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Natural pyrite as an electrochemical sensor for potentiometric titrations with EDTA, mercury(II) and silver(I)

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Abstract The results obtained in potentiometric titrations of copper(II), mercury(II) and iron(III) with standard EDTA solutions are presented. The titration of copper(II) at pH values in the range from 8.11 to 10.99 (ammonia buffer) and the titration of mercury(II) and iron(III) at pH values from 3.59 to 5.65 (acetate buffer) were performed. The titration end-point (TEP) was detected with an indicator electrode made from natural crystalline pyrite as an electrochemical sensor. The results obtained in potentiometric titration with the pyrite electrode were compared with those obtained using a platinum electrode (Fe^{3+}), a Cu ion selective electrode (Cu^{2+}) and a Hg electrode (Hg^{2+}). Accurate and reproducible results with good agreement were obtained, but higher potential changes at the TEP were obtained using the pyrite electrode. In the course of the titration the potential was established within less than 1 min, whereas at the TEP it was within about 2–3 min. The potential changes at the TEP were in the range from 60 to 200 mV per 0.1 ml EDTA, according to the stability constant of the complex formed. The highest potential changes, ranging from 160 to 200 mV, were obtained in the titration of iron(III) at pH 3.59. Reverse titration was also performed and accurate and reproducible results were obtained. Moreover, titration of halogenide and thiocyanate with standard mercury(II) solutions, as well as cyanide with silver(I) solution, were performed and accurate and reproducible results were again obtained.

Key words Pyrite sensor · Complexometric titrations · EDTA · Mercury(II) · Silver(I)

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Introduction

Pyrite, FeS_2, is a mineral with characteristic electrical and magnetic properties, as a result of which its application and behaviour as an anodic depolarizer for the production of hydrogen [1], or a cathode material in galvanic cells [2], or a material for the production and uses of solar energy [3] have been investigated. The pyrite electrode can be successfully used in acid-base titrations in aqueous [4] and non-aqueous [5] media, and in precipitation [6] as well as redox [7] titrations, as investigations have shown. Since a pyrite electrode is a redox electrode [7] and silver, copper, gold, etc., can be inserted in pyrite's crystal grating ($Fe^{2+}S_2^{2-}$), it is very probable that an electrode with this sensor can be applied for titration end-point (TEP) detection in complexometric titrations. Because of the presence of iron(II) and S_2^{2-} ions in pyrite's crystal lattice it can be supposed that the pyrite potential will depend on the iron(II) and/or iron(III) ions and also from all ion species that are able to react with the S_2^{2-} group. This paper presents the results obtained in titrations of copper(II), mercury(II) and iron(III) ions with standard EDTA solutions, halogenides and thiocyanate ion with mercury(II) solution and cyanide ion with standard silver(I) solution.

Experimental

Reagents

For 0.1 mol/dm^3 EDTA, 37.2240 g of complexone III were weighed in a 1 dm^3 flask and dried for 2 h at 120 °C. A 0.1 mol/dm^3 Fe(III) solution was prepared by dissolving ~20 g of $Fe_2(SO_4)_3$ (calculated as anhydrous salt) in 1 dm^3 of distilled water and standardized by EDTA titration, using a Pt electrode. A solution of 0.1 mol/dm^3 Cu(II) was prepared by dissolving ~25 g $CuSO_4 \cdot 5H_2O$ in 1 dm^3 of distilled water and standardized by EDTA titration, detecting the end point with a copper ion selective electrode (Cu ISE). A solution of 0.1 mol/dm^3 Hg(II) was prepared by dissolving 20.059 g of chemically pure Hg in nitric acid and diluting to 1 dm^3 with distilled water. Ammonia buffer solution was

prepared by mixing 0.2 mol/dm^3 of ammonia solution and 0.2 mol/dm^3 of ammonia chloride in appropriate proportions; pH values were controlled by means of a pH meter. Acetate buffer solution was prepared by mixing 0.2 mol/dm^3 of $MeCO_2Na$ and 0.2 mol/dm^3 of $MeCO_2H$ in various ratios. The pH values of the buffer obtained were controlled by means of a glass electrode. A 0.1 mol/dm^3 Ag(I) solution was prepared by dissolving 16.9873 g of dry $AgNO_3$ (analytical grade purity) in 1 dm^3 distilled water. The 0.1 mol/dm^3 solutions of Cl^-, Br^-, I^-, SCN^- and CN^- were prepared by dissolving 5.845 g of NaCl, 11.901 g of KBr, 16.601 g of KI, 9.718 g of KSCN and 6.512 g of KCN, respectively, in 1 dm^3 of distilled water, and standardized by Ag(I) solution using the Ag electrode.

