\beta_2{}^*$, respectively, were taken or computed from literature.[6]

The changes in potential values, ΔE, were calculated by using equation (5) and plotted *versus* pH, for two analytical concentrations of iron in Figure 1. Both curves in Figure 1 indicate the highest change of potential in the pH range from 2 to 3, and this acidity of solution has been selected for the study of $FeFi^{(3-i)+}$ formation reaction.

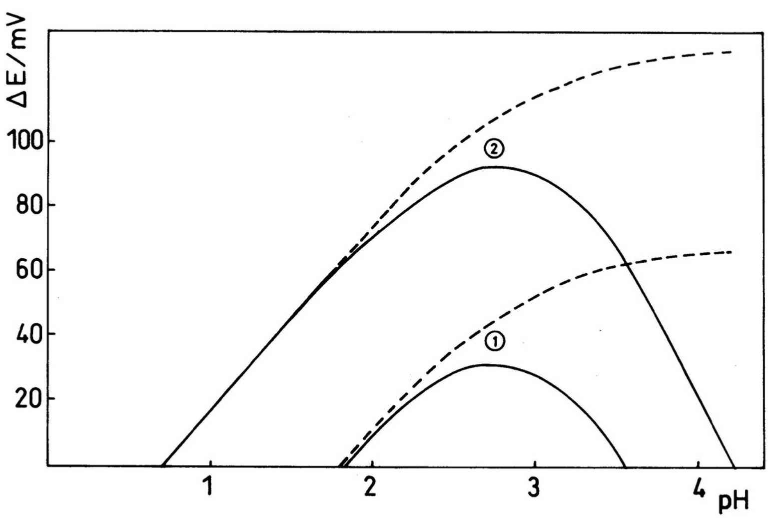

Figure 1. Changes in potential values, calculated by using equation (5), *versus* pH for two analytical concentrations of iron: 1. 1 x 10^{-4} M; 2. 1 x 10^{-3} M. Fluordie, c_F = 6.9 x 10^{-6} M. The dashed curves represent the change in potential values when the formation of $FeOH^{2+}$ and $Fe(OH)_2{}^+$ was omited.

Analytical Study of $FeFi^{(3-i)+}$ Formation

The reaction of iron with fluoride is carried out at pH 1.8 or 2.5. Typical cell potentials *versus* time curves recorded during the reaction between ferric and fluoride ions are shown in Figure 2. The potential of FISE becomes more positive indicating a decrease in the free fluoride ion concentration resulting from the formation of iron-fluoride complex and/or decrease of pH. At this point, it should be stressed that, at constant pH values, addition of the same quantity of iron, which was reduced from Fe(III) to Fe(II), does not alter the potential of FISE. Under the experimental conditions where $c_{Fe(III)} >> c_F$, FeF^{2+} formation may be expected through two paths in accordance with equations (3) and (8):

$$Fe^{3+} + HF \rightleftharpoons FeF^{2+} + H^+ \qquad (8)$$

If reaction (3), or (8), represents a bimolecular reaction, then the formation rate of products may be given by a simplified equation

$$d\,[FeF^{2+}] / dt = k_1\,[Fe^{3+}]\,[F^-] \qquad (9)$$

or

$$d[FeF^{2+}]/dt = k_2\,[Fe^{3+}]\,[HF]$$

where k_1 (k_2) is the specific rate constant.

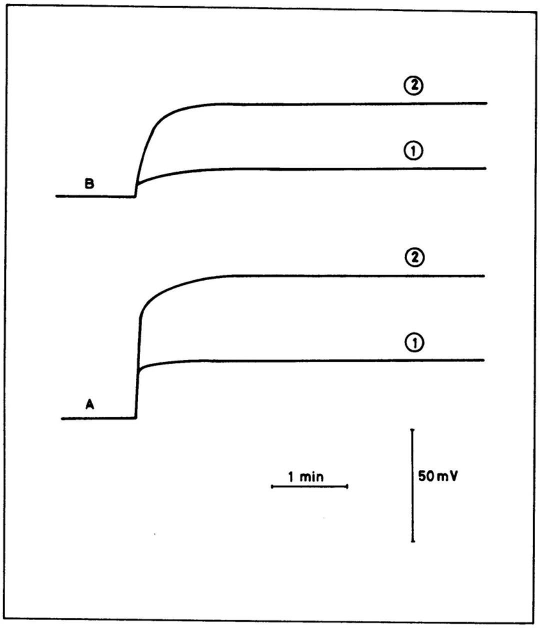

Figure 2. Dynamic response curves of the cell with FISE after adding 4 μmol of Fe(III), to the reaction solution containing 0.2 μmol of total fluoride at different pH; A, pH 3.4; B, pH 2.0. Curves A-1 and B-1 blank.

