Int. J. Electrochem. Sci., 7 **(2012)** 2928 - 2937

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Interference Effect of Various Ions on Determination of Iron with Flow Injection Analysis Using the Potentiometric Technique

Marija Bralić[1], *Maša Buljac*[1,*], *Marijo Buzuk*[1], *Slobodan Brinić*[2]

[1]Department of Environmental Chemistry, Faculty of Chemistry and Technology, Teslina 10/V, 21000 Split, Croatia
[2]Department of General and Inorganic Chemistry, Faculty of Chemistry and Technology, Teslina 10/V, 21000 Split, Croatia
[*]E-mail: masa@ktf-split.hr

Received: 13 February 2012 / *Accepted:* 14 March 2012 / *Published:* 1 April 2012

Fluoride-selective electrode (FISE) was used for determination of Fe^{3+} using home-made cell for flow injection analysis (FIA). Lowest signal obtained for this system was 10^{-5} M, with slope of 28.9 mV per decade at pH 3.4 and flow rate of 2.86 mL/min. Influence of various cations and anions on determination of Fe^{3+} was examined. In the presence of 0.01 M cations significant interference did not noticed, except slightly parallel shift (within 10 mV) in the slope of the calibration curves. Contrariwise, determination of Fe^{3+} in the presence of various anions (particularly SCN^-, $S_2O_8^{2-}$, SO_3^{2-}) was significantly obstructed. However, these interferences can be occurred at high concentration of interfering anions and does not disturb determination of Fe^{3+} in real samples. The results of real samples analysis, with this system, were compared to those obtained by FAAS.

Keywords: FISE, iron (III), flow injection analysis, interference

1. INTRODUCTION

In the environment one element can be present in different chemical forms which differ for their chemical behavior, bioavailability and toxicity. This is the case of iron, since the role that this element plays in biogeochemical cycles depends greatly on its redox and complexation speciation [1]. Iron is vital for almost all living organisms due to the fact that it occurs in a wide variety of metabolic process, including oxygen transport, DNA synthesis, and electron transport. However, iron concentrations in body tissue damage as a result of formation of free radicals [2].

Iron can exist as inorganic species of Fe^{3+} or Fe^{2+}, be organically complexed, exist as colloids of oxides, oxyhydroxides or mixed with organic material, and be suspended as both biotic and abiotic particles. [3]. Iron is an essential nutrient and is abundant in many mineral oxides that exchange iron with surface and ground waters trough dissolution and precipitation.

Numerous analytical techniques for determining aqueous iron concentration have been developed and deployed, including titrimetric, electrochemical, chromatographic, ultracentrifugation and photometric methods [4]. Also, potentiometric determination of iron was reported [5, 6]. Most of electrodes used in potentiometry were either solid-state or ionophore-free, ion-exchange electrodes; ionophore-based membrane sensors for Fe^{3+} ion are quite spares. Moreover, most of these electrodes suffer a lack of stability, selectivity or long response time [7]. Furthermore, even less papers were publicized in which FISE has been described as a detector for the determination of iron [8, 9]. When determining Fe^{3+} with ISE, correct choice of pH is important as it affects both the formation of Fe^{3+} complex and the linearity of FISE response [10]. The selectivity of ion-selective electrodes (ISE), i. e., their behavior in the presence of interfering ions, has been of interest as long as ISE have existed.

The available literature [11, 12, 13] describes the various methods for determination of trace amount of various metals.

In this paper, we report a novel potentiometric method and effect of various ions on determination of Fe^{3+}, in flow injection analysis (FIA) with home-made flow cell.

2. EXPERIMENTAL

2.1. Instrumentation

An Orion fluoride ion-selective electrode (FISE) Model 94-09 SC was placed into conducts of the flow and flow injection system as shown in Figure 1.Potentiometric data were recorded with a millivoltmeter (Model MA 5741, Iskra, Slovenia) coupled to a personal computer and recorder.

The flow system consisted of a peristaltic pump (Minipuls 2, Gilson, France), fitted silicone rubber tubing of 0.8 mm id. and an injection valve (model V-100, Tecator, Sweden). The outlet of the injector was connected to the flow cell via silicone tubing of 0.8 mm id.

The measurements were provided at constant temperature of 25 ± 1 °C.

