

Natural Monocrystalline Pyrite as Sensor for Potentiometric Redox Titrations. Part I. Titrations with Permanganate

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Abstract: Results obtained in potentiometric titrations of Fe(II), Mn(II), $\text{Fe}(\text{CN})_6^{4-}$, $\text{C}_2\text{O}_4^{2-}$ and As(III) with standard potassium permanganate solution, are presented. The titration end point (TEP) was detected with a universal electrode whose sensor is natural crystalline pyrite. The titrations of As(III) were carried out in HCl (1.2 M) and H_2SO_4 solutions (0.1-4.5 M), whereas oxalate was determined in H_2SO_4 (0.1-4.5 M). Iron(II) and hexacyanoferrate(II) were titrated in H_2SO_4 and also in H_3PO_4 solutions (0.1-4.5 M). The titrations of Mn(II) were performed in $\text{H}_2\text{P}_2\text{O}_7^{2-}$ media at pH 4.0, 5.0, 6.0 and 7.0. The results obtained by using the pyrite electrode were compared with those obtained by the application of a Pt-electrode, and good agreement, reproducibility and accuracy were obtained. The potentials in the course of the titration and at the end-point (TEP) are rapidly established. The potential changes at the TEP ranged from 90 to 330 mV/0.1 mL, depending on the titrated system. The highest changes were observed in titrations of Fe(II) in H_3PO_4 (240-330 mV/0.1 mL). Reversed titrations were also performed and accurate and reproducible results were obtained.

Keywords: Pyrite, Sensor, Permanganate, Potentiometry, Reductants

Introduction

Mn(II) can be determined in several ways: iodometrically¹, by differential stripping voltammetry², polarographically³, fluorometrically⁴, amperometrically⁵, by indirect titration with EDTA⁶,

spectrophotometrically^{7,8}, by the potentiometric titration with Mn(VII) in pyrophosphate media⁹ as well as by potentiometric titration with polyamine ligands in acetonitrile¹⁰.

Fe(II) can be determined by volumetric titration with cerium(IV) using ferroin as indicator¹¹, by liquid chromatography¹², photometrically^{13,14}, polarographically¹⁵, ferrocenometrically¹⁶, by using XeF₂ as a standard titrating solution¹⁷ as well as potentiometrically^{10,18-22}.

Hexacyanoferrate(II) can be determined by infrared spectroscopy²³, or amperometrically^{24,25}, coulometrically^{26,27} as well as potentiometrically²⁸⁻³².

Arsenic(III) can be determined potentiometrically and by visual titration with bromoamine²⁸, by potentiometric stripping analysis³³, AFS method³⁴, cerimetrically^{11,35}, by potentiometric titration with XeF₂ and also bipotentiometrically with Mn(III) and Mn(IV).

Oxalate can be determined chromatographically³⁶, spectrophotometrically³⁷, gasometrically³⁸ as well as by potentiometric precipitation titrations.

From this short survey of methods for the determination of reducing substances it is seen that the potentiometric methods are of great importance for these determinations. Therefore, it is desirable to reveal and develop new sensors for the TEP detection. In the hitherto published papers the following indicator electrodes were used: Cu-wire, graphite electrode, Pt-electrode, Ag-electrode coated with Ag₂S and Ag₃Fe(CN)₆ and picrate ion-selective electrode. All theafore-mentioned determinations were carried out either in aqueous or nonaqueous media, and are based on redox reactions, complex formation reactions or formation of precipitates.

In addition, Au, stainless steel, various inert electrodes can be also used as indicator electrodes in redox titrations, and one among the latter ones is the pyrite electrode which was found to be very effective in acid-base titrations in aqueous⁴⁰ and non-aqueous⁴¹ solutions, as well as for complexometric titrations^{42,43} and redox titrations^{44,32}.

In this paper results obtained in investigating pyrite as sensor of the indicator electrode in redox titrations with standard Mn(VII) solution, are presented.

