

Flow injection potentiometric determination of Fe(III) using a fluoride-selective electrode as detector*

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Abstract. Flow injection analysis (FIA) system incorporating a fluoride ion-selective electrode (FISE) as detector is described. Laboratory-built cascade flow cell equipped with FISE and reference electrode is used for flow injection potentiometric determination of Fe(III) based on monitoring of the formation of FeF_2^+ in acid solution. Under optimized flow conditions (4.0 mL min^{-1} , $300 \mu\text{L}$ samples, $10^{-5} \text{ mol L}^{-1}$ sodium fluoride in the carrier stream) a rectilinear calibration graph is obtained by plotting the peak height *versus* concentration of iron in the range of Fe(III) concentration from 1×10^{-4} to $1 \times 10^{-1} \text{ mol L}^{-1}$ in a 0.01 mol L^{-1} perchloric acid or acetate buffers (pH 2.8; 3.4).

Key words. Flow-injection analysis – iron(III) – fluoride ion-selective electrode.

Introduction

Flow injection analysis (FIA) with different sensors is rapidly developing into a powerful analytical tool with many merits, such a broad scope and rapid sample throughput.

Over many years, there has been a great deal of research and development in flow injection systems using ion-selective electrodes (ISEs) as detectors [1]. Many systems were evaluated using ISEs in flow injection potentiometry (FIP), and continuous flow modes [2,3].

The fluoride ion-selective electrode (FISE) with LaF_3 membrane is probably the most widely applied ion-selective electrode used for practical measurements. Since the FISE was developed (1966), the formation constants of many metal fluoro complexes in aqueous solution have been determined. However, there are very few reports in which the FIA determination of metal ions, or their influence on the response characteristics of the fluoride ion-selective electrode, based on metal fluoride complex formation are discussed [4-7].

Suitability of the FISE for monitoring a reasonably fast reaction of the formation of FeF_2^+ in acidic solution has been previously established [8]. Oehme and Dolezalova [9] reported the possibility of direct potentiometric determination of Fe^{3+} based on iron-fluoride complex formation but no detailed information was given.

Previous investigation [10] has shown that FISE can be applied successfully for kinetic potentiometric determination of Fe(III) in batch experiment. 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.

In this work we developed a simple FIA system with an commercial FISE as detector. This system was applied for the determination of iron in the range of concentration from $10^{-4} \text{ mol L}^{-1}$ to $10^{-1} \text{ mol L}^{-1}$.

Experimental

Reagents

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

Standard sodium fluoride solution, 0.1 mol L^{-1} , was prepared in a polypropylene calibrated flask from dried (0.1 MPa , $110 \text{ }^\circ\text{C}$) sodium fluoride. Dilute standard fluoride solution was prepared from the stock solution, using polypropylene flask and a pipette.

A stock iron(III) solution of approximately 0.1 mol L^{-1} was prepared by weighing and dissolving an appropriate amount of iron(III) nitrate in 1 mol L^{-1} perchloric acid. Other solutions of iron were prepared from the stock solution by dilution with 0.01 mol L^{-1} 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.

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Apparatus

An Orion fluoride ion-selective electrode (FISE) Model 94-09 SC was incorporated into conducts of the flow injection system as shown in figure 1. The indicator electrode was used with an Orion 90-02 single-junction reference electrode. Potentiometric data were recorded at room temperature with an millivoltmeter (Model MA 5740, Iskra, Ljubljana, Slovenia) coupled to a personal computer and recorder.

The flow system consisted of a peristaltic pump (type Minipuls 2, Gilson, France) fitted with silicone rubber tubing of 2.0 mm i.d. and an injection valve (model V-100, Tecator, Sweden). The outlet of the injector was connected to the flow cell *via* silicone tubing of 0.5 mm i.d.

A diagram of the cascade flow cell design with the commercial FISE and a reference electrode is given in figure 1. The carrier solution is pumped over the ion-sensitive surface of the electrode and the level of liquid in conical funnel is maintained constant.

Procedure

The carrier stream was pumped through the two-position injection valve using a flow-rate of 4.0 mL min⁻¹ in a single-line flow manifold. While one loop served as the carrier stream, a sample (standard) was drawn through the other loop at the same flow rate. The carrier stream was sodium fluoride, typically at a concentration of 1 × 10⁻⁵ mol L⁻¹ with 0.01 mol L⁻¹ perchloric acid or appropriate buffer as a pH and ionic-strength adjustor. Solutions of iron were injected into the carrier stream by means of the loop injection valve with 300 μL loop volume. The potentiometric response of the electrochemical cell to injected iron was then monitored with millivoltmeter and potentiometric data were captured continuously by a personal computer.