Apparatus and electrodes

The experiments were carried out with a sample of pyrite mineral from the Veliki Krivelj copper mine (Bor, Serbia). Analytical data of the pyrite analysis were as follows: Fe 46.14%, S 53.18%, As 0.17%, Sb 0.001%, Ag 0.001%, Cu 0.43%, Zn 0.09%, Au 0.0009%.

The apparatus and pyrite electrode were prepared as described in previous papers [4, 7]. Moreover, in this work the following electrodes were also used: a Cu ISE (Orion model 9429A); an Ag electrode (sheet metal); a Hg electrode manufactured in our laboratory; a Pt electrode (Platinum wire); a glass electrode (Radelkiz model OP-0808 P); a reference electrode (SCE Radiometer type 401); the pH meter was an Iskra model MA 3740.

Procedure

Potential measurement

The stationary potential measurement of the pyrite electrode was carried out in a series of iron(III) and mercury(II) solutions at concentrations in the range from 1×10^{-1} to 1×10^{-6} mol/l, the potential of the pyrite electrode being followed with time. The ionic strength of the solution was maintained with sodium nitrate. The potential values determined in this way were used for the slope (n) and correlation coefficient (c_{corr}) calculations. The time needed for the equilibration of a stable potential was measured for the Fe(III)/Fe(II) couple, at various c_{Ox}/c_{Red} ratios, viz., 1/9, 3/7, 5/5, 7/3 and 9/1.

Potentiometric titrations

The optimal pH range for iron(III), mercury(II) and copper(II) potentiometric titrations with EDTA was determined as follows. An appropriate volume of titratable ion was diluted to 80 ml with water, followed by the addition of 10 ml of buffer at the corresponding pH value, viz., for ammoniacal copper(II) and for mercury(II) and iron(III) acetate. The pyrite indicator electrode connected to the SCE was immersed in the solution. The potentiometric titration was then carried out by adding EDTA titrant in portions and measuring the potential difference after each addition. A similar procedure was used in determining Cl^-, Br^- and SCN^- ions with mercury(II) solution. The behaviour of the pyrite electrode in CN^- titration with standard silver(I) solutions was investigated in a similar way.

Determination of iron with EDTA in steel, pyrite concentrate and chalcopyrite mineral

A sample of the steel (~0.5 g) or pyrite concentrate or chalcopyrite mineral (~1 g) was dissolved in HNO_3 containing sulfuric acid in a flask, with heating. The solution was evaporated to the minimum volume, transferred to a 500-ml volumetric flask, and water added to the mark. Using a pipete, 100 ml of the solution was transferred to another 250-ml flask, 5 ml of ammonia solution were added, and the mixture boiled for 5 min. $Fe(OH)_3$ was separated by filtration, the iron(III) hydroxide dissolved in 0.2 M sulfuric acid, the iron solution transferred to a 100-ml flask, and water added to the mark. An aliquot (5.00 ml) was transferred to a 150-ml flask, acetate buffer (pH 3.66) and water added and the potentiometric titration carried out. Indicator electrodes were Pt and FeS_2.

Results and discussion

Potential of the pyrite

Nernstian dependence of the pyrite electrode was performed by following the potential of the pyrite electrode with time in solutions of various iron(III) and mercury(II) concentrations. The slope and correlation coefficient were calculated from the dependencies E versus pFe and pHg obtained by plotting the electrode potential against the logarithm of the corresponding concentration (Fig. 1). It was found that the pyrite electrode showed a linear dependence (2–6) with a slope of 0.055 V decade^{-1} for Hg^{2+} and (1–4) with a slope of 0.034 V decade^{-1} for Fe^{3+}, respectively (Fig. 1). Similarly, for the redox couple $c_{Fe(III)}/c_{Fe(II)}$ the potential of the pyrite electrode was followed for various c_{Ox}/c_{Red} ratios (Fig. 2) and the following equation was found:

$$E_{FeS_2} = E_{const} + 0.051 \text{ V} \log(c_{Fe(III)}/c_{Fe(II)}) \quad (1)$$