2.2. Cell design

On the basis of literature data and our laboratory experience [14, 15, 16] a cell for flow measurements was designed. The cell is manufacture from polymethylmetaacrylate (PMMA), (Figure 1). Unlike the previously laboratory-designed types of cell [14, 15], here the cell was manufactured in the way that the working electrode (FISE) was placed on the upper side of the cell at right angle, while the reference electrode was placed at the angle of 70^{o}. The border rings enable one electrode to be always in the same position in relation to the other electrode.The nozzle, which is at the lower side of the cell, is vertically positioned un relation to the FISE membrane, from which it is approximately 1 mm away. The stream of the solution wets the whole area of the membrane and, pouring down the reference electrode, effectuates the electric contact between the working and reference electrode. The reference electrode is in contact with rest of the solution, the volume of wich is about 2 mL. The opening for out flow (2) is positioned at a high of 5 mm from the cell bottom. The reference electrode is always dipped 2 mm above the cell bottom.

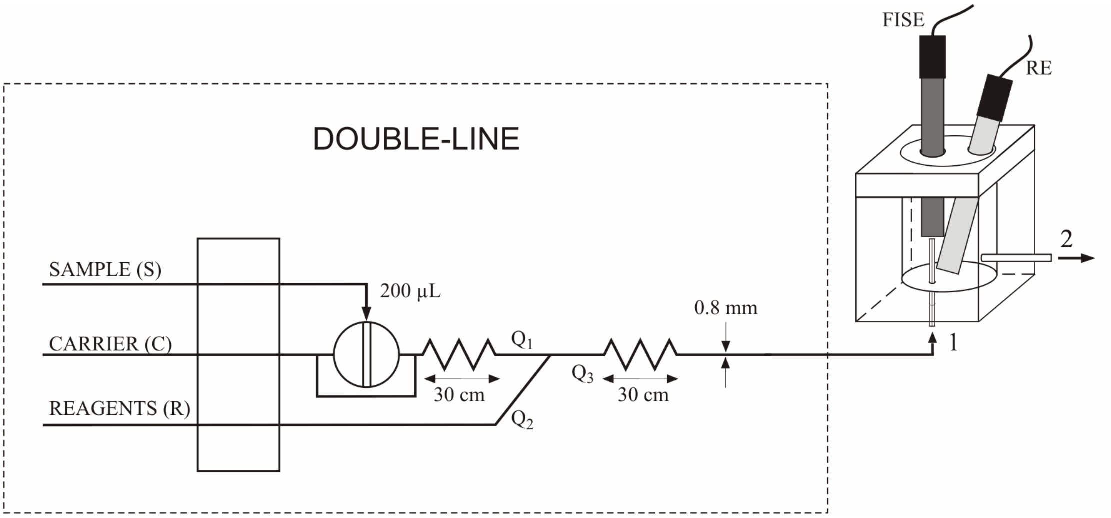

Figure 1. The home-made cell and apparatures used in flow analysis

2.3. Reagents

All chemicals were of analytical reagent grade. Solutions were prepared with doubly distilled water.

Standard sodium fluoride solution, 0.1 M was prepared in a calibrated polypropylene flask from dried (110 C°) sodium fluoride. Dilute standard fluoride solution was prepared by mixing standard sodium fluoride with 0.1 M KNO_3 and acetate buffer, using propylene flask and pipettes. pH 2.8 or 3.4 buffers were prepared by diluting glacial acetic acid and sodium acetate. The stock Fe^{3+} solution 0.1 M was prepared by weighing and dissolving an appropriate amount of Fe^{3+} nitrate in 0.1 M KNO_3 and acetate buffer (pH 2.8 or 3.4). The Fe^{3+} was titrated by a standardized 0.01 M EDTA solution. Other solutions of iron were prepared from the stock solution by dilution with 0.1 M KNO_3 and acetate buffer (pH 2.8 or 3.4). Solutions of interfering ions were prepared on same way as Fe^{3+} solution.

2.4. Measurement Procedure

The flow injection analysis (FIA) was performed with injection valve. While one loop served as the carrier stream with flow-rate of 2.86 mL/min or 3.45 mL/min the sample was drawn through the other loop with the same flow rate and then was injected into carrier stream by means of the injection valve with 200 μL loop volume. In the measurements the carrier stream was the base solution 0.1 M potassium nitrate buffered on pH 2.8 or 3.4 with acetate buffer and 2×10^{-6} M sodium fluoride solution which mixed together. After the injection valve such a mixture came on the FISE.