Parameters of the FIA system were varied in order to maximize the dynamic range, the precision and sampling rate. The carrier stream concentration, 1 × 10⁻⁵ mol L⁻¹ sodium fluoride, was chosen as the compromise between sampling rate, linear dynamic range and lower detection limit.

Results and discussion

The performance of the potentiometric cascade cell with the FISE detector was examined for fluoride and iron(III). Figure 2 shows flow injection peaks recorded with the above FIP system, with fluoride or iron(III) concentrations, ranging from 1 × 10⁻⁴ to 1 × 10⁻¹ mol L⁻¹ in a 0.01 mol L⁻¹ perchloric acid. The carrier stream was 1 × 10⁻⁵ mol L⁻¹ fluoride in a 0.01 mol L⁻¹ perchloric acid.

When fluoride or iron(III) was injected into the carrier stream of fluoride ions the electrode potential was determined by the surface concentration of free fluoride ions and was therefore dependent on the rate of transport of analyte to the electrode surface and/or complexation kinetics. At a

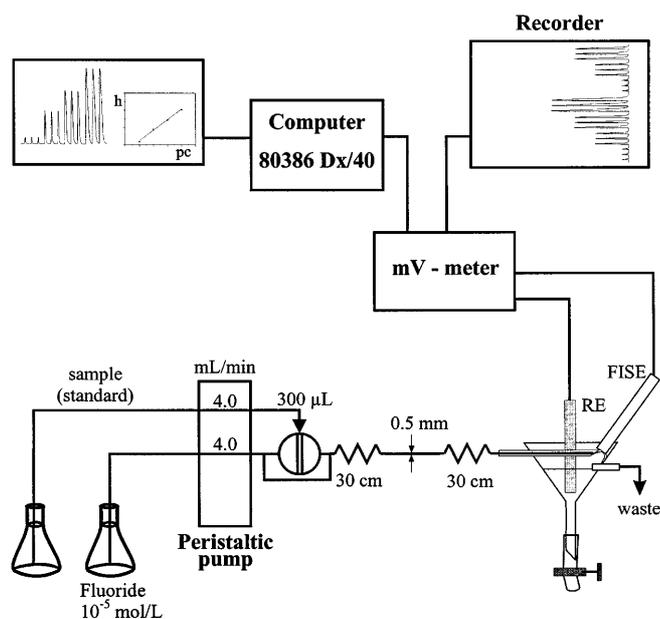


Fig. 1. Manifold and flow diagram of the FIA system. FISE - fluoride ion-selective electrode. RE - Orion 90 - 02 single-junction reference electrode.

constant flow rate the electrode potential may be expressed in terms of the Nernst equation. When a buffered carrier solution with fluoride ions is pumped, the potential of the electrode is given by

$$E_1 = E' - S \log \{c'_F / (1 + K_{HF} [H^+])\} \quad (1)$$

where S , c'_F and K_{HF} denote the Nernstian slope (59 mV), total or analytical concentration of fluoride in carrier stream and the formation constant of HF ($K_{HF} = 7.93 \times 10^2 \text{ mol}^{-1} \text{ L}$), respectively.

When a sample containing fluoride ions is injected into the carrier stream, the free fluoride ions will be altered to a new value. In the flow-injection measurements of fluoride sample the potential of the peak is described by the following equation:

$$E_2 = E' - S \log \{(c'_F + mc''_F) / (1 + K_{HF} [H^+])\} \quad (2)$$

where m and c''_F denote the dilution constant and the analytical fluoride concentration in the sample. Since the peak height, h , in flow-injection measurements is equal to the potential difference,