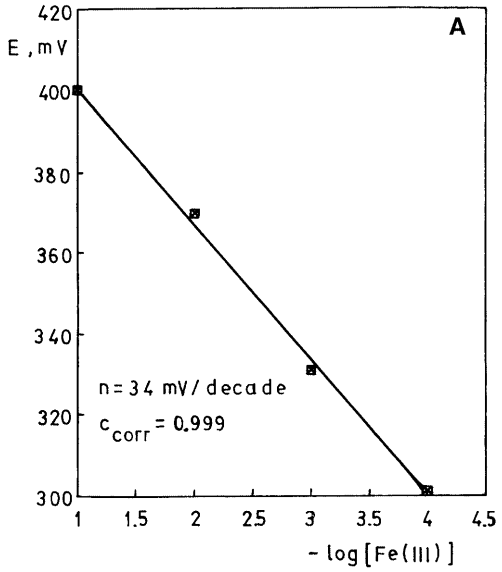
The slopes of the systems E vs. log[Fe^{3+}] and E vs. log[Fe^{3+}]/log[Fe^{2+}] are different. In the former system the Fe^{2+} concentration is not defined because of a developing reaction (see Eq. 4 below) but in the latter system the solution potential is defined and can be measured by means of redox electrodes.

The behaviour of the pyrite electrode as a redox electrode is shown by Eq. 1. The potential change at the TEP during the redox titration using the pyrite electrode as the indicator electrode can be explained by the following. The electronic structure of crystalline pyrite indicates that this mineral is a low-spin complex with d^2sp^3 hybridization. All hybrid orbitals are occupied with electrons, which makes pyrite a diamagnetic and nonreactive compound. Since pyrite is a semiconductor of n or p type, it is possible to use it, as a result of its chemical inactivity, for measurements of the redox potentials. The potential changes in potentiometric titrations in this case can be explained by polarization curves for pyrite and the components taking part in the redox reaction (Fig. 3).

It is known that in acid media pyrite dissolves slightly (becomes corroded), giving rise to soluble products:

$$FeS_2 + 8H_2O \rightarrow Fe^{3+} + 2SO_4^{2-} + 16H^+ + 15e^- \quad (2)$$

The rest potential of pyrite in open-circuit is 0.62 V vs. SCE, and at more positive potentials the dissolution of pyrite occurs, which may be shown by the anodic polarization curve. The degree of pyrite oxidation is equivalent to the corrosion current and depends on several parameters (temperature, state of the pyrite



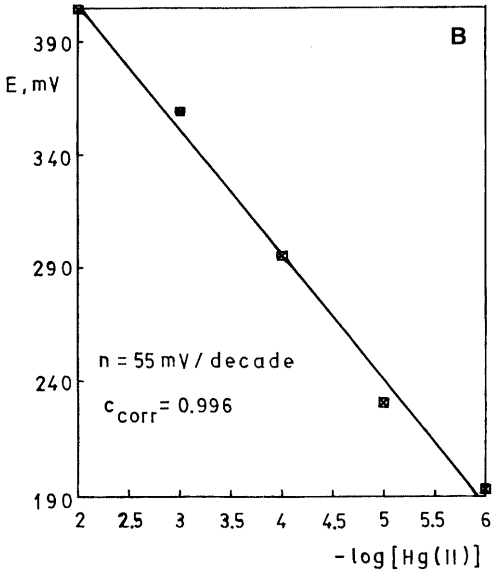


Fig. 1 Dependence of the pyrite electrode potential on log $c_{M^{n+}}$

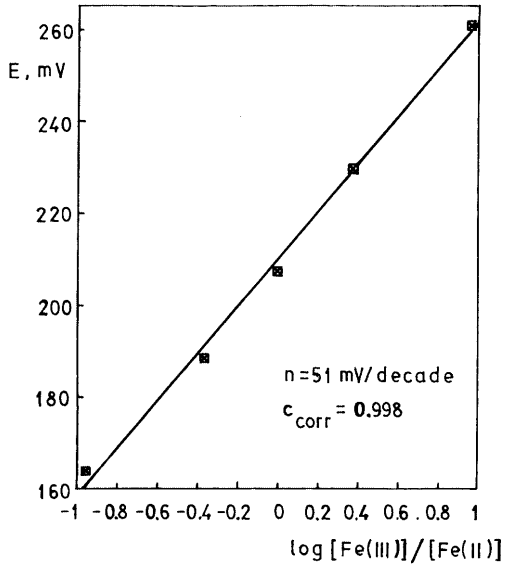


Fig. 2 Dependence of the pyrite electrode potential on time at different $\log(c_{Ox}/c_{Red})$ values