Experimental

Chemicals and solutions

All solutions used in this paper were prepared from p.a. chemicals and distilled water.

The concentrations of standard solutions were determined titrimetrically by using visual or potentiometric TEP detection.

H₂P₂O₇²⁻ solutions with pH values 4.0, 5.0, 6.0 and 7.0 respectively, were prepared by adding H₂SO₄ or NaOH to 0.02 M pyrophosphate solution, the pH being adjusted pH-metrically.

Apparatus and electrodes

The apparatus used and the preparation of electrodes are described in an earlier paper⁴⁰.

Procedure

Measurement of the stationary potential

The stationary potential of the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ systems was measured at $I = 0.1$ M. The ionic strength was adjusted by the addition of NaNO_3 . The measurements were carried out for the following concentration ($c_{\text{Ox}}/c_{\text{Red}}$) ratios: 9:1, 7:3, 5:5, 3:7 and 1:9. The stationary potential was measured by noting the potential changes after each minute, in the course of 15 minutes. Potential values measured after 15 minutes were taken for the calculation of the slopes and correlation coefficients.

Potentiometric titrations

An appropriate volume of the reductant solution was placed in a 150 mL beaker and made up to 80 mL with an acid solution of known concentration (or pyrophosphate solution of known pH value, in the case of $\text{Mn}(\text{II})$ determination), the electrode couple SCE- FeS_2 was then dipped into the solution, the magnetic stirrer was switched on and the potential change was measured after the addition of each increment of $\text{Mn}(\text{VII})$. The exact amount of consumed $\text{Mn}(\text{VII})$ solution was calculated by the mathematical method from the second derivative.

Results and Discussion

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 non-reactive compound. Since pyrite is a semiconductor of n or p type, it is possible to use it, on account of its chemical inactivity, for the 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.1.).

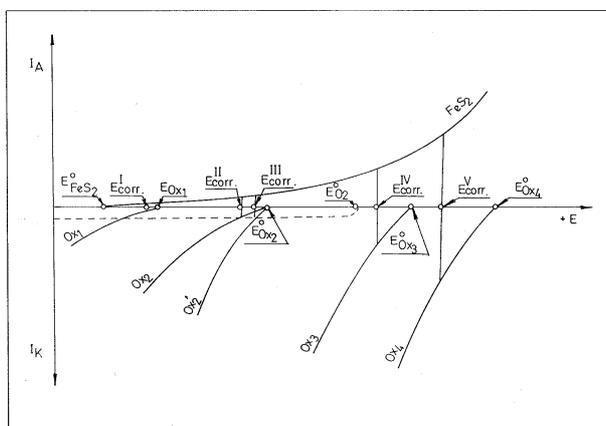


Figure 1. Anodic and cathodic polarization curves by means of which potential changes at the titration end-point are explained [Ox_1 , Ox_2 (Ox'_2), Ox_3 and Ox_4 are different oxidants].

It is known that in acid media pyrite dissolves slightly (becomes corroded), giving rise to soluble products⁴⁵:



The rest potential of pyrite in open-circuit is 0.62 V vs. SCE, and at more positive potentials the dissolutions 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 pyrite 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.1.). 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_{corr}^I). It may be assumed that the solutions contain 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:



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_{corr}^{II} 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 that results in the shift of the corrosion potential to E_{corr}^{III} . 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_{corr}^{III} to E_{corr}^{IV} makes possible the applications of the pyrite electrode as the indicator electrode in potentiometric redox titrations. From Fig.1. it is also seen that higher potential changes of the pyrite electrode at the titration end-point are observed in case 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 titration end-point in that case are small. Similar consideration hold for titrations of oxidizing agents with reducing agents, but then, the corrosion potential of pyrite is shifted towards the more negative region.

The measurements of the standard potential were carried out with solutions having different c_{Ox}/c_{Red} ratios of the $Fe(III)/Fe(II)$ and $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ systems, and the results obtained are shown in Fig. 2.

