Research Article

Iron(II) as a new electron transfer reagent in buffer medium and in presence of oxalate for the selective determination of Chromium(VI) and some related analytical applications of the reagent in the medium.

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Abstract

Iron(II) in buffer medium and in presence of oxalate has been proposed as a new electron transfer reagent or reducing agent for the selective determination of chromium(VI) in presence of several other metal ions such as Mo(VI), U(VI), V(IV) etc. The method consists in taking a chromium(VI) solution [containing 3-11mg of Cr] into a buffer medium of pH ~ 4.0- 5.2 containing about 0.04-0.10M potassium oxalate and then titrating it against iron(II) solution. By reversing the above redox process i.e. by taking iron(II) in buffer-oxalate medium [pH 1.5-2.5 and oxalate concentration 0.04- 0.10M] and titrating it against chromium(VI) solution taken in the burette, a new method for the selective determination of iron(II) [containing 9-30mg of Fe] has also been developed. The end-point in both the methods can be detected either potentiometrically or using a thiazine dye as a redox indicator. In combination with one of our methods reported earlier using iron(II) as a reducing agent in phosphoric acid medium, the method now proposed for the determination of chromium(VI) allows the quantitative analysis of metal ions present in synthetic mixtures such as : (1). Cr(VI) - Mo(VI) ;(2). Cr(VI) -U(VI); and (3). Cr(VI)- V(V). Similarly, in combination with the stannous chloride method for the estimation of iron(III) available in literature, the method new now developed for the determination of iron(II) permits the quantitative analysis of Fe(II) and Fe(III) present in synthetic mixtures and for analysis of iron ore for iron content. The formal redox potentials of Cr(VI)/Cr(III) and those of Fe(III)/Fe(II) couples have been measured in the buffer media of varying pH and oxalate ion concentrations under the optimum titration conditions. Based on these potentials data, an explanation for the conditions needed in the determination of chromium(VI) with iron(II) has been offered. The transition potentials of the indicators used have been measured. Based on these potentials data the suitability of the indicators in the present redox processes has been explained. The advantages of the present reductant over the other conventional reductants have been brought out. The reaction conditions under which Cr(VI) is reduced to Cr(III) by oxalate were investigated with a view that these findings may help to mitigate the ground water pollution due to Cr(VI) which is more toxic than Cr(III).

Keywords: Iron(II) reductant, buffer- oxalate medium, chromium(VI), metal ion mixtures.

1. Introduction

Chromium is known to be one of the most useful of all transition metals as it is mainly used in the production of ferroalloys, stainless steel and hard chromium steel which are the source of material for the manufacture of several scientific equipment, electrical materials and surgical apparatus etc. Chromium forms a number of salts/compounds with different oxidation states starting from +2 to + 6; of which those with +3 and +6 oxidation states are the most stable. Chromium(III) oxide, sulfate, halides etc. are some important salts of chromium(III) while chromium(VI) oxide, potassium or sodium dichromate are the well known salts of chromium(VI). Potassium dichromate is the most useful of all chromium(VI) compounds as it serves as a chief raw

material in the large scale production of several technologically useful chemicals such as chrome alum, chrome red, zinc yellow, chrome yellow etc. It is one of the most stable of all chromium(VI) compounds and hence used as a primary standard volumetric reagent in the laboratory. Being a powerful oxidising agent [E^0 = +1.33V] [1 (p66)] it is extensively used in the estimation of several substances of industrial importance and the procedures are well documented [1 (p375-378), 2 p(169-197)] in the standard analytical chemistry text books.

Surprisingly, for such a useful reagent, no convenient and suitable methods are available for its determination. A survey of literature reveals that the recent methods reported [3-8] are found to be highly expensive as they have to be carried out using the state of the art technology and useful to determine only the minute quantities of chromium(VI) present in certain samples. However, the earlier methods available are very limited in number and utilize the reducing agents like iron(II) [2 (p606), 9,10] , arsenic (III) [2 (p655)] , iodide [2 (p 237)] , ,tin(II) [2 (p622)] & vanadium(III) [2 (p629)], titanium(III) [2 (p617)] ,11], uranium(IV) [2 (p631), 9], hexacyanoferrate(II) , hydroquinone & molybdenum(V) [9], ascorbic acid [12] etc. Recently, a redox procedure for the determination of chromium(VI) using iron(II) as a reducing agent in acetic acid medium and in presence of pyrophosphate was reported from our laboratories [13].

Most of these methods suffer from the common disadvantage that metal ions like Mo(VI), U(VI), V(IV), Sb(V), As(V), Tl(III) etc, interfere. Further each method has its own disadvantages. For example one of the iron(II) methods [10] requires high concentration of phosphoric acid which is expensive and makes the medium more viscous. The arsenic(III) method is an indirect one and needs the use of an expensive catalyst. In the iodometric method, the concentration of acid must be carefully controlled to prevent the formation of air sensitive hydroiodic acid and the solution must be kept in darkness for about 10 minutes for completion of the reaction, further, the method is expensive. Some of the reagents like tin(II), titanium(III), ascorbic acid must be stored in a special apparatus under inert atmosphere as the reagents are air sensitive. In the case of ascorbic acid, a stabilizer must be added to prevent its decomposition. The procedures involved in the preparation and preservation of the reductants like V(III), U(IV), Mo(V) etc.[which are utilized for the determination of Cr(VI)] is a tedious task. The formation of Prussian blue colour due to the combination of ferrate(II) and ferrate(III) in the reaction medium in the hexacyanoferrate(II) method was stated to impair the detection of the end-point . Pyrophosphate used as a complexing agent in our recent method is an expensive reagent and causes to precipitate some metals as metal-pyrophosphates.