The potentiometric response of electrochemical cell was monitored with milivolltmeter and potentiometric data were continuously recorded by a personal computer.

2.5. Real Sample-Soil

Before analysis, the soil sample was dried and sieved trough a 2 mm stainless steel sieve in order to remove the coarse material. The following procedures were implemented for the extraction and determination of Fe^{3+} and /or total iron.

A) A portion of sample (50 g) was shaken with 0.1 M HCl (500 mL) for 24 hours to extract the fraction of Fe. After filtration, in the clear filtrate, Fe^{3+} was determined.

B) An amount of soil (50 g) was shaken with 2.5% HAc (500 mL) for 24 hours to extract the fraction of Fe. After filtration, in the clear filtrate, Fe^{3+} was determined.

3. RESULTS AND DISCUSSION

3.1. Mechanism of potentiometric response

The optimized flow conditions (FC) were similar to those found in early studies [8].

It was noticed that the potential change per concentration decade is a function of the time and resources necessary to perform measurements at the same time.

Figure 2 presents results obtained with FI (A) and classic potentiometric (B) measurements. A linear response at flow rate of 2.86 mL/min for Fe^{3+} concentration higher than 1.0×10^{-3} M, with slopes of 28.5 and 28.9 mV per decade (at pH 2.8 and 3.4 respectively), was observed. When flow rate was 3.45 mL/min, the slope was 25.9 mV at both pH values. Furthermore, at classic potentiometric measurement slope was 56.2 mV per decade and 55.3 mV per decade at pH 2.8 and 3.4 with linear range down to 4.5×10^{-4} M.

In the presence of fluoride, electrode potential at different pH is given by following expression:

$$E = konst. - S \log \{c'_F / (1 + K_{HF}\,[H^+])\} \qquad (1)$$

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 ($K_{HF} = 7.93 \times 10^2$ M), respectively.

However, at sufficient Fe^{3+} concentration, formation $FeF_n^{(3-n)+}$ complexes induce decreasing of fluoride concentration by reaction:

$$Fe^{3+} + n\,F^- \rightleftarrows FeF_n^{(3-n)+} \qquad (2)$$

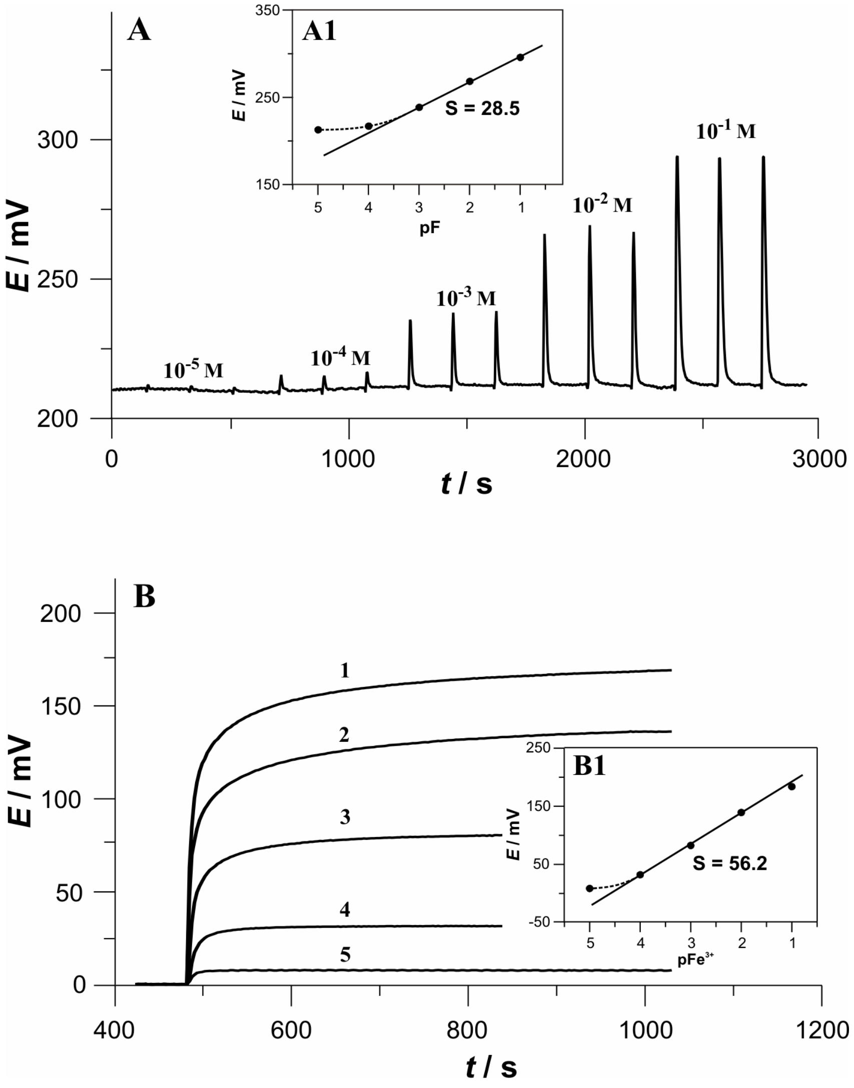

Figure 2. (A) The peaks obtained for injection of Fe^{3+}; (A1) relationship between peak height and concentration of Fe^{3+}; (B)The dynamic response curve of the cell with FISE after adding 2.0 ml Fe^{3+} , (B1) The relationship between the potential and concentration of Fe^{3+}.

For $c_{Fe(III)} >> c_F$, n is expected to be 1 and consequently, the slope should be 59 mV per decade (theoretical), respect to our investigation it should be 56.2 and 55.3mV per decade.

According above stoichiometry, electrode potential after injection of Fe^{3+} can be presented by equation (3)

$$E = konst. - S \log \left\{ \frac{c'_F}{\left\{ \left(c_{Fe} - c'_F \right) / \left(1 + \beta^*_1 / \left[H^+ \right] + \beta^*_2 / \left[H^+ \right]^2 \right) \right\} \beta_1} \right\} \tag{3}$$

where β_1 *i* β_i^* (i= 1,2) represent stability constant of FeF^{2+} and hydrolysis of Fe^{3+}

$$\beta^*_i = \left\{ \left[Fe(OH)_i^{(3-i)+} \right] / \left[Fe^{3+} \right] \right\} \left[H^+ \right]^i \tag{4}$$

After injection of Fe^{3+} peak hight in FIA experiment can be given by equation (5)

$$h = S\left\{\log\left(c_{Fe} - c'_{F}\right) + \log\beta_1 - \log\left(1 + K_{HF}\left[H^+\right]\right) - \log\left(1 + \beta^*{}_1/\left[H^+\right] + \beta^*{}_2/\left[H^+\right]^2\right)\right\} \quad (5)$$

Response toward F^-, in the concentration range between 10^{-5} to 10^{-1} M, was fast (within few seconds) and reproducible. Respecting the last equation (5), when only one complex was dominant, stoichiometry of the reaction product can be determined from dependence between peak height (h) and log c(Fe^{3+}). According above, from experimental slope of 28.5 and 25.9 mV per decade (in dependence of pH, respectively), formation of FeF_2^+, instead expected FeF^{2+}, can be assumed.

3.2. Interferences

The selectivity of ion-selective electrodes (ISE), i.e., their behavior in the presence of interfering ions, has been of interest as long as ISE have existed. In the available literature, only interference on the determination of fluoride ions were examined [17,18,19].