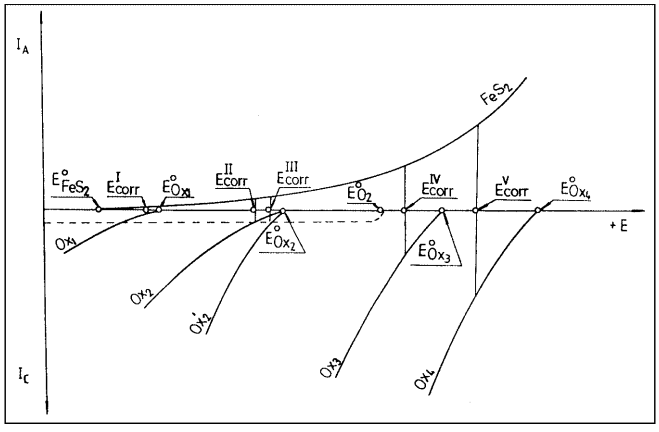


Fig. 3 Anodic and cathodic polarization curves by means of which the potential changes at the titration end-point are explained [Ox_1, Ox_2 (Ox_2'), Ox_3 and Ox_4 are different oxidants]

surface, oxidant concentration, oxidant nature, acidity of medium, etc.). In potentiometric titrations, however, a polished mineral (small surface area), room temperature and low oxidant concentrations are used, so that all these conditions ensure an insignificant dissolution of pyrite. These data indicate that in the absence of oxidizing agents the value of the corrosion potential will be more negative (Fig. 3). Under these conditions the value of the corrosion current is also small. Such a state of the pyrite electrode occurs at the beginning of the potentiometric titrations. The effect of oxygen in the solution may be eliminated by bubbling nitrogen through the solution. Besides, the initial solutions may contain some ions which might cause the corrosion of pyrite at low potentials (E^{I}_{corr}). It may be assumed that the solution contains a reducing species (Red_2) which on oxidation gives Ox_2, when being titrated with the oxidant Ox_3. Under these conditions the following reaction takes place in the solution:

$$Red_2 + Ox_3 \rightleftharpoons Red_3 + Ox_2 \qquad (3)$$

where Ox_2/Red_2 and Ox_3/Red_3 denote corresponding redox pairs. After the first addition of the oxidizing agent Ox_3 a corrosion potential E^{II}_{corr} is established at the pyrite electrode, whereby pyrite is oxidized by the oxidizing form of the reducing species (Ox_2). On further addition of the oxidizing agent Ox_3, the concentration of the Ox_2 species increases (Ox_2') and results in the shift of the corrosion potential to E^{III}_{corr}. At the end-point, when in the solution the oxidant Ox_3 is in excess, the corrosion potential is abruptly shifted towards the more positive region, since under these conditions the dissolution of pyrite is defined by the Ox_3/Red_3 system. This change of the corrosion potential from E^{III}_{corr} to E^{IV}_{corr}

makes possible the applications of the pyrite electrode as the indicator electrode in potentiometric redox titrations. From Fig. 3 it is also seen that higher potential changes of the pyrite electrode at the TEP are observed when oxidizing agents with more positive equilibrium potentials (stronger oxidants) are used. The reagents which display a great overvoltage in cathodic reduction at pyrite are not suitable as titrating agents, since the potential changes at the TEP in that case are small. A similar consideration holds for titrations of oxidizing agents with reducing agents, but then the corrosion potential of pyrite is shifted towards the more negative region.

Reagents of oxidant character, i.e., Hg(II), Cu(II), Fe(III) and others, are often used for complexometric determination and their concentrations are determined with EDTA. For that reason it is useful to know the behaviour of the pyrite electrode in solutions of these components.

The following reaction takes place in iron(III) solution:

$$2Fe^{3+} + FeS_2 \rightleftharpoons 3Fe^{2+} + 2S^0 \quad (4)$$

and Gibbs' free energy for this reaction is: $\Delta G_{25} = -67.255$ kJ/mol. By investigation of the reaction kinetics [8] it was found that the pyrite decomposition rate for low iron(III) concentrations was negligible. Therefore the pyrite electrode can be used for iron(III) determination and iron(III) can be applied as a titrating agent. As a result of the reaction of Eq. 4, in the electrode layer there will always be present concentrations of Fe^{3+} and Fe^{2+} and their ratio will define the pyrite potential. In the case of iron(III) determination in complexometric titrations with EDTA, the potential jump at the TEP occurred because the whole iron(III) [Ox] was complexing and the pyrite electrode potential decreased. In the reverse titration the excess of iron(III) gives the potential jump at the TEP. Besides, in our previous paper [4] it was shown that the formation of the iron(III) and iron(II) hydroxide occurred on the pyrite surface in aqueous solution. Iron hydroxide in the presence of EDTA dissolves according to the following equations:

$$Fe(OH)_3 + Y^{4-} \rightleftharpoons FeY^- + 3OH^- \quad (5)$$

$$Fe(OH)_3 + Y^{4-} \rightleftharpoons FeY(OH)^{2-} + 2OH^- \quad (6)$$

$$Fe(OH)_2 + Y^{4-} \rightleftharpoons FeY^{2-} + 2OH^- \quad (7)$$

Soluble complexes of iron(II) and iron(III) are formed, as can be seen from the equations. The potential of the FeS_2 electrode depends on the concentration ratio of FeY^- and FeY^{2-} (Eq. 8). The excess of Fe^{3+} or EDTA in the solution causes the potential jump at the TEP:

$$E_{FeS_2} = E_{const} + nV \log[FeY^-]/[FeY^{2-}] \quad (8)$$

Regarding thermodynamics, the Hg(II) ion can react with pyrite according to the following equations:

$$2Hg^{2+} + FeS_2 \rightleftharpoons Hg_2^{2+} + Fe^{2+} + 2S^0$$
$$\Delta G_{25} = -93.98 \text{ kJ/mol} \quad (9)$$

$$Hg^{2+} + FeS_2 \rightleftharpoons Hg^0 + Fe^{2+} + 2S^0$$
$$\Delta G_{25} = -83.14 \text{ kJ/mol} \quad (10)$$

Mercury(II) can be reduced to mercury(I), as can be seen from the equations, and also the formation of the elemental mercury on the pyrite surface is possible. Therefore the pyrite potential will depend on the redox couples Hg(II)/Hg(I) and Hg(II)/Hg^0. Reactions 9 and 10 are very slow, similar to the reaction of Ag^+ with pyrite [6], and that gives the possibility to apply the pyrite electrode in Hg(II) ion solutions. The characteristics of the pyrite electrode could be improved, since elemental mercury covered most of the pyrite sensor surface.

The following reaction between pyrite and Cu^{2+} has been investigated by Holdich and Broadbent [9]:

$$FeS_2 + 2Cu^{2+} \rightleftharpoons Fe^{2+} + 2Cu^+ + 2S^0 \quad (11)$$

The pyrite decomposition influenced by Cu^{2+} ions proceeds very slowly, as was established by those investigators. High concentrations of copper(II) ions (118 g/l) are necessary for pyrite oxidation. The decomposition rate of pyrite depends on the size of the pyrite particles, as the above investigators have shown. Reaction 11 takes place when the particle diameters are less than 0.013 mm. The reaction between Cu(II) and FeS_2 proceeds very slowly at temperatures below 180 °C, as was stressed by Naboichenko et al. [10], in spite of the negative Gibbs' free energy. The dimension of the pyrite crystal used for the pyrite electrode was about 0.5 cm^2 and was also polished. That was the reason for the negligible decomposition of pyrite by the copper(II) ions. However, reaction 11 occurs in the layer close to the electrode, with the copper(II) ions causing the corrosion of the pyrite sensor and shifting the pyrite potential towards the more positive region. The disappearance of the copper(II) ions caused by the complete complexing at the TEP shifts the pyrite potential towards the more negative region, and the jump of the potential is registered. This enables application of the pyrite electrode in complexometric titrations with copper(II) ions as a titrating agent.

These considerations indicate that the FeS_2 electrode can be applied for the TEP detection in complexometric titrations using Fe^{3+}, EDTA, Hg^{2+} or Cu^{2+}.

Potentiometric titrations

Potentiometric titrations with EDTA

The titrations of Ni(II), Bi(III), Cd(II), Co(II), Fe(III), Hg(II) and Cu(II) were investigated. When both ions of higher and lower valence were present in the solution, e.g., Fe(III)/Fe(II), Hg(II)/Hg(I) or Cu(II)/Cu(I), suc-

cessful potentiometric titrations were obtained, indicating that the pyrite electrode behaved in the titrations as a redox electrode. Since both components of the redox couple were present in the solution, EDTA would react with one of them, making a more stable complex, e.g., $K_{FeY^-} = 1.26 \times 10^{25}$ and $K_{FeY^{2-}} = 1.99 \times 10^{14}$. Therefore the concentration ratio between the oxidized and reduced forms was established at the TEP, causing the redox potential change with reference to the initial state.

In the titration of iron(III) with the pH increasing, the total potential changes were decreasing. The potential change decrease was caused by iron(III) properties that enabled the formation of the basic acetate and stable hydroxide, which influenced the complexing rate of iron(III) with EDTA. Those were the reasons for the iron(III) determination at pH 3.59. The potential value of the pyrite electrode at the beginning of titration was given by Eq. 1 and in the course of the titration by Eq. 8.