The present paper describes a new redox procedure for the selective determination of chromium(VI) in presence of several other metal ions such as Mo(VI), U(VI), V(IV), Sb(V), As(V), etc., using iron(II) as a reducing agent or electron transfer reagent in buffer medium and in presence of oxalate. The method consists in taking a chromium(VI) solution in buffer medium of pH 4.0-5.0 [obtained by mixing HCl / H_2SO_4 with sodium acetate] in presence of 0.04-0.10M potassium oxalate and titrating it against iron(II) solution taken in the burette. The procedure now developed is accurate, convenient and does not suffer form any of the disadvantages of the earlier ones mentioned above ; further all the reagents needed in preparing the reducing agent [HCl, H_2SO_4, sodium acetate, potassium oxalate, iron(II) etc.] are inexpensive and readily available in a state of high purity. By reversing the above process, i.e., by taking iron(II) solution in the buffer-oxalate medium [pH 1.5-2.5 ; oxalate ion concentration ~ 0.05-0.10 M] and titrating it against chromium(VI) solution taken in the burette, a new method for the selective determination of iron(II) with chromium(VI), has also been developed. In both the determinations, the end-point can be detected either potentiometrically or using a thiazine dye as a redox indicator. The buffer solutions of desired pH are obtained by mixing required volume of hydrochloric acid/sulphuric acid [1N] with that of sodium acetate [1M] and diluted to a definite volume as suggested by Walpole [14] . In combination with one of our earlier methods developed using iron(II) as a reducing agent in phosphoric acid medium[15], the method now proposed for the determination of chromium(VI) enables us the quantitative analysis of metal ions present in the synthetic mixtures such as (1). Cr(VI) - Mo(VI) ;(2). Cr(VI) -U(VI); and (3). Cr(VI)- V(V). Similarly, in combination with the stannous chloride method for the determination of iron(III) available in literature [1 p415], the method now developed for iron(II) permits the analysis of iron(III) and iron(II) contents present in a synthetic mixture and for the analysis of an iron ore for iron content.

Further, based on the formal redox potentials of Cr(VI)/Cr(III) couple and those of iron(III)/iron(II) couple obtained at different pH and oxalate ion concentrations and considering the stoichiometric chemical equations involved in the redox procedures, plausible explanations to the conditions needed in the determination of chromium(VI) with iron(II) and iron(II) with chromium(VI) have been offered. Moreover, based on the transition potentials of the indicators obtained in the determination, a reasonable explanation to the suitability of thiazine dyes as redox indicators in the determination of chromium(VI) with iron(II) has been placed. The present paper also furnishes valid reasons for iron(II) to be a good reducing agent in buffer-oxalate medium and the advantages of the present reducing agent over the conventional reducing agents such as Ti(III), Sn(II), Cr(II), V(II) etc.

The authors, in addition, have studied the conditions under which chromium(VI) is reduced to chromium(III) by oxalate and presented them in the paper, with a view that these findings may help to mitigate the ground water pollution due to Cr(VI) which is more toxic than Cr(III). . It has been reported earlier [16] that corrosion inhibition and electroplating industries improperly dispose of Cr(VI) containing waste water into the environment causing contamination of soils and water with Cr(VI) and this is often controlled by treating with oxalate which reduces Cr(VI) to Cr(III).

2. Experimental

2.1. Preparation of solutions:

Potassium dichromate or chromium(VI) solution: A standard solution of 0.1N of potassium dichromate has been prepared by dissolving exactly 4.903 grams of the AR grade salt in distilled water in one litre standard flask and diluting up to the mark. The strength of the solution has been checked by the iodometric method [2 (p237)] . From the stock solution a 0.05N solution has been prepared by suitable dilution.

Chromium(III) solution: An approximately 0.05M solution of chromium(III) has been prepared from an AR grade potassium chromium(III) sulphate dodecahydrate in one litre standard flask and the solution standardised by titrating it against a standard solution of permanganate[2 (p101)]

Iron(II) solution: An approximately 0.1N solution of iron(II) has been prepared from an A.R. grade ammonium iron(II) sulphate hexahydrate in 0.1N sulphuric acid medium and standardised by titrating it against a standard solution of potassium dichromate[1 p375] as described in literature. From this solution a 0.05N solution of iron (II) has been prepared by suitable dilution.

Iron (III) solution: An approximately 0.1N solution of iron (III) has been prepared from an A.R. grade ammonium iron(III) sulphate dodecahydrate in 0.2 N sulphuric acid medium and standardised by stannous chloride method [1 p415]. From the solution a 0.05N solution of iron (III) has been prepared by suitable dilution.

Molybdenum(VI), Vanadium(V) and Uranium(VI) solutions : 0.1N solutions of molybdenum(VI) [from an AR grade Na_2MoO_4. $2H_2O$], [2 (p153)] vanadium(V) [from an AR grade sodium metavanadate, $NaVO_3$] [2 (p606)] and uranium(VI) [from from an AR grade uranyl acetate [$UO_2(CH_3COO)_2$. $2H_2O$] [2 (p189)] have been prepared by dissolving the requisite quantities of their respective salts [mentioned in parenthesis] in distilled water in standard flasks. The strength of each solution

has been determined adopting the standard methods [2 (p153, 606, 189)] described in literature.

Sodium acetate solution: A stock solution of 1M sodium acetate has been prepared from its A.R. grade salt [$CH_3COONa.3H_2O$] in distilled water.

Acid solutions: Stock solutions of hydrochloric acid [2M and1M] and sulphuric acid [2N and 1N] have been prepared from their respective A.R. grade samples in distilled water. The solutions were standardized by titrating them against a standard solution of sodium carbonate using methyl orange as an indicator.