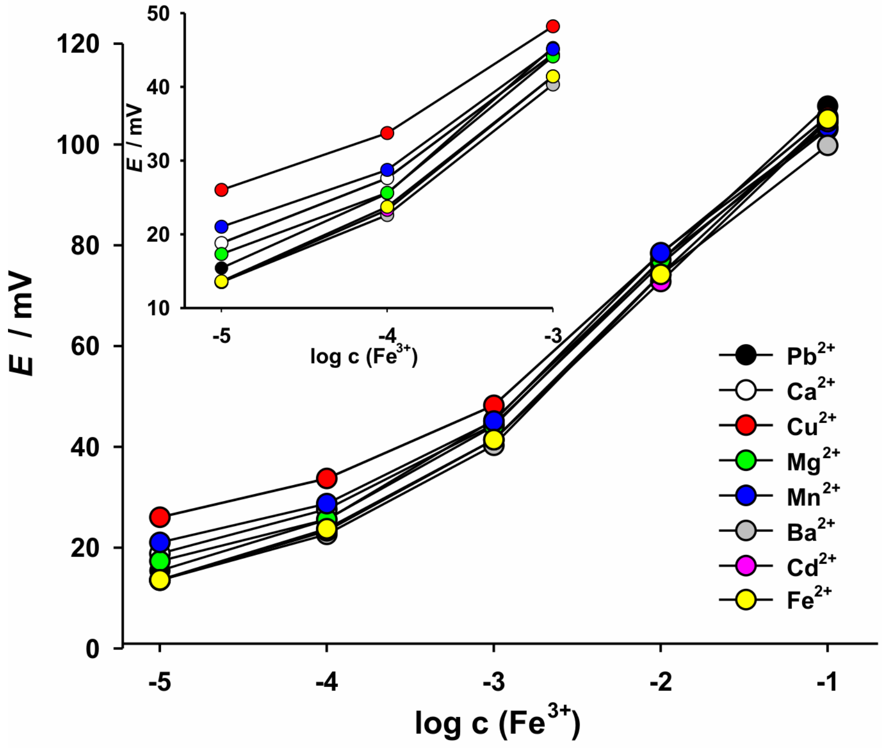

Figure 3. Dependence of peak height vs. log c (Fe^{3+}) in the presence of various cations (c= 0.01 M) at pH=2.8. Inlet: Enlarged region around detection limit.

These experiments were performed by preparation of series of sample solution by mixing a different concentration of Fe^{3+} (between 10^{-2} and 10^{-5} M) with different concentration (between 10^{-2} to 10^{-5} M) of potentially interfering ions followed by injection in the sample stream at different flow rate (2.8 and 3.45 mL/min). These conditions provide enough time for completing the reaction between involved species.

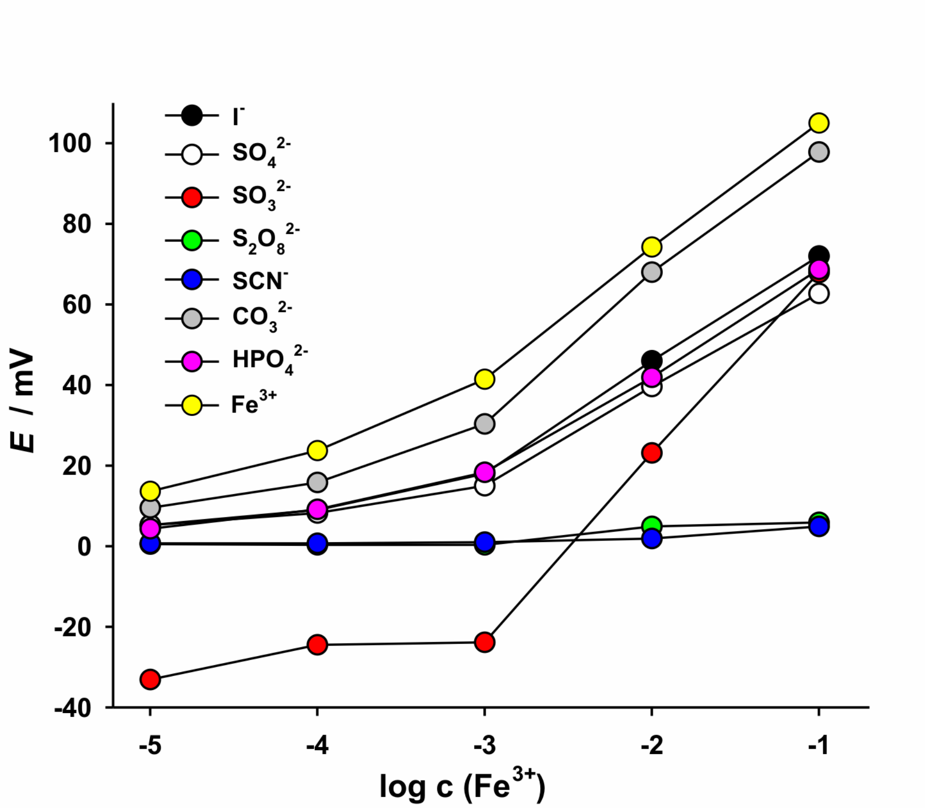

Figure 4. Dependence of peak height vs. log c (Fe^{3+}) in the presence of various anions (c= 0.01 M except c(HPO_4^{2-})= 1 × 10^{-5} M; c(CO_3^{2-})= 1 × 10^{-3} M) at pH= 2.8