The titrations of iron(III) with EDTA at pH 3.59 were carried out by means of the platinum electrode as the indicator electrode. The potential changes (70–90 mV per 0.1 ml EDTA) were smaller in comparison with changes registered using the pyrite electrode (Table 1). The results obtained in potentiometric titrations of Fe(III) with EDTA solution, detecting the TEP by means of the Cu ISE, have been reviewed [11] and it was found that the standard deviation range was ±(0.6–1.2)%. Using the pyrite electrode, reliable results were obtained in this work with similar deviations.

Al-Daher and Kratochvil [12] have found that in the potentiometric titration of iron(III) in acetonitrile the jumps at the TEP were in the range from 120 to 300 mV, similar to the jumps at the TEP obtained by employing the pyrite electrode as described in this paper.

Copper(II) was titrated in ammoniacal buffer at pH values which ranged from 8.11 to 10.99 for the optimal pH value determination. With the increase of the pH values in the titrated solution up to pH 10.00, the results have shown an increase of the total changes as well as the potential changes at the TEP. For pH higher than 10.00, when EDTA has mainly the form of Y^{4-} ions, the potential changes cannot be influenced by the increase of the pH values. Nevertheless, copper(II) titration with EDTA in ammoniacal buffer could be performed at pH values less than 10.00 and accurate and reproducible results with smaller potential changes could be obtained. However, the titration should be performed at pH 10.00 because of the higher potential changes.

In titration of copper(II) with EDTA at pH 10.00 by means of the Cu ISE electrode, jumps were obtained at the TEP in the range from 80 to 100 mV per 0.1 ml EDTA. The potentiometric titrations using the pyrite electrode were found to give higher total potential changes as well as higher potential changes at the TEP in comparison with those obtained with the Cu ISE electrode (Table 1). Smith and Manahan [13] determined copper(II) in the concentration range 9–900 μg/l using an electrode based on copper sulfide. The results obtained were in the range from 98.9 to 101.1%, the same as in this paper. In the determination of copper the error achieved was less than 1%, obtained by Van der Meer et al. [14]. Schafer [15] determined Cu(II) with EDTA in a potentiometric titration by means of an electrode sensitive to copper(II) ions, with results similar to those given here.

For the optimal pH value determination, the titrations of mercury(II) were performed at various pH values in the acetate buffer solution. The influence of the pH values on the potential changes at the TEP was investigated. It was found that the difference in potential changes at the TEP occurred within the pH range 3.59–4.25 and also within the pH range 4.25–5.65. The titration of mercury(II) with EDTA can be carried out within the whole pH range mentioned, but because of the higher potential it is better to perform it at pH > 4.25. In this paper the titrations were carried out at pH 4.75. The titration of mercury(II) with EDTA by means of the Hg electrode was performed at the same

Table 1 Results obtained in potentiometric titrations of Cu(II), Hg(II) and Fe(III) with EDTA using the pyrite electrode for detection of the TEP

Species to be determined	Amount (mmol)	pH	Titrating agent	Total change E (mV)	Change in E at the TEP (mV/0.1 mL)	Found (%)[f]
Cu(II)	0.15	10.00[a]	EDTA	120–130	80–90	99.8 ± 0.1
Cu(II)	0.39	10.00	EDTA	120–130	60–80	99.9 ± 0.1
Cu(II)	0.15	10.00	EDTA	120–150	80–100	100.0 ± 0.0[c]
EDTA	0.10	10.00	Cu(II)	140–160	60–90	100.3 ± 0.2
Hg(II)	0.09	4.75[b]	EDTA	210–230	120–140	99.2 ± 0.1
Hg(II)	0.15	4.75	EDTA	220–240	110–130	99.4 ± 0.1
Hg(II)	0.09	4.75	EDTA	200–205	100–120	100.0 ± 0.0[d]
EDTA	0.07	4.75	Hg(II)	170–180	100–110	100.9 ± 0.1
Fe(III)	0.09	3.59[b]	EDTA	220–250	180–200	100.0 ± 0.1
Fe(III)	0.27	3.59	EDTA	310–330	160–180	100.5 ± 0.1
Fe(III)	0.09	3.59	EDTA	130–160	70–90	100.0 ± 0.0[e]
EDTA	0.07	3.59	Fe(III)	260–280	190–220	100.5 ± 0.1

[a] Ammoniac buffer
[b] Acetate buffer
[c] Cu ISE
[d] Hg electrode
[e] Pt electrode
[f] Six determinations

pH value and the TEP jumps obtained were in the range from 100 to 120 mV. These changes were smaller in comparison with the changes obtained when the pyrite electrode was used (Table 1), indicating the advantage of the pyrite electrode over the Hg electrode. Somer [16] determined Hg(II) using the iodide ISE for the TEP detection and the potential change at the TEP was 189 mV/0.1 ml NaI. Compiglio [17] also titrated Hg(II) and the TEP detection was obtained by an iodide ISE. The results obtained ranged from 98.40 ± 0.11 to 100.03 ± 0.04, depending on the Hg(II) concentration. By titrating mercury(II) with EDTA and determining the TEP by means of the pyrite electrode, accurate and reproducible results, in accordance with the above results, were obtained in this work.