Buffer solution: Buffer solutions of desired pH are prepared by mixing a suitable volume of 1N or 2N solution of HCl or H_2SO_4 with that [generally 10ml] of 1M solution of sodium acetate and diluted to a definite volume [generally 50ml] as suggested by Walpole [14].

Potassium oxalate solution: Stock solution of 1M potassium oxalate [$K_2C_2O_4.H_2O$] has been prepared by dissolving the required quantity of the A.R. grade salt in distilled water.
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Indicator solution: 0.1% (w/v) aqueous solution the dyes: Methnylene Blue (MTB) (Merck, Germany), Toluidine Blue (TLB). Azure A (AZA) and Azure B (AZB) [all from Gurr & Co England], Resorufine (RSF) [from Aldrich, USA] have been prepared and utilized as redox indicators in the methods.

Apparatus

pH meter: A digital pH meter of Elico- make [Elico L 1610] together with a glass electrode assembly has been made use of in pH measurements.

Potentiometer: Equip-Tronics Eq-602 Digital potentiometer with inbuilt STD cell and Magnetic stirrer was utilized for potential measurements, a bright platinum electrode and a saturated calomel electrode have been used as indicator and reference electrodes respectively.

Reaction vessel fitted with four/ two holed rubber stopper : To carryout the titrations potentiometrically as well as to measure the redox potentials under inert atmosphere a Pyrex glass beaker of 150ml capacity [called the reaction vessel] fitted with four holed rubber stopper has been made use of. One of the holes serves to accommodate an inlet tube for passing purified nitrogen gas into the solution, the second and third holes accommodate the indicator electrode [platinum] and the reference electrode [calomel] respectively. The fourth one serves as an out let for nitrogen gas [in potential measurements] as well as to accommodate the nozzle of the burette for the addition of a titrant into the reaction vessel in the potentiometric

titrations. When the titrations employing redox indicators [visual end – point methods] are carried out under inert atmosphere, the reaction vessel is covered with only two holed rubber stopper. One of the holes accommodates the inlet tube for passing purified nitrogen gas into the solution and the other one serves as an outlet for passage of the gas and simultaneously it accommodates the nozzle of the burette for adding the titrant into the reaction vessel during the titration.

2.2. Selective determination of chromium(VI) with iron(II) in buffer-oxalate medium.

2.2.1. Potentiometric Method:

Preliminary investigations of the author indicated that the potentiometric determination of chromium(VI) using iron(II) as a reductant in buffer-oxalate medium is feasible provided the pH of the reaction medium and that of the oxalate ion concentrations are in the range of 4.00 – 5.20 and 0.04 – 0.10M respectively. Further, it is found that the titration has to be carried out under inert atmosphere. In view of these findings the author has recommended the following procedure for the selective determination of chromium(VI) with iron(II) in buffer – oxalate medium using the potentiometric technique.

Recommended Procedure for the potentiometric method:

To an aliquot (3-12 ml) of chromium(VI) solution (0.05N) taken in a 150 ml beaker fitted with a four holed rubber stopper (described above to maintain inert atmosphere), about 10 ml of 1M sodium acetate, 5ml of 1N sulphuric or hydrochloric acid, 15 ml of distilled water and 3ml of 1M potassium oxalate solution are added and the total volume diluted to about 50 ml. The pH of the solution is found to be about 5.0 and the overall concentration of oxalate ion is about 0.06M. Purified nitrogen gas is passed through the reaction mixture to expel any dissolved oxygen. The contents are now titrated against a standard solution of iron(II) (0.05M) potentiometrically under inert atmosphere [arrangements described above] in the usual way, while the solution is being stirred with the help of a magnetic stirrer. Stable potentials are recorded throughout the titration for the addition of each instalment of iron (II), except near the end-point at which it takes about 30-40 seconds. Maintenance of inert atmosphere helps us to record the stable potentials during the titration. The jump in potential at the equivalence point is found to be 65 - 75 mV for the addition of 0.05ml of 0.05M iron(II) solution. Some of the typical results obtained by the recommended procedure have been show in Table-2.1.

Table-2.1: Determination of Cr(VI) with Fe(II) in buffer-oxalate medium-Potentiometric Method.

S.No	Amount of chromium(VI) Found[*], mg		Pooled Standard Deviation (S_g)	$\dfrac{1.96 \times sg}{\sqrt{n}}$	95% Confidence Levels $\bar{x} \pm \dfrac{1.96 \times sg}{\sqrt{n}}$
	Reference Method [2 (p237)]	Author's Method			
1	3.029	3.017			3.007 to 3.027
1	3.901	3.916			3.906 to 3.926
2	4.928	4.912			4.902 to 4.922
3	6.066	6.086			6.076 to 6.096
4	7.097	7.079	0.013	0.010	7.069 to 7.089
5	8.235	8.251			8.241 to 8.261
6	9.268	9.284			9.274 to 9.294
7	10.39	10.37			10.36 to 10.38

*Average of six determinations.

2.2.2. Indicator Method:

Based on the preliminary studies, it has been ascertained that for a satisfactory and selective determination of chromium(VI) with iron(II) in buffer medium containing oxalate, employing some thiazine group of dyes as redox indicators, the pH and oxalate

ion concentrations must be in the range of 4.0 – 4.8 and 0.06 - 0.12M respectively and no inert atmosphere need be maintained during the titration. In view of these findings the following procedure has been recommended for the visual end-point/ indicator method.

Table –2. 2 : Determination of Cr(VI) with Fe(II) in buffer-oxalate medium-indicator method.