Theoretically, the initial rate of reaction is directly proportional to the Fe^{3+} concentration, but the exact relationship between the rate and concentration for a given reaction can be established only by experiment.

After addition of lower concentrations of iron into the reaction solution, the cell potential showed a monotonic and asymptotic approximation to the final steady state. Also, in experiments where $c_{Fe(III)} \leq 5 \times c_F$, the total changes in potentials are too small for useful analytical application. However, when a wide concentration range of iron was tested, $c_{Fe(III)} \geq 10 \times c_F$, the change in potential during fixed time (1 minute) was found to be linear with the iron concentration in solution (Figure 3). Good linearities (r = 0.9979, pH 1.8; r = 0.9958, pH 2.5) were achieved in the range of iron concentration from 3.5×10^{-5} M to 1.4×10^{-3} M. In addition, for the experiments where $c_{Fe(III)} / c_F \geq 10$, the rate of the process is sufficiently high. Otherwise, the main portion of the total change in potential occurs during a short time interval, and the initial rate can be calculated with non-steady-state potentials recorded 1 minute after the addition of iron, by using the next equation

$$\Delta[FeF^{2+}] / \Delta t = \Delta E / \Delta t \text{ (mV min}^{-1}) = (\Delta E)_{1\ \mathrm{min}} \qquad (10)$$

The recorded change in potential values, ΔE, or the calculated initial rate, $\Delta E / \Delta t$, are plotted *versus* log $c_{Fe(III)}$, for different analytical fluoride concentrations. It was found that a rectilinear range increases with a decrease of total fluoride concentration in the reaction solution.

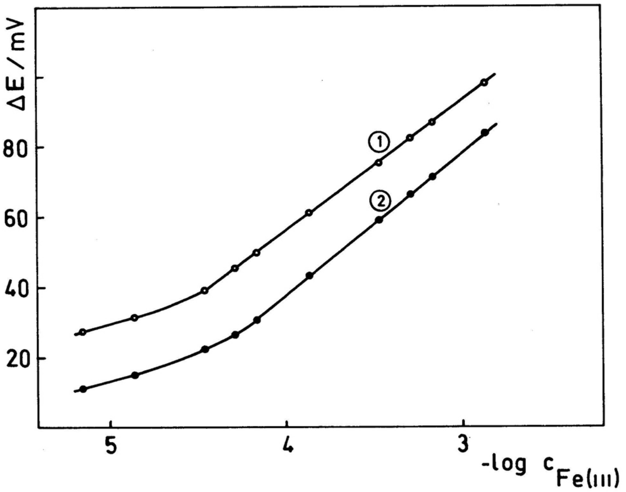

Figure 3. Relationship between the change in potential for a fixed time interval (1 minute) and the concentration of iron in the reaction solution at different pH; 1. pH 2.5; 2. pH 1.8. $c_F = 6.9 \times 10^{-6}$ M.

However, as the initial concentration of fluoride should be about ten times the actual detection limit of the utilized electrode, the sensitivity of the kinetic determination of iron is limited by c_F and pH. The initial concentration of fluoride, calculated by using equation (7) for the lowest total concentration of fluoride, $c_F = 6.9 \times 10^{-6}$ M, in solution with pH 2, was 8×10^{-7} M. This value is above the detection limit of the utilized electrode in acidic solution.[7]

After addition of the highest concentration that produces a linear relationship between the change in potential and iron concentration, the net cell potential was altered by more than 70 mV and the calculated concentration of fluoride was 3.28×10^{-8} (see below). This concentration of free fluoride in solution is very close to the one calculated from the solubility product of LaF_3-membrane ($K_{sp}^{LaF_3} = 10^{-29}$).