The potentiometric titrations curves for the titration of copper(II), mercury(II) and iron(III) at the optimal pH values are represented in Fig. 4.

From the figure it can be seen that with an increase in stability constant of the complex formed, the total potential changes as well as the potential at the TEP were increased. Since the stability constant of CuY^{2-} was the smallest ($K = 6.91 \times 10^{18}$), the potential changes in the titration of copper(II) were also the smallest. With an increase in stability constant ($K_{HgY^{2-}} = 6.31 \times 10^{21}$) the potential changes increased. The highest potential changes were obtained in the titration of iron(III), since the stability constant of FeY^{-} is the highest ($K = 1.26 \times 10^{25}$). The results obtained in direct and reverse titrations were satisfactory accurate and reproducible (Table 1).

Since the pyrite electrode is a redox electrode, there is a possibility of interference when determining some components [Fe(III), Cu(II), Hg(II)] in a solution that contains some chemical species that can influence the electrode potential of pyrite. On that account the content of Fe(III) in a solution which contains copper(II) ions was determined. The determinations were performed at pH 3.59 for different mole ratios of Fe(III)/Cu(II) (Table 2.) The results obtained show that the total potential changes, as well as the potential changes at the TEP, in those titrations decreased and a fivefold amount of Cu(II) did not prevent the determination of the Fe(III). For the mole ratio Fe(III):Cu(II) = 1:5 and using the platinum electrode for the detection of the TEP, the potential jumps at the TEP were almost halved. Such behaviour of the pyrite electrode indicates that this electrode could be used as the indicator for the determination of iron(III) in diverse technological solutions, for example solutions obtained by dissolving steel, chalcopyrite mineral, pyrite concentrate (Table 3), printed circuits, etc. The results from this experiment are summarized in Table 3.

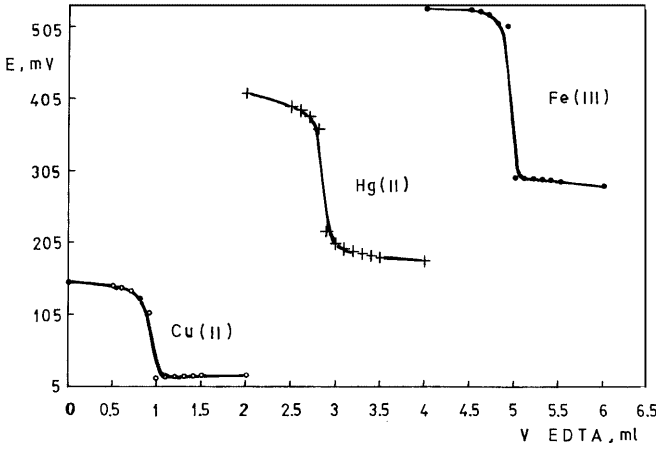


Fig. 4 Potentiometric titration curves for the titration of Cu(II) (pH 10.00), Hg(II) (pH 4.75) and Fe(III) (pH 3.59). Pyrite was the indicator electrode sensor

In potentiometric titrations of halogenide and thiocyanate with the standard mercury(II) solution, the pyrite electrode was used as the indicator electrode. The potential of the pyrite electrode after the TEP can be described by the following equation (see Fig. 1):

$$E = E_{\text{const}} + nV \log c_{\text{Hg(II)}} \tag{12}$$

and the excess of mercury(II) ions caused the potential jump. The results of these titrations are given in Table 4. From the results it is evident that the pyrite electrode showed regular behaviour. Comparing the stability constants of the complexes formed [18] the following order was obtained:

$$K_{HgCl_2} < K_{Hg(CNS)_2} < K_{HgBr_2} < K_{HgI_2} \tag{13}$$

The increase of the total potential changes, as well as the potential changes at the TEP in the titrations investigated, were in the same order. In our previous paper [6] X,SCN^{-} were determined by potentiometric titrations with $AgNO_3$ and the TEP was detected by means of the