Name Of the indicator	Chromium(VI) found, mg.*		Pooled Standard deviation (Sg)	$\dfrac{1.96 \times sg}{\sqrt{n}}$	95% Confidence Levels $\overline{x} \pm \dfrac{1.96 \times sg}{\sqrt{n}}$
	Reference Method(mg) [2 (p237)]	Author's method(mg) $\overline{x}$			
Methylene Blue [260]	3.464 5.191 6.936 8.651 10.39	3.485 5.170 6.955 8.634 10.42	0.014	0.011	3.474 to 3.496 5.159 to 5.181 6.944 to 6.966 8.623 to 8.645 10.41 to 10.43
Toluidine Blue [264]	3.371 4.769 6.631 8.503 10.22	3.357 4.786 6.649 8.521 10.24	0.013	0.010	3.347 to 3.367 4.776 to 4.796 6.439 to 6.459 8.511 to 8.531 10.23 to 10.25
Azure-A [263]	3.551 5.617 7.208 8.829 10.13	3.568 5.595 7.224 8.807 10.16	0.012	0.010	3.558 to 3.578 5.585 to 5.605 7.214 to7.234 8.797 to 8.817 10.15 to 10.17
Azure-B [253]	3.901 5.461 7.263 9.029 10.29	3.920 5.483 7.245 9.042 10.27	0.014	0.011	3.909 to 3.931 5.472 to 5.494 7.234 to 7.256 9.031 to 9.053 10.26 to10.28

*Average of six determinations.

Recommended Procedure for the visual end-point/indicator method:

To an aliquot (3-12ml) of chromium(VI) solution (0.05M) taken in the reaction vessel, about 10ml of sodium acetate (1M), 8.0ml of hydrochloric/sulphuric acid (1N), about 15ml of distilled water followed by 4ml of potassium oxalate (1M) are added and the solution diluted to about 50ml. [The pH of the solution is now found to be about 4.4 and the overall oxalate ion concentration is about 0.08M]. After passing purified nitrogen gas through the reaction mixture for about 2minutes to expel any dissolved oxygen, 4-5drops of an indicator solution [[0.1% w/v aqueous solution of a thiazine dye mentioned above] are added. The reaction mixture is now titrated against a standard solution of iron(II) (0.05M) to the sharp colour transition of the indicator from blue to colourless [with a light green ting due to the presence of Cr(III) ions] and this is sharp and reversible. Some of the typical results obtained by the procedure were given above in Table 2.2. In both the methods, to avoid the any possible reduction of Cr(VI) by oxalate ion, the reaction medium is diluted by adding about 15ml of distilled water prior to the addition of oxalate.

2.3. Selective Determination of Iron(II) with Chromium(VI) in Buffer-Oxalate Medium.

The authors found that the above redox procedure can be reversed for the selective determination of iron(II) with dichromate . In this method, iron(II) solution taken into a buffer medium is titrated against chromium(VI) solution taken in a burette. Preliminary investigations revealed that iron(II) can be determined satisfactorily and selectively in presence of several other metal ions using dichromate or chromium(VI) as an oxidimetric titrant involving both potentiometric and visual end-point or indicator [thiazine dyes as indicators] methods provided the pH of the buffer and that of oxalate ion concentrations in the reaction medium are in the range of 1.5 -2.5 and 0.05 – .0.10M respectively. However, it has been noticed that inert atmosphere must be maintained in both the methods for precise detection of the end-point. In view of these findings the following procedure is recommended for the selective determination of iron(II) with chromium(VI) using potentiometric and indicator methods.

2.3.1. Recommended Procedure – Potentiometric Method :

To an aliquot (3-12ml) of iron (II) solution [0.05M] taken in a reaction vessel fitted with a four holed rubber stopper [described above to maintain inert atmosphere] , about 10ml of 1M sodium acetate [1M] , 8ml of H_2SO_4 or HCl solution [2N], 10 ml of distilled water and 4ml of potassium oxalate [1M] are added. The solution is diluted to about 50ml and stirred well [the pH of the solution is found to be about 1.5 and the overall oxalate ion concentration is about 0.08M]. Purified nitrogen gas is passed through the reaction mixture to expel any dissolved oxygen. The contents are now titrated against a standard solution of potassium dichromate or chromium(VI) (0.05N) potentiometrically under inert atmosphere while the reaction mixture is being stirred by a magnetic stirrer. Stable potentials are recorded immediately after the addition of each instalment of a chromium(VI) solution. The break in potential at the equivalence point is found to be about 65mV for the addition of 0.05 ml of 0.05N dichromate solution.   Inert atmosphere has been maintained during the titration to prevent aerial oxidation of iron(II) as well as to get stable potentials during the titration. Some of the typical results obtained by the method have been recorded in Table-2.3.

Table -2.3 : Selective determination of iron(II) with chromium(VI) in buffer-oxalate medium- potentiometric method.