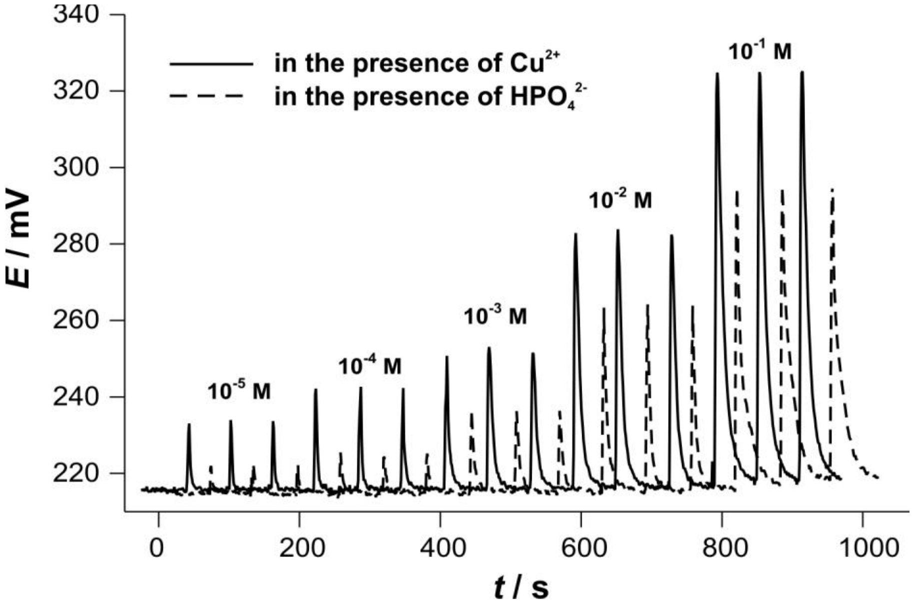

Figure 5. Interference effect Cu^{2+} and $S_2O_8^{2-}$ on the peak height at the iron determination with flow injection analysis (c (HPO_4^{2-})= 1 × 10^{-5} M; c(Cu^{2+})= 1 × 10^{-2}) at pH=2.8

Although interferences of investigated cations, according available data for complex formation and solubility products, were not expected, slightly parallel shift (within 10 mV) of calibration curves (peak height vs. concentration of Fe^{3+}) were obtained in the presence of various cations (c(X) = 0.01 M) (see Figure 3). This shift, which is more discernible at low concentration of Fe^{3+} (see inlet of Figure 3) and it is followed by deterioration in detection limit, can be attributed to change of ionic strength in the sample stream, if we bearing on mind high concentration of interfering cations.

Table 1. Relative error (in %) calculated[a] from peak height obtained, at pH 2.8, by injection of different Fe^{3+} concentration in (h') and without (h) presence of interfering ion (c(X) = 0.01 M).

Interfering ion (X)	relative error (in %)[a] at different c(Fe^{3+}) / M				
	1.0×10^{-5}	1.0×10^{-4}	1.0×10^{-3}	1.0×10^{-2}	1.0×10^{-1}
Ca^{2+}	38.2	16.4	7.2	2.7	-0.6
Cu^{2+}	91.2	42.2	16.4	5.5	0.5
Mg^{2+}	27.2	4.6	6.5	3.9	-1.9
Mn^{2+}	54.4	21.1	8.9	5.8	-1.5
Ba^{2+}	-0.7	-4.6	-2.6	-0.1	-5.0
Cd^{2+}	-0.7	-1.7	0.0	-1.9	-0.5
Pb^{2+}	13.2	7.6	9.4	3.6	2.5
I^-	0.0	-2.2	-6.7	-8.6	-
SO_4^{2-}	0.0	-10.8	-22.3	-14.3	-17.7
SO_3^{2-}	-736.5	-366.3	-223.8	-50.0	-10.9
$S_2O_8^{2-}$	-90.4	-96.7	-98.4	-89.4	-92.3
SCN^-	-86.5	-92.4	-94.8	-95.9	-93.6
[b]CO_3^{2-}	-34.5	-26.5	-14.6	-1.3	0.0
[c]HPO_4^{2-}	-17.3	-1.1	-5.2	-10.3	-9.8

[a] $\{(h' - h)/h\}\times 100$
[b] $c = 1\times10^{-3}$ M
[c] $c = 1\times10^{-5}$ M

For clearer representation of deviation of obtained peak high in the presence of 0.01 M (except CO_3^{2-} and HPO_4^{2-}) interfering ions, relative errors at each concentration of Fe^{3+} are given in Table 1.