The calculated correlation coefficients (c_{corr}) shown the linearity of the results obtained, whereas the hitherto performed investigations point out the effectiveness of the pyrite electrode as the indicator electrode for potentiometric titrations.

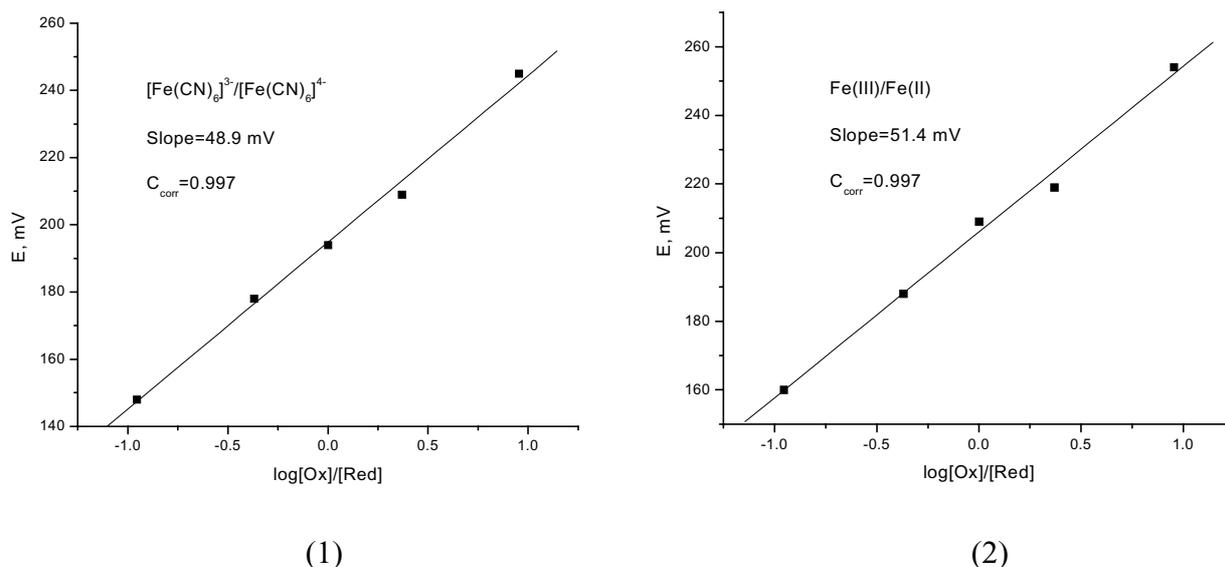


Figure 2. Plots of E against $\log (c_{\text{Ox}}/c_{\text{Red}})$: (1) $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$; (2) $\text{Fe}(\text{III})/\text{Fe}(\text{II})$.

The chemical process taking place in the potentiometric titration of the Mn(II) with permanganate in pyrophosphate media is given by the following equation:



The main factor of this process is the concentration of $\text{H}_2\text{P}_2\text{O}_7^{2-}$ on account of the stabilization of Mn(III) in the form of the pyrophosphate complex. The titrations were performed at pH values 4.0, 5.0, 6.0 and 7.0 (Fig. 3).

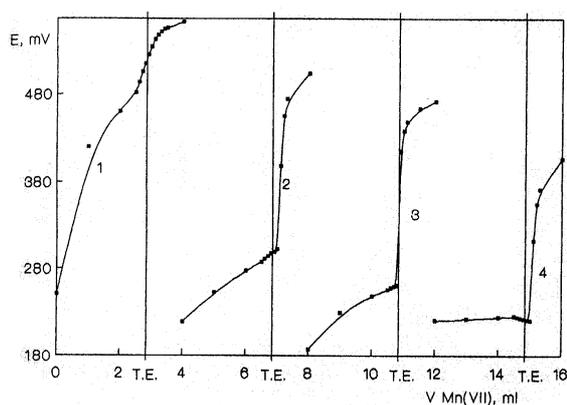


Figure 3. Potentiometric titrations of Mn(II) in pyrophosphate at various pH values (1. pH 4.00; 2. pH 5.00; 3. pH 6.00; 4. pH 7.00).