S.No	Amount of Iron(II) Found[*], mg		Pooled Standard Deviation (S_g)	$\dfrac{1.96 \times sg}{\sqrt{n}}$	95% Confidence Levels $\bar{x} \pm \dfrac{1.96 \times sg}{\sqrt{n}}$
	Reference Method [1 (p375)]	Author's Method			
1	9.23	9.26			9.25 to 9.27
2	10.62	10.58			10.57 to 10.59
3	12.91	12.94			12.93 to 12.95
4	16.21	16.17			16.16 to 16.18
5	20. 31	20.26	0.02	0.01(6)#	20.25 to 20.27
6	25. 81	25.84			25.83 to 25.85
7	30. 31	30.36			30.35 to 30.37
8	32.20	32.14			32.13 to 32.15

*Average of six determinations.   # the digit in the third decimal is not significant, hence it is not considered in computing the confidence limits

2.3.2.Recommended procedure - Indicator Method:

The conditions for the indicator or visual end-point method are almost similar to those in the potentiometric method described above, excepting that a few drops of a redox indicator [a thiazine dye] are added to detect the end-point of the titration. The procedure in brief is as follows :

To an aliquot (3-12ml) of iron (II) solution [0.05M] taken is a 150ml beaker [reaction vessel], all the reagents are added in the same quantity and order as in the case of potentiometric method described above and the solution diluted to about 50ml [pH of the solution is about 1.5 and the overall concentration of oxalate ion is 0.08M] . After passing purified nitrogen gas through the reaction mixture for about two minutes to expel any dissolved oxygen, 4-5 drops of (0.1% W/V) of a thiazine group of dye solution are added. The reaction vessel is now covered with a two holed rubber stopper [described above and it is an arrangement for the circulation of inert gas] and the contents are titrated against a standard solution of dichromate   or chromium(VI) (0.05N), while the solution is being stirred with the help of a magnetic stirrer, to the sharp colour transition of the indicator . Purified nitrogen gas [inert gas] is circulated in the solution throughout the titration to prevent the aerial oxidation of iron(II). Only three thiazine dyes, mentioned in table 2.4, are found suitable as redox indicators in the present procedure. The colour transition of the indicators at the end-point is from colourless to blue and it is sharp and reversible. Some of the typical results obtained by the above procedure are given in Table 2.4.

Table –2.4 : Determination of Fe(II) with Cr(VI) in buffer-oxalate medium-indicator method.

Name Of the indicator	Iron(II) found, mg.*		Pooled Standard deviation (Sg)	$\dfrac{1.96 \times sg}{\sqrt{n}}$	95% Confidence Levels $\overline{x} \pm \dfrac{1.96 \times sg}{\sqrt{n}}$
	Reference Method(mg) [1 (p375)]	Author's method(mg) $\overline{x}$			
Toluidine Blue [268]	10.09 14.82 20.15 25.54 30.83	10.14 14.75 20.07 25.61 30.89	0.03	0.02(4)#	10.12 to 10.16 14.73 to 14.77 20.05 to 20.09 25.59 to 25.63 30.87 to 30.91
Azure-A [273]	10.63 15.96 20.70 26.07 31.58	10.58 16.03 20.62 26.14 31.51	0.04	0.03(2)#	10.55 to 10.61 16.00 to 16.06 20.59 to 20.65 26.11 to 26.17 31.48 to 31.54
Azure-B [260]	11.49 17.08 23.20 28.51 33.34	11.54 17.15 23.12 28.44 33.41	0.03	0.02(4)#	11.52 to 11.56 17.13 to 17.17 23.10 to 23.14 28.42 to 28.46 33.39 to 33.43

*Average of six determinations. [verified]   # the last digit is not significant, hence it is not considered in computing the confidence limits

2.4 . Selective Determination of Chromium(VI) in presence of molybdenum(VI), uranium(VI) and vanadium(V) and the quantitative analysis of metal ions present in the synthetic binary metal ion mixtures consisting of (1). Cr(VI) - Mo(VI) ;(2). Cr(VI) -U(VI); and (3). Cr(VI)- V(V).

The above mentioned three binary metal ions mixtures have been prepared by mixing their respective solutions of 0.1N strength in various propositions in different 50ml standard flasks and diluted to volume. In preparing these solutions care has been taken to see such that the total concentration of the two metal ions combined together does not exceed 0.05N in 50ml.

The authors found that chromium(VI) can be selectively determined by iron(II) in presence of other similar metal ions such as molybdenum(VI), uranium(VI) and vanadium(V) by titrating an aliquot of a metal ion mixture against iron(II) in a buffer - oxalate medium described in procedure in 2.2.2 . The total content of both the metal ions present in a mixture can be found by titrating a similar aliquot of the metal ion mixture against iron(II) in 9-10M phosphoric acid medium using resorufin as a redox indicator[15]. From the two titrations, the quantity of each metal ion present in a binary metal ion mixture can be found. Based on these facts the following procedure has

been recommended for the quantitative analysis of metal ion mixtures.

2.4.1. Recommended Procedure for the quantitative analysis of binary metal ion mixtures:

A 10ml aliquot of a metal ion mixture is taken into a buffer medium of pH ~ 4.4 containing an oxalate ion concentration of about 0.08M [in 50ml], then it is titrated against a standard solution of 0.05M iron(II) using a thiazine group of dye as a redox indicator as described in procedure 2.2.2. The volume of iron(II) consumed to get the end-point of the titration is noted as titre-1[or T_1]. In the similar way another 10ml aliquot of the metal ion mixture is titrated against same iron(II) solution in 9-10M phosphoric acid medium using resorufin as a redox indicator to the sharp colour transition of the indicator from red to blue – green as described in the method [15]. The volume of iron(II) consumed is noted as titre-2 [or T_2] . From the two titre values, the amount of each metal ion present in a mixture can be computed as elucidated below.

In the present procedure, the metal ion mixtures are titrated against iron(II) in two different media : (1) in buffer-oxalate medium and (2) in high phosphoric acid medium. In the former medium, iron(II) reduces Cr(VI) to Cr(III) and V(V) to V(VI) while Mo(VI) and

24

U(VI) remains unaffected; whereas in the latter medium, iron(II) reduces Cr(VI) to Cr(III) , V(V) to V(III) , Mo(VI) to Mo(V) and U(VI) to U(IV).