Drastically deviations were observed in the presence of various anions (see Figure 4). These deviation were manifested in decreasing of slope and deterioration of detection limit (for HPO_4^{2-}, I^-, SO_4^{2-}) and can be explain by oxidoreduction reactions in the case of I^-, SO_3^{2-}. Precluding of determination in the presence of SCN^- is probably due to strong complexation of Fe^{3+} with SCN^- ($K_{Fe(SCN)_3} \approx 10^9$). Same problem was probably responsible for interference occurred in the case of HPO_4^{2-}, even at concentration of 1.0×10^{-5} M (at this pH dominant form is $H_2PO_4^{2-}$; $K_{FeH_2PO_4^+} = 10^{24}$). Influence of $S_2O_8^{2-}$ can be attributed to decomposition of $S_2O_8^{2-}$ in weak acid media to HSO_4^- and O_2 and strong interference of produced oxygen, as it is known that LaF_3 was used as potentiometric sensors for detection of O_2 in water [20]. Presence of CO_3^{2-} did not significantly influenced on the determination of Fe^{3+} comparing to other examined anions.

FIA response on Fe^{3+} in the presence of interfering ions (Cu^{2+} and HPO_4^{2-}) is shown at Figure 5. Interference of Cu^{2+} is characterized in increase of peak height, while in the presence of HPO_4^{2-} opposite behavior was noticed.

Insufficient number of published papers, concerning FIA method for determination of Fe^{3+}, does not allow a quality comparison of proposed method in this paper. Chen and Alexander [21] proposed use of tungsten oxide electrode in FIA for determination of Fe^{3+}. However, lack of selectivity was noticed, as tungsten oxide electrode was also selective for Cu^{2+}, Pb^{2+} and Ca^{2+}. Teixeira and authors [22] reported construction and analytical evaluation of graphite-epoxy ion-selective electrode in FIA for determination of Fe^{3+}. Ion-selective membrane was based on ion-pair incorporated in PVC and limitation in useful lifetime was noticed (which is disadvantage of PVC based selective membrane). Furthermore, this method was characterized by complex construction (tubular electrodes, complex membrane composition and complicated electrode construction that included graphite-epoxy resin coated with PVC membrane). Measuring range and detection limit was similar in both mentioned methods to those obtained with method described in this paper.

3.2. Analytical applications

We studied the possibility of applying the FIA to the determination of iron in the soil sample (Figure 6) and results obtained are compared with results of tests of soil samples from the FAAS.

Earlier studies have shown that aluminum interferes with the strongest potentiometric determination of iron, so, FAAS used to determine the concentrations of Al and Fe in the sample. The result of analysis showed that the concentration of Al 10^{-3} M and Fe 10^{-5} M.

The implementation of the proposed method (FIA) in real samples showed good agreement of the results with those obtained when using FAAS for sample treated with HAc, while in the soil sample treated with HCl signal is greater than the gain of only Al and Fe only. Actually, obtained signal was summed signal of Fe and Al, suggesting the possibility of using the FIA for determining the controlled extraction of Fe.

Similar observations was obtained in earlier investigation [22]