From the graph in Fig. 3. it is seen that pH 6.0 is the optimum pH, and that the titrations at pH-values 4.0, 5.0 and 7.0 do not afford good results since the TEP is shifted. At pH 6.0 the concentration of $\text{H}_2\text{P}_2\text{O}_7^{2-}$ ion in the solution is maximal which enables the stabilization of Mn(III) form, a decrease of the standard Mn(III)/Mn(II) potential and shifts the reaction to the right.

Pastor et al.⁹ carried out the determination of Mn(II) under the same conditions but they applied Pt and graphite electrodes as indicator electrodes. Comparison of results obtained by the application of the pyrite, Pt and graphite electrodes, is given in Table 1.

Table 1. Comparison of the results obtained with the pyrite, Pt and carbon indicator electrode in pyrophosphate media.

Titrated ion	Titrant	pH	Electrode	Potential change at the TEP	Reference
Mn(II)	Mn(VII)	6.2	Pt	110 - 130	9
Mn(II)	Mn(VII)	6.2	Carbon	165 - 190	9
Mn(II)	Mn(VII)	6.0	FeS ₂	100 - 190	Results presented in this paper

From Table 1 it is seen that the pyrite electrode is applicable to the titrations of Mn(II) in pyrophosphate media at pH 6.0 with the same effectiveness as the Pt and graphite electrodes. The total potential changes range from 200 to 260 mV, whereas the jumps at the TEP from 100 to 190 mV/0.1 mL, depending on Mn(II) concentration in the titrated solution.

An increase in sulphuric acid concentration has a small effect on the increase of the total potential changes in the course of iron(II) titration, but not on the potential changes at the TEP.

However, an increase in H₃PO₄ concentration effects considerably both the potential changes in the course of the titration and the potential changes at the TEP. These observations are expected since Fe(III) which is formed in the course of the titration, in phosphoric acid solution forms the complex Fe(HPO₄)⁺ whose formation constant is $2.3 \cdot 10^{9(46)}$. The formation of such a stable complex causes a decrease of the potential of the Fe(III)/Fe(II) system and in this manner the potential differences with respect to the Mn(VII)/Mn(II) is increased. All that results in an increase of total potential changes in the course of the titration and also of potential changes at the TEP (Table 2).

Table 2. Results obtained in potentiometric titrations of reducing substances with standard potassium permanganat solution (electrode couple FeS₂-SCE).

Taken (mol)	c _{acid} (mol.dm ³)	Titrant	Total change of E (mV)	Change of E at the TEP (mV/0.1ml)	Found
Fe(II) ¹		Mn(VII)			
0.0027	0.1		280 - 360	90 - 120	99.4±0.1
0.0027	4.5		340 - 350	90 - 120	99.7±0.2
0.0010	0.5		290 - 300	140 - 150	100.6±0.4
0.0019	0.5		305 - 310	100 - 130	100.1±0.3
0.0029	0.5		745 - 750	450 - 500	100.0±0.0*
Mn(VII)		Fe(II)			
0.0007	1.5		260 - 270	50 - 60	99.9±0.2
0.0007	4.5		260 - 300	40 - 70	99.2±0.2
0.0004	1.5		280 - 290	75 - 80	99.2±0.1
0.0006	1.5		270 - 290	50 - 60	100.0±0.6