Based on these considerations, titre-1 or T_1 in the case of mixture -1[Cr(VI) - Mo(VI)] and mixture-2 [Cr(VI) - U(VI)] corresponds to the amount of chromium(VI) present in the mixture, where as T_2 corresponds to the sum total Cr(VI) and Mo(VI) in the case of mixture-1 and Cr(VI) and U(VI) in mixture-2. Hence the difference between T_2 and T_1 corresponds to the amount of Mo(VI) in the case of mixture-1 and uranium(VI) in the case of mixture-2.

In the case of mixture-3 [Cr(VI)- V(V)] , however, both T_1 and T_2 correspond to the sum total of Cr(VI) and V(V) present in the mixture. But there is a difference, because, T_1 relates to the reduction of Cr(VI) to Cr(III) and V(V) to V(IV) by iron(II) while T_2 corresponds to the reduction of Cr(VI) to Cr(III) and V(V)] to V(III) [but not to V(IV) as in T_1]. Based on these findings it can be concluded that $T_2 - 2 \times [T_2 - T_1]$ corresponds to the amount of Cr(VI) present in the mixture, while $2 \times [T_2 - T_1]$ corresponds to the amount of V(V)] present in the mixture. Thus, the amounts of metal

ions present in the three mixtures can be analysed. Some of the typical results obtained by the recommend procedure for the content of each metal ion present in a total volume of 50ml have been furnished in table- 2. 5.

2.5. Quantitative analysis of iron(II) and iron(III) ions present in aqueous solutions.

In the present communication, the authors have proposed new methods for the selective determination of iron(II) with dichromate in buffer medium and in presence of oxalate in parts 2.3.1 and 2.3.2, It is known that iron(II) solutions are always found to be associated with trace quantities of iron(III) ions. Therefore, the determination of iron(III) content present in iron(II) solutions is of considerable significance in analytical chemistry. However, it has been found that in combination with the well known stannous chloride method [1 (p415)] reported in literature for the determination of iron(III), the present method described above for the determination of iron(II) , enables us to develop a new method for the quantitative analysis of iron(II) and iron(III) ions present in aqueous solutions.

Table-2.5:Quantitative Analysis of :(1).Cr(VI) -Mo(VI) ; (2) Cr(VI) -U(VI) and (3) Cr(VI)-V(V) Metal Ion Mixtures with Iron(II).

(A). Chromium(VI) and Molybdenum(VI) mixture [13&15]					
Amount of chromium(VI) found in 50 ml, mg			Amount of molybdenum(VI) found in 50 ml, mg		
Reference method [13,15,17 &18]	Present method*	R.S.D % @	Reference method [13&15]	Present method*	R.S.D % @
17.32	17.41	0.41	143.4	143.1	0.20
20.77	20.68	0.33	124.7	125.1	0.26
24.27	24.35	0.28	105.5	105.1	0.35
27.73	27.64	0.22	86.20	86.60	0.41
(B). Chromium(VI) and uranium(VI) mixture [13 &18]					
Amount of chromium(VI) found in 50 ml, mg			Amount of uranium(VI) found in 50 ml, mg.		
19.08	18.98	0.42	166.8	167.2	0.18
22.53	22.62	0.39	142.6	142.2	0.25
25.99	25.91	0.30	118.8	119.3	0.32
29.58	29.65	0.21	95.21	94.91	0.43
(C). Chromium(VI) and vanadium(V) mixture [13 & 17]					
Amount of chromium(VI) found in 50 ml, mg			Amount of vanadium(V) found in 50 ml, mg.		
15.58	15.65	0.44	22.95	22.99	0.16
17.28	17.30	0.32	20.40	20.45	0.22
19.04	18.98	0.26	17.85	17.79	0.31
20.78	20.73	0.14	15.30	15.23	0.45

*Average of six determinations.   @ Relative Standard Deviation Percent

2.5.1. Recommended Procedure:

Metal ion mixtures having different concentrations of iron(II) and iron(III) have been prepared by mixing 0.1N solutions of the two metal ions in different proportions in different100ml standard flasks such that their total strength of the two metal ions does not exceed 0.05N in a total volume of 100ml and the

solution diluted to volume. A 10 ml aliquot of a metal ion mixture is taken into a buffer-oxalate medium of pH~ 1.5 containing about 0.08M oxalate and titrated against a standard solution of chromium(VI) [0.05M] using a thiazine dye as a redox indicator as per the procedure 2.3.2. The volume of Cr(VI) consumed is noted as titre-1 or T_1.

Another 10ml aliquot is transferred into a 150 ml beaker, treated with about 20 ml (1+1) HCl solution and it is heated just to boiling. To the hot solution a 6% solution of stannous chloride solution is added drop-wise [to reduce iron (III) to iron (II)] until the solution becomes completely colourless. The solution is rapidly cooled under tap water and about 5 ml of 5% solution of mercuric chloride is added [to remove the excess stannous chloride] [1 (p415)] . To the solution, about 5 ml of 10N sulphuric acid, 5 ml of syrupy phosphoric acid are added and the solution diluted to about 50 ml. The contents are now titrated against a standard solution of chromium(VI) (0.05N) as described in literature using diphenylamine as an indicator [1 (p415)]. The volume of dichromate consumed in noted as titre-II or $[T_2]$.

Obviously in this procedure, T_1 corresponds to the amount of iron(II), while T_2 corresponds to the sum total of iron(II) and iron(III) present in the mixture. Therefore, the difference between T_2 and T_1 corresponds to the amount of iron(III) present in the mixture. Thus, the amount of iron(II) and iron(III) present in a mixture can be computed. Some of the representative results obtained by the above method have been shown in table-2.6 and compared with the standard methods of analysis given in the references [1 (p375) ,1 (p415)].