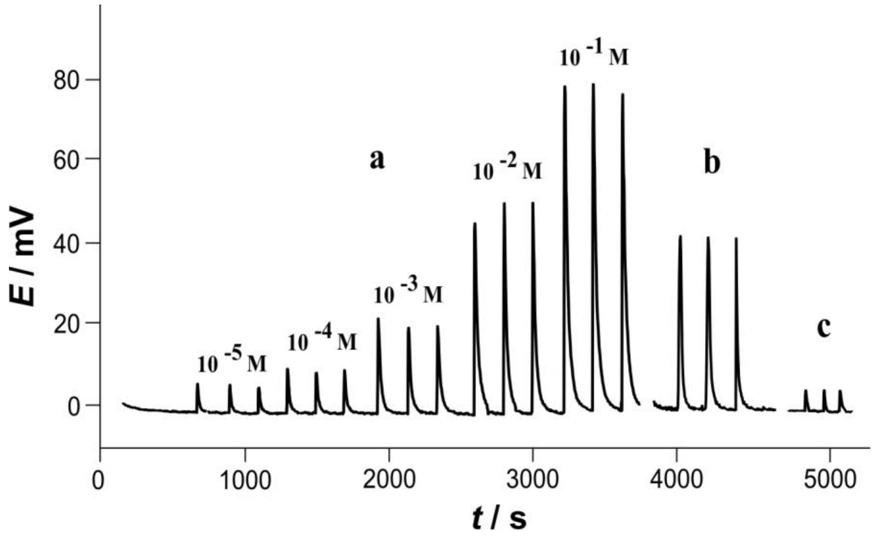

Figure 6. The peaks obtained for injection of Fe^{3+}: (a) standard solution; (b) real samples treated with HCl; (c) real samples treated with HAc (standard procedure at pH 2.8)

4. CONCLUSION

This work presents a novel procedure for the reliable determination of free Fe^{3+} in real samples between 10^{-5} to 10^{-1} M.

Investigation concerning peak height for Fe^{3+} in the presence of various cations revealed small influence of reported cations. However, significantly influence of anions was observed when concentrations of anions were extremely high (0.01 M). The described method was used for determination of the Fe^{3+} in real samples (soil). These results were significantly influenced by sample preparation method.

The results (in the real samples) obtained by proposed method, are in good agreement to those obtained by FAAS.

References

1. P. Ugo, L. M. Moretto, A. De Boni, P. Scopece, G.A. Mazzocchin, *Anal. Chim. Acta,* 474 (2002) 147
2. Ç. A. Şahin, I. Tokgöz, S. Bektaş, *J. Hazard. Mater.*, 181 (2010) 359
3. D. A. Weeks, K. W. Bruland, *Anal. Chim. Acta*, 453 (2002) 21
4. V. K. Gupta, B. Sethi, N. Upadhyay, S. Kumar, R. Singh, L. P. Singh, *Int. J. Electrochem. Sci.*, 6 (2011) 650
5. M. H. Mashhadizadeh, I. S. Shoaei, N. Monadi, *Talanta*, 64 (2004) 1048
6. C. J. Borman, B. P. Sullivan, C. M. Eggleston and P. J. S. Colberg, *Sensor*, 9 (2009) 4390
7. A. R. Fakhari, M. Alaghemand and M. Shamsipur, *Anal. Lett.*, 34 (2001) 1097
8. M. Bralić, S. Brinić, E. Generalić, L. Vrsalović, *Talanta*, 63 (2004) 777
9. B. Sun, Y. Ye, H. Huang, Y. Bai, *Talanta*, 40 (1993) 891
10. R. De Marco, D.J. Mackey, *Mar. Chem.*, 68 (2000) 283
11. M. B. Gholivand and F. Raheedayat, *Electroanalysis*, 16 (2004) 1330
12. M. B. Gholivand and F. Sharifpour, *Talanta*, 60 (2003) 707
13. P. L. Croot, P. Laan, *Anal. Chim. Acta*, 466 (2002) 261
14. M. Bralić and Nj. Radić, *Analusis*, 27 (1999) 57
15. M. Bralić, E. Generalić, S. Krka, *Anal. Lett.*, 33 (2000) 1811
16. J. A. Boržitsky, A. V. Divini, O. M. Petrukhin, Y. I. Urusov, *Analyst,* 118 (1993) 859
17. W. Frenzel and P. Brätter, *Anal. Chim. Acta*, 187 (1986) 1
18. R. Bock and S. Strecker, *Fresenius Z. Anal. Chem.*, 235 (1968) 322
19. P. Kauranen, *Anal. Lett.*, 10 (1997) 451
20. N. Yamazoe, J. Hisamoto, N. Miura, *Sensors and Actuators*, 12 (1987) 415
21. Z. Chen, P. Alexander, *Electroanalysis*, 9 (1997) 141
22. C. D. Stalikas, A. Ch. Pappas, M. I. Karayannis and P. G. Veltsistas, *Microchim. Acta*, 142 (2003) 43