As shown by Baumann,[9] the linear response of FISE holds right down to 3.2×10^{-10} M fluoride in fluoride ion buffers consisting of metal-fluoride complexes. With regard to all these observations, the utilized electrode can be used with confidence in the proposed kinetic experiment.

Reversibility of the iron-fluoride complex formation and the potential-time response of the FISE have been examined by using a common analytical system. The basic buffered fluoride solution was stirred and monitored throughout successive additions of known amounts of iron(III), EDTA and fluoride (see Figure 4). The time response was recorded on an X – Y recorder.

When EDTA is added to a solution containing FeF^{2+} species, we can expect displacement of some fluoride ions because $K_{FeEDTA} > K_{FeF^{2+}}$. In the experiment, after each increment of EDTA before equivalence point, the potential of the FISE became more negative. The stable potential of the cell, recorded when the equivalence point was exceeded, indicates total iron in the Fe-EDTA form.

However, addition of sodium fluoride solution altered the potential of the cell and a steady-state potential was achieved within 1 minute. All these observations indicate that the potential of FISE satisfactorily follows free fluoride through the postulated equilibria in acidic solution.

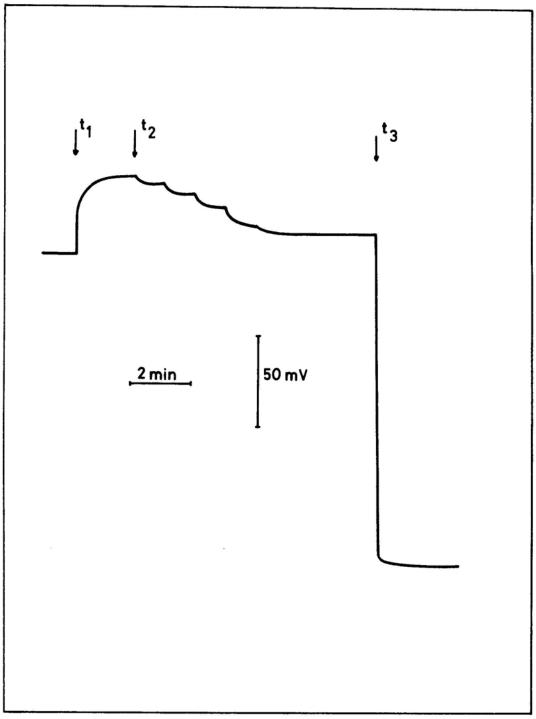

Figure 4. Dynamic response curves of the cell with FISE after adding 4 μmol of Fe(III) (t_1), 1 μmol EDTA (t_2) 7 X, and 200 μmol NaF (t_3) to the reaction solution, initially containing 0.2 μmol of total fluoride, pH 2.

According to the experimental results, the end point of the titration of Fe^{3+} with EDTA or other ligands that form a more stable complex than the fluoride may be indicated using the utilized electrode.

Calculation of Free Fluoride Concentration

In order to confirm which form of iron-fluoride complex is predominant under the experimental conditions, the free fluoride concentration was calculated. Using the recorded net change in potential for a fixed interval (1 minute), ΔE, during the kinetics experiments, the concentration of fluoride was calculated by equation (5) in the following rearranged form:

$$-\log [F^-] = \Delta E / S - \log [F^-]_{\text{initial}} \qquad (11)$$

In the experimental solution where $c_{Fe(III)} >> c_F$, the free fluoride concentration may also be calculated from the over-all formation constant of iron-fluoride complexes, which is the equilibrium expression for the over-all formation reaction $Fe^{3+} + iF^- \rightleftharpoons FeF_i^{(3-i)+}$:

$$[F^-] = \left\{ \frac{[FeF_i^{(3-i)+}]}{[Fe^{3+}] \times \beta_i} \right\}^{1/i} \tag{12}$$

The concentration of iron-fluoride complex with i number of ligands can be expressed in the form:

$$[FeF_i^{(3-i)+}] = 1 / i \times \left\{ c_F - [F^-]_t \times (1 + K_{HF} \times [H^+]) \right\} \tag{13}$$

The free concentration of iron in acidic fluoride solution is given by

$$[Fe^{3+}] = \frac{c_{Fe(III)} - [FeF_i^{(3-i)+}]}{1 + (\beta_1^* / [H^+]) + (\beta_2^* / [H^+]^2)} \tag{14}$$

The calculated concentrations of fluoride for the experimental range of total iron concentration from 6.9 x 10^{-6} M to 1.4 x 10^{-3} M, are plotted *versus* the recorded experimental changes in potential (see Figure 5). As mentioned above, all the constant values, including β_2 = 1.49 x 10^9, were taken from literature.