Table – 2. 6 : Quantitative Analysis of Iron(II) and Iron(III) present in a mixture.

Amount of iron(II) found in 100ml*, mg.			Amount of iron(III) found in 100ml*, mg.		
Reference method [1 (p375)]	Present method	R.S.D % @	Reference method [1 (p415)]	Present method	R.S.D % @
111.70	112.25	0.45	167.55	167.21	0.20
139.62	139.06	0.40	139.62	140.03	0.23
167.68	168.22	0.32	111.70	111.36	0.31
195.47	194.88	0.30	83.71	84.10	0.36
223.51	224.07	0.19	55.85	55.57	0.42

*Average of six determinations.   @ Relative Standard Deviation Percent

2.6 . Determination of iron content present in an iron ore :

The new method now proposed in the present communication for the Determination of iron(II) together with the stannous chloride method stated above , has been extended for the estimate of iron content present in an iron ore. The main steps involved in the method are : (1) to dissolve the ore sample in dilute hydrochloric acid (2) to reduce all iron(III) to iron(II) by stannous chloride method (3) to neutralise the ore solution thus obtained to pH~ 1.0 and then diluting the solution to 100 in a standard flask and (4) to titrate an aliquot of the solution as per the present procedure[2.3.2] and another same aliquot as per the standard procedure against a standard solution of chromium(VI) and to compare the iron contents obtained by the two methods.

2.5.2.   Recommended   procedure   for   the determination of iron content present in an iron ore:

About 2 gm of accurately weighed iron ore sample is taken in a 150 ml beaker and about 50 ml of (1+1) HCl are added [20 (p478)] . The solution is stirred for about 5 min and then it is heated gently to half of its original volume. The solution is cooled to room temperature and filtered using Whatman No. 41 filter paper. The precipitate is washed with about 10 ml of hot HCl [1+1], followed by 10 ml of hot water. The solution is heated to boiling and to the hot solution a 6% (w/v) solution of stannous chloride is added drop-wise until the solution becomes completely colourless [this confirms all Fe(III) is converted to Fe(II)] [20 (p478)]. The solution is cooled to room temperature; then about 10 ml of mercuric chloride solution [5%w/v] is added to remove excess Sn(II); the white precipitate of mercury(I) chloride is removed by filtration thorough Whatman No.41filter paper and the precipitate washed with 10ml hot water twice. The filtrate and washings are neutralised by the drop-wise addition of 2M NaOH solution until the pH of the solution is ~ 1-1.5 and it is collected into a 100ml standard flask and diluted to volume.

The solution is used as a stock solution for the analysis of iron content. A 5.0 ml aliquot of the solution is taken into a buffer medium of pH~ 1.5 containing about 0.08M potassium oxalate and titrated against a standard solution of chromium(VI) [0.1N] employing a thiazine group of dye as a redox indicator as described in procedure 2.3.2. Another similar aliquot [5.0ml] is taken into a dilute sulphuric acid [1-2 N] and phosphoric acid [0.5-1.0M] medium and then titrated against a standard solution of dichromate or chromium(VI) [0.1N] using barium salt of diphenyl amine sulfonate as a redox indicator[standard method] as described in literature [20 (p451)   ].From the volume of chromium(VI) consumed in each method, the percent iron content present in the ore sample were calculated and the results presented in table 2.7.

26

Table -2.7 : Determination of iron content present in an iron ore

Iron content found,%	Iron content found, % [by the present method using indicators]		
Reference Method [20 (p478)]	Toluidine Blue	Azure- A	Azure- B
44.9	45.12 ± 0.15*	44.92 ± 0.18*	45.25 ± 0.12*

* Standard Deviation

3. Results and Discussion

In the experimental part described above, evidently, tables 2.1and 2.2 relates to the results of the determination of chromium(VI) [in the range 3-10mg] with iron(II), while tables 2.3 and 2 4 pertains to those of iron(II) [in the range 10-30mg] with chromium(VI) in buffer medium and in presence of oxalate involving both potentiometric and visual end-point [or indicator] techniques. The accuracy or the two potentiometric methods [determination of chromium(VI) and iron(II)] is found to be ± 0.4%, while that of the two indicator methods it is ± 0.6%. The precision of all these methods has been determined by computing the pooled standard deviation and 95% confidence limits and the values were shown in the tables 2.1 to 2.4.

Out of several thiazine dyes tried, only four in the determination of chromium(VI) and three in the determination iron(II) are found to function satisfactorily as redox indicators. In these methods, when chromium(VI) is titrated against iron(II) (which is taken in the burette) the dyes are reduced by iron(II) to their colourless leuco-bases, in a two electron reduction step [21&22] at the end-point . However, when iron(II) is titrated against chromium(VI) (which is taken in the burette), the dyes are first of all reduced to their colourless leuco-bases by iron(II) present in the medium but, at the end-point, the colourless leuco bases are oxidised to their corresponding original blue form by chromium(VI) most probably in a two electron oxidation process. The colour transitions of the indicators in both the methods are sharp and reversible.

In the present paper, the table 2.5 presents the results relating to the quantitative analysis of three synthetic binary metal ion mixtures consisting of (1). Cr(VI) - Mo(VI) ;(2). Cr(VI) -U(VI); and (3). Cr(VI)- (V) ; while table 2.6 furnishes the results pertaining to those of iron(III)-iron(II) mixture. The accuracy of all these procedures is found to be ± 0.6%. The precision of these methods has been found by computing the relative standard deviation percent and the values have been incorporated in the tables 2. 5 and 2.6. The results pertaining to the analysis iron ore for iron content have been placed in table 2.7 and found them to be in good agreement with the standard methods of analysis.