Table 2 Results obtained in potentiometric determinations of Fe(III) with EDTA at pH 3.59 and for different mole ratios of Fe(III)/Cu(II)

Weighed Fe (mmol)	Molar ratio Fe(III): Cu(II)	Total change E (mV)	Change in E at the TEP (mV/0.1 mL)	Indicator electrode	Found (%)[a]
0.25	5:1	300–320	160–200	FeS_2	100.1 ± 0.2
0.25	1:1	290–300	190–200	FeS_2	99.9 ± 0.1
0.25	1:5	250–280	150–170	FeS_2	100.1 ± 0.1
0.25	1:5	160–210	80–100	Pt	100.0 ± 0.0

[a] Six determinations

Table 3 Determination of iron with EDTA in steel, pyrite concentrates and chalcopyrite mineral (pH = 3.66, acetate buffer)

	Fe content (%)[a]	
	Pt electrode	FeS_2 electrode
Steel	93.3 ± 0.2	93.2 ± 0.1
Chalcopyrite	29.9 ± 0.1	29.8 ± 0.2
Pyrite concentrate	41.5 ± 0.1	41.6 ± 0.2

[a] Five determinations

Table 4 Results obtained in potentiometric titrations of halogenide and thiocyanate with a standard Hg(II) solution and of cyanide with a standard Ag(I) solution

Ion to be determined	Amount (mmol)	Titrating agent	Total change E (mV)	Change in E at the		Found (%)[a]
				TEP_1 (mV/0.1 ml)	TEP_2 (mV/0.1 ml)	
Cl^-	0.20	Hg(II)	210–290	–	40–60	100.9 ± 0.2
Cl^-	0.50	Hg(II)	250–300	–	25–40	100.4 ± 0.1
Hg(II)	0.12	Cl^-	130–170	–	30–35	99.6 ± 0.2
Br^-	0.19	Hg(II)	260–330	–	110–140	100.3 ± 0.1
Br^-	0.50	Hg(II)	310–350	–	100–120	100.1 ± 0.1
Hg(II)	0.11	Br^-	220–240	–	80–100	99.6 ± 0.1
CNS^-	0.10	Hg(II)	240–310	–	110–140	99.6 ± 0.3
CNS^-	0.50	Hg(II)	270–390	–	60–90	99.9 ± 0.1
Hg(II)	0.27	CNS^-	280–290	–	60–70	100.7 ± 0.1
I^-	0.22	Hg(II)	360–380	–	200–220	100.6 ± 0.1
I^-	0.42	Hg(II)	380–440	–	190–230	100.3 ± 0.1
Hg(II)	0.10	I^-	280–340	–	130–200	100.7 ± 0.1
CN^-	0.30	Ag(I)	440–480	–	115–150	98.4 ± 0.2
CN^-	0.47	Ag(I)	455–505	–	160–185	100.1 ± 0.1
CN^-	0.47	Ag(I)	1020–1030	210–230	150–180	100.0 ± 0.0[b]
Ag(I)	0.44	CN^-	320–395	70–80	–	99.1 ± 0.1

[a] Six determinations
[b] Ag electrode

pyrite electrode. Similar potential changes at the TEP were obtained in this paper by titrating X,SCN^- with standard Hg(II) solution. This indicates that Hg(II) can be successfully applied for X,SCN^- ions' determinations by means of the FeS_2 electrode as the indicator. Other authors [19] also used Hg(II) for X,SCN^- determination and obtained good results.

In reverse titrations, the results were similar to those obtained for the direct titrations. The rate of potential equilibration at the pyrite electrode in the course of these titrations was fast, less than 1 min. At the TEP, the potential was established within 1–2 min or 2–3 min in direct or reverse titration, respectively. The results obtained were accurate and reproducible in direct as well as in reverse titrations.

The reaction of CN^- ion as a monodentate ligand with Ag(I) ion is suitable for volumetric determination. The TEP indication can be followed by the potentiometric application of silver and ion selective electrodes. The pyrite electrode was used in this investigation. In the titration followed by potentiometric detection of the TEP, two jumps could be registered: the first after $Ag(CN)_2^-$ formation and the second after AgCN was formed. Previous investigations have shown that the pyrite electrode could be used in precipitation titration and its potential could be expressed as a function of the $c_{Ag(I)}$ ion [6]. In the course of CN^- titration with Ag(I) by means of the pyrite electrode, the potential was established for less than 1 min, whereas in the vicinity of the TEP for about 1–2 min. Accurate and reproducible results were obtained both in direct and reverse titrations (Table 4).

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