The concentration values plotted in Figure 5 are calculated using equation (11), curve 1, and equation (12), curves 2, 3. From the computed points, it may be concluded that FeF^{2+} is the predominant form of iron-fluoride complex in the proposed kinetics experiment.

In conclusion, the proposed method is a simple and rapid way of determining Fe^{3+} in the concentration range from 3.5 x 10^{-5} M to 1.4 x 10^{-3} M. The life time of utilized FISE is not being shortened by repeating runs in the described experiment. The work also points to the usefulness of ISE in kinetic studies.

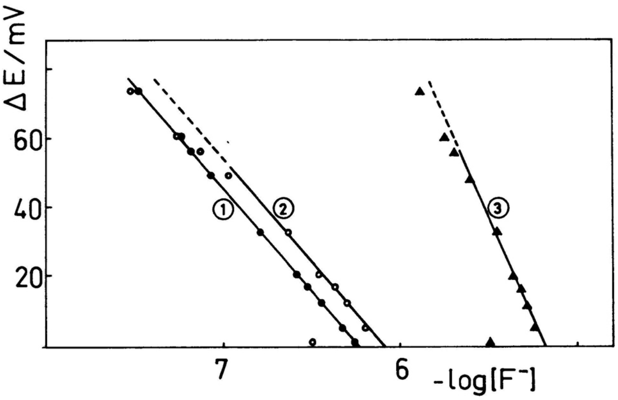

Figure 5. Relationship between the net change in potential for a fixed time interval (1 minute) and the concentration of fluoride, calculated by using equations (11) and (12), pH 1.8. 1. equation (11). 2. equation (12), i = 1, β_1 = 1.62 x 10^5. 3. equation (12). i = 2, β_2 = 1.49 x 10^9.

Acknowledgement. – This work was supported by the Ministry of Science, Republic of Croatia (Grant 1-07-025).

REFERENCES

1. K. Srinivasan and G. A. Rechnitz, *Anal. Chem.* **40** (1968) 1818.
2. F. Oehme and L. Dolezalova, *Z. Anal. Chem.* **251** (1970) 1.
3. Yu. G. Vlasov and E. A. Bychkor, *Ion-Selective Electrode Rev.* **9** (1987) 5.
4. Y. S. Fung and K. W. Fung, *Anal. Chem.* **49** (1977) 497.
5. Nj. Radić and M. Vudrag, *J. Electroanal. Chem.* **178** (1984) 321.
6. J. Inczedy, *Analytical Applications of Complex Equilibria*, Ellis Horwood, Chichester, 1976. p. 320.
7. Nj. Radić and M. Bralić, *Analyst* **115** (1990) 735.
8. J. J. Lingane, *Anal. Chem.* **39** (1967) 881.
9. E. W. Baumann, *Anal. Chim. Acta* **54** (1971) 189.

SAŽETAK

Kinetičko-potenciometrijsko određivanje Fe(III) uporabom elektrode selektivne na fluorid-ion

Nj. Radić i J. Komljenović

Opisana je kinetičko-potenciometrijska metoda određivanja Fe^{3+}, temeljena na praćenju reakcije nastajanja FeF^{2+} u kiseloj sredini, korištenjem fluorid-selektivne elektrode. Istražen je utjecaj pH i koncentracije fluorida u otopini na kinetiku proučavane reackije. Za konstrukciju kalibracijskih dijagrama uporabljene su izračunane početne brzine nastajanja kompleksa ili zabilježene promjena potencijala u određenomu vremenskom intervalu (1 min.). Utvrđena je linearna ovisnost (r = 0.9979) početne brzine nastajanja kompleksa $(\Delta E)_{1\ \mathrm{min}}$ i koncentracije Fe^{3+} u reakcijskoj otopini. Opisana metoda omogućuje pouzdano određivanje Fe^{3+} u koncentracijskom području 3.5 x 10^{-5} mol/L 1.4 x 10^{-3} mol/L.