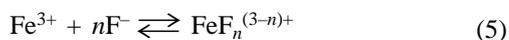
$$h = E_2 - E_1 \quad (3)$$

using equations (2) and (1) at constant pH one can obtain

$$h = S \{ \log c'_F - \log (c'_F + mc''_F) \}. \quad (4)$$

In the other flow-injection experiment, when a sample containing iron(III) at a sufficient high concentration to form

iron-fluoride complexes is injected into the carrier stream, the fluoride-ion concentration will be lowered to a new value. Under the experimental conditions in batch experiment, when $c_{\text{Fe(III)}} \gg c_{\text{F}}$, FeF_n^{2+} was estimated as the predominant form of iron-fluoride complex [10]. In this FIP experiment the potential of the peak may be described based on the following equations:



$$\beta_n = \frac{[\text{FeF}_n^{(3-n)+}]}{[\text{Fe}^{3+}][\text{F}^-]^n} \quad (6)$$

$$[\text{F}^-] = \left(\frac{[\text{FeF}_n^{(3-n)+}]}{[\text{Fe}^{3+}] \beta_n} \right)^{1/n} \quad (7)$$

$$E_2 = E' - S \log \left(\frac{c_{\text{F}}/n}{\left(\frac{m_{\text{cFe}} - c_{\text{F}}/n}{1 + \beta_1^*[\text{H}^+] + \beta_2^*[\text{H}^+]^2} \right) \beta_n} \right)^{1/n} \quad (8)$$

where β_n and β_i^* ($i = 1, 2$) denote the stability constant of $\text{FeF}_n^{(3-n)+}$ and hydrolysis constants of Fe^{3+} , respectively

$$\beta_i^* = \left(\frac{[\text{Fe}(\text{OH})_i^{(3-i)+}]}{[\text{Fe}^{3+}]} \right) [\text{H}^+]^i \quad (9)$$

The values of $1.62 \times 10^5 \text{ mol}^{-1} \text{ L}$, $1.5 \times 10^9 \text{ mol}^{-2} \text{ L}^2$, $7.2 \times 10^{11} \text{ mol}^{-3} \text{ L}^3$, $1.00 \times 10^{-3} \text{ mol L}^{-1}$ and $5.01 \times 10^{-7} \text{ mol}^2 \text{ L}^{-2}$ for β_1 , β_2 , β_3 , β_1^* and β_2^* , respectively were taken or computed from literature [11].

The peak height for iron(III) flow-injection experiment is also equal to the potential difference ($E_2 - E_1$). For this experiment the peak height is given by

$$h = -\frac{S}{n} \left\{ \log(c_{\text{F}}/n) - \log(m_{\text{cFe}} - c_{\text{F}}/n) + \log \left(1 + \beta_1^*[\text{H}^+] + \beta_2^*[\text{H}^+]^2 \right) + \log \beta_n \right\} + S \left\{ \log c_{\text{F}} + \log \left(1 + K_{\text{HF}}[\text{H}^+] \right) \right\} \quad (10)$$

or

$$h = k - \frac{S}{n} \left\{ \log(c_{\text{F}}/n) - \log(m_{\text{cFe}} - c_{\text{F}}/n) + \log \left(1 + \beta_1^*[\text{H}^+] + \beta_2^*[\text{H}^+]^2 \right) + \log \beta_n \right\} \quad (11)$$

The FIP system exhibited a fast response to fluoride, taking 6 seconds to attain the potential of the peak height for a concentration range from $1 \times 10^{-4} \text{ mol L}^{-1}$, but return of the potential to a stable base line consumes much more time. The slope of the experimental curve (Fig. 2B, curve 1)