Taken (mol)	$c_{\text{acid}} (\text{mol.dm}^3)$	Titrant	Total change of E (mV)	Change of E at the TEP (mV/0.1ml)	Found
Fe(II) ²		Mn(VIII)			
0.0029	0.1		390 - 400	180 - 240	100.5±0.1
0.0029	1.5		440 - 470	260 - 330	100.5±0.1
0.0021	0.5		430 - 440	260 - 270	100.0±0.0
0.0037	0.5		440 - 445	240 - 250	99.9±0.1
		Fe(II)			
0.0007	0.1		340 - 350	130 - 160	99.5±0.2
0.0007	1.5		430 - 440	130 - 190	99.8±0.3
0.0004	0.5		410 - 420	190 - 200	99.2±0.1
0.0007	0.5		400 - 405	170 - 190	99.8±0.1
Fe(CN) ₆ ⁴⁻		Mn(VII) ¹			
0.0031	0.1		470 - 480	180 - 190	99.9±0.0
0.0031	1.5		370 - 380	60 - 65	99.9±0.1
0.0018	0.5		380 - 390	100 - 120	100.4±0.1
0.0038	0.5		400 - 410	90 - 100	100.3±0.1
0.0031	0.5		730 - 770	430 - 460	100.0±0.0*
Mn(VII)		Fe(CN) ₆ ⁴⁻			
0.0004	0.1		320 - 330	140 - 150	100.3±0.1
0.0004	1.5		205 - 210	30 - 35	99.9±0.3
0.0004	0.5		260 - 270	75 - 80	99.9±0.3
0.0005	0.5		280 - 285	60 - 80	99.6±0.2
Fe(CN) ₆ ⁴⁻		Mn(VII) ²			
0.0031	0.5		440 - 450	150 - 180	99.7±0.1
0.0031	4.5		330 - 350	20 - 40	99.7±0.2
0.0012	0.5		420 - 430	170 - 180	101.1±0.1
0.0038	0.5		440 - 470	130 - 150	100.1±0.1
0.0031	0.5		710 - 780	440 - 510	100.0±0.0*
As(III) ³		Mn(VII)			
0.0013	1.2		230 - 290	150 - 200	100.7±0.1
0.0020	1.2		240 - 270	150 - 200	99.9±0.1
As(III) ¹		Mn(VII)			
0.0020	0.1		280 - 330	160 - 230	100.3±0.2
0.0020	1.5		260 - 380	200 - 310	100.2±0.1
0.0009	0.5		230 - 250	150 - 160	98.9±0.1
0.0020	0.5		300 - 340	180 - 270	100.1±0.1
0.0013	0.5		690 - 740	350 - 620	100.0±0.0*
C ₂ O ₄ ²⁻		Mn(VII) ¹			
0.0014	0.1		180 - 250	90 - 140	101.8±0.2

Taken (mol)	c_{acid} (mol.dm ³)	Titrant	Total change of E (mV)	Change of E at the TEP (mV/0.1ml)	Found
0.0014	4.5		230 - 280	40 - 50	101.9±0.8
0.0014	0.5		220 - 280	110 - 160	101.0±0.2
0.0020	0.5		230 - 320	120 - 200	100.4±0.1
0.0014	0.5		550 - 560	360 - 420	100.0±0.0*

1- Titrations in H₂SO₄; 2- Titrations in H₃PO₄; 3- Titrations in HCl; *-Titrations by the use of a Pt-el.

The increase in H₂SO₄ and H₃PO₄ concentrations has a more significant influence of potential changes in titrations of hexacyanoferrate(II). At lower H₂SO₄ concentrations the process of hexacyanoferrate(II) oxidation takes place more readily since a small amount of H⁺ is available for the formation of H₄Fe(CN)₆.