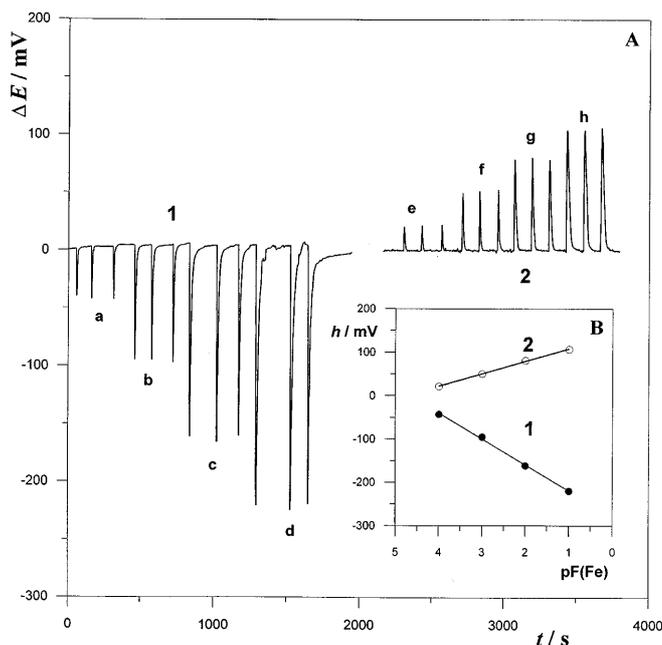


Fig. 2. (A) Recording of peaks obtained for 300 μL injection of fluoride (1) and iron (2) into a carrier stream of $10^{-5} \text{ mol L}^{-1}$ fluoride at pH 2 and a flow rate of 4.0 mL min^{-1} . Concentrations of injected standards were as follows: a) 1×10^{-4} , b) 1×10^{-3} , c) 1×10^{-2} , d) $1 \times 10^{-1} \text{ mol L}^{-1}$ fluoride, e) 1×10^{-4} , f) 1×10^{-3} , g) 1×10^{-2} , h) $1 \times 10^{-1} \text{ mol L}^{-1}$ iron(III). (B) Relationships between the peak height and the concentration of fluoride (1) and iron (2) standards injected into the carrier stream.

59.8 mV pF^{-1} obtained for the tested concentrations of fluoride was in good agreement with theoretical values.

As predicted by equation (11) at constant pH and constant analytical concentration of fluoride, the stoichiometry of the reaction product can be determined from the slope of the plot of h versus $\log c_{\text{Fe}}$, if one complex is predominant. From the slope of the experimental curve, 28.6 mV pFe^{-1} (Fig. 2B, curve 2), obtained at pH 2 may be concluded that FeF_2^+ is the predominant form of iron-fluoride complexes in the proposed FIP experiment.

The fluoride-containing species in acidic solution are F^- , HF , HF_2^- and possibly the dimer $(\text{HF})_2$. At pH of this experiment HF_2^- is very small and can be neglected. If we assume HF and F^- to be the predominant fluoride-containing species in FIA experiments their concentrations, with variation in pH, can be calculated from the formation constant of HF . Previous investigation [8] has shown that both species can take part in iron-fluoride complex formation. Also, for the same total fluoride and iron concentrations, the rate of formation of iron-fluoride complex depends on the acidity of the solution.

In previous paper [10], it has been shown that the highest change of potential based on the $\text{FeF}_n^{(3-n)+}$ formation

reaction may be expected in the pH range from 2.5 to 3.2. However, FIP experiments carried out in acetic solution (pH 2.8 or 3.4) where iron forms labile complexes with acetate, showed the same sensitivity as in perchloric acid solution (pH 2) with slopes 30 ± 2 mV pFe⁻¹.

For the chosen fluoride concentration in stream solution (see Procedure), at all tested pH values, the lower detection limit of iron was 10^{-4} mol L⁻¹.

As mentioned above, in batch experiment the formation of FeF²⁺ complex has been justified based on steady-state potential values. It is likely that, under the chosen flow conditions, the stoichiometry of iron-fluoride complexes and the rate of the complex formation is different than in batch experiment. Also, the recorded peak value does not reach the equilibrium potential of iron-fluoride complexation. Presumably, within the time of experiment, FeF₂⁺ is the predominant form of iron-fluoride complexes at the surface of electrode.

Interferences from other metal ions which react with fluoride have been investigated. Aluminium ions interfere strongly and should be separated or masked before iron determination by using the proposed method. Among other ions (Ca²⁺, Cu²⁺, Hg²⁺, Mg²⁺, Pb²⁺) which form precipitate or complexes with fluoride the main interfering cation is Ca²⁺. The effect of this ion was measured when injected into fluoride carrier and also when was present in iron standards. When Ca²⁺ ions at a concentrations from 10^{-4} mol L⁻¹ to 10^{-1} mol L⁻¹ was injected into 10^{-5} mol L⁻¹ F⁻ in acetate buffer a significant peak response was recorded. However, when the largest concentration of Ca²⁺, 0.1 mol L⁻¹, was present in all iron standards the height of the peak was altered only for the lowest, 10^{-4} mol L⁻¹, concentration of iron.

Conclusions

The above results show that the flow injection potentiometry with fluoride ion-selective electrode is a simple and rapid

way of determining Fe³⁺ in the large concentration range from 10^{-4} mol L⁻¹ to 10^{-1} mol L⁻¹. For all injected concentrations of iron the observed baseline is stable. The lifetime of the utilised FISE is not being shortened by repeating injection even for the largest concentrations of iron in the proposed experiment. 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.

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