With increasing H⁺ concentration the reaction of H₄Fe(CN)₆ formation is favoured, and in conditions of satisfactory high H⁺ concentration (4.5 M H₂SO₄) the process of hexacyanoferrate(II) oxidation is very slow. At low H₂SO₄ concentrations (0.1, 0.5 and 1.5 M) the process of hexacyanoferrate(II) oxidation proceeds with a more considerable decrease in potential changes with the increasing acidity. However, since H₃PO₄ is a weaker acid than H₂SO₄, a H₃PO₄ solution of the same concentration as that of H₂SO₄ will contain less H⁺ ions, and therefore, with increasing H₃PO₄ concentration the formation of H₄Fe(CN)₆ will have less priority. On account of these reasons the titration of hexacyanoferrate(II) in 4.5 M H₃PO₄ is possible (Table 2).

With standard solutions of Mn(III) in 1.0 M H₂SO₄ and Mn(IV) in 2.0 M H₂SO₄ the bipotentiometric titrations (Pt-electrodes) of hexacyanoferrate(II) were performed with a total potential change of 400-750 mV. The results obtained with Mn(III) were 99.2±0.2% and those with Mn(IV) 100.2±0.3%. Hexacyanoferrate(II) can be determined also by potentiometric precipitation reactions with AgNO₃, the indicator electrode being based on a mixture of Ag₂S and Ag₄Fe(CN)₆, whereby the obtained jumps amounted to about 150 mV/0.1 mL³⁰, or a picrate ion-selective electrode can be used.

The titrations of As(III) were carried out in HCl (1.2 M) and H₂SO₄ (0.1 - 4.5 M). Because the reaction of As(III) with Mn(VII) is slow, it had to be catalyzed. In titrations of As(III) in HCl, only the concentration of As(III) was changed. The changes in As(III) concentration had no significant effect either on the potential changes or on the accuracy of the results. An increase in H₂SO₄ concentration in titrations of As(III) had a more significant effect on potential changes. With increasing acidity the oxidizing ability of Mn(VII) is increased, and because of that the difference in potential is increased which causes an increase in potential changes (Table 2).

The titrations of oxalate were carried out in H₂SO₄ (0.1-4.5 M). It is known that the presence of higher amounts of H₂SO₄ inhibits the reaction of oxalate with Mn(VII) making it slow, which has a considerable effect on the decrease of potential change at the TEP (with increasing acidity the potential change is decreased for about 90 mV/0.1 mL) (Table 2).

In reversed titrations the behaviour of the pyrite electrode was similar to that in direct titrations. The total potential changes and the potential changes at the TEP were smaller with respect to those in direct titrations. The highest changes at the TEP were observed in titrations of Mn(VII) with iron(II)

in 1.5 M H_3PO_4 (130 - 190 mV/0.1 mL), whereas the smallest ones in titrations of Mn(VII) with iron in H_2SO_4 (50 - 60 mV/0.1 mL).

The accuracy and the reproducibility in direct and reverse titrations were satisfactory (Table 2).

In all direct and reverse titrations, in the presence of MnO_4^- ion in excess, potential oscillations were observed ($\pm 5\text{mV}$). These oscillations are most probably due to unequal rates of MnO_4^- reduction on the pyrite surface. A change in the reduction rate (cathodic current density) causes a change in the position of the corrosion potential, which gives rise to its oscillations.

In the course of the titration and also at the TEP the potential was rapidly established (<1) except in titrations of oxalate where on account of a slow reaction a somewhat longer time-interval was required, as well as in the determination of As(III) where the reaction had to be catalyzed.

Data in Tables show that the behaviour of pyrite in all the investigated systems is in accordance with the expected one: higher jumps were obtained with those systems where the difference between the standard potential values was greater. Also higher jumps at the TEP were registered in cases where the medium can influence the reaction equilibrium (titration of Fe(II) in H_3PO_4 or Mn(II) in pyrophosphate medium at the pH 6.0). In addition, taking into account the accuracy and the reproducibility as well as the rate of potential establishment at the FeS_2 electrode in the course of the titration and at the TEP, it may be concluded that pyrite as sensor of the indicator electrode is suitable for the TEP detection in redox potentiometric titrations where standard Mn(VII) solution is used as the titrant.

Acknowledgments

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