Most of the chemists aware that iron(II) is only a mild reducing agent under normal experimental conditions or in dilute acid medium , its standard redox potential [E^o] being reported to be + 0.68V in 1M H_2SO_4 medium [1(p364)]. However, it functions as a powerful reducing agent in the presence of certain complexing substances/ions such as phosphoric acid, pyrophosphate, oxalate, fluoride, triethanolamine etc. Thus, iron(II) in presence of these complexing ions finds numerous redox analytical applications and it is beyond the scope of the paper to summarise them. These ions bind iron(III) in the form of a complex, causing considerable decrease in the redox potential of iron(III)/ iron(II) couple [or iron system], there by enhance the reducing ability of iron(II). However, the use of iron(II) as a reducing agent in buffer medium [pH range 1-5] and in presence of oxalate was introduced from our laboratories in late seventies [23]. Subsequently, it has been utilised for the determination of several inorganic & organic substances, quinones, dyes etc., [22 , 24-32] .

Raju and co-workers measured the formal redox potentials of iron system [22] and found that at a fixed pH of ~ 4.0 the potential of iron system decreases from about 475mV to 80 mV with increase in oxalate ion concentration from 0.00M to 0.12M. They further reported that at a fixed oxalate ion concentration of 0.06M, the potential of iron system decreases from 375mV to 85mV with increase in pH form about 0.85 to 5.3. These potentials data thus manifest that the reducing ability of iron(II) increases with increase in pH as well as with increase in oxalate ion concentration. With the help of a computer program these authors identified [32] that iron(III) is bound by oxalate ion in the form of trisoxalatoferrate(III) in the pH region 2 to 5.

The reagent, namely iron(II) as a reducing agent in buffer medium and in presence of oxalate , offers several advantages over the conventional/ powerful reductants such as titanium(III), tin(II), chromium(II) etc. For example, unlike the conventional reductants, which are air sensitive, iron(II) solutions need not be stored in a special apparatus under inert atmosphere to prevent air oxidation. Several metal ions like Mo(VI), U(VI), V(IV), Sb(V), As(V) etc. which interfere in the reductions involving the conventional reductants do not interfere in the case of the present reagent [iron(II) in buffer oxalate medium]. Titrations involving the conventional reductants are often carried at elevated temperatures, but in the case of the present reductant, the reaction goes to completion at room temperature. Further, buffer solutions of desired pH

required for the medium can be readily obtained by mixing suitable volumes of a mineral acid solution [1N HCl or H_2SO_4] with those of sodium acetate[1M] as described in literature [14].

It has already been stated earlier that the potentionmetric determination of chromium(VI) with iron(II) [2.2.1] is found feasible provided the pH of the reaction medium and oxalate ion concentrations are in the range of 4.0-5.2 and 0.04-0.10M respectively.

If the concentration of oxalate ion exceeds 0.10M in the pH range 4.0-5.2 and 0.04M in the pH range 1.0-3.5, potential jump corresponding to the lower titre values for chromium(VI) taken are recorded, indicating some of the Cr(VI) is consumed probably by being reduced to Cr(III). The authors contemplate that, in buffer- oxalate medium, lower pH values of the buffer and higher oxalate ion concentrations favours the reduction of Cr(VI) to Cr(III) by oxalate, hence causing to record lower values for Cr(VI) in the potentiometric determination. Our assumption is strengthened by Njoku and Nweze's [16] findings that increased concentration of oxalic acid increases the reduction of chromium(VI) to chromium(III) more effectively at lower pH values in the soil minerals. Our present redox process observed between chromium(VI) and oxalate ion is of considerable significance and useful one in the context of mitigating pollution due to chromium(VI) in the ground water. This is because, contamination of chromium(VI) which is more toxic than chromium(III) and leached into ground water from various industries like corrosion inhibition and electroplating, is often controlled by its reduction to

chromium(III) using a variety of organic compounds including oxalic acid [33].

Further, It is interesting to note that, in the buffer medium of pH 4.0- 5.0 , the lower values for chromium have been recorded when the concentration of oxalate ion in the reaction medium exceeds 0.12M in the indicator method [2.2.2] , but such lower values are recorded even at 0.10M in the case of potentiometric method [2.2.1] . The most probable reason for this is that the time in which oxalate ion remains in contact with the chromium(VI) in the potentiometric method is more than that in the case of indicator method. In general, the latter method [indicator method] can be completed within 10-15 minutes while in the case of former method [potentiometric] it takes nearly 40-50 minutes for its completion. Because of this reason, the reduction of Cr(VI) by oxalate ion is expected to take place even at lower concentrations of oxalate ion than in the case of indicator method.

In order to explain the conditions needed in the selective determination of chromium(VI) with iron(II) in buffer [pH 4.0-5.2] oxalate [0.04- 0.10M] medium, the authors have measured the formal redox potentials of Cr(VI)/Cr(III) couple [chromium or oxidant system] and those of iron(III)/iron(II) couple [iron or reductant system] in pH range 4.0-5.2, keeping the concentration of oxalate ion fixed at 0.06M adopting the method of Gopal Rao and Dikshitulu[17]. The potentials of both the couples have been recorded in table 3.1 and depicted graphically in figure- 3.3 for the sake of comparison. From these potentials data, it is interesting to note that the formal potentials of chromium system increase, while those of iron system decrease with increase in pH in presence of 0.06M potassium oxalate.

Table – 3.1 : Formal redox potentials of chromium and iron systems in a buffer medium of varying pH [range 4.00 – 5.22] and at a fixed oxalate ion concentration of 0.06M.

Temp = 28ºC ± 0.5ºC ; Concentration of Cr(VI) = Cr(III) = 0.005N.

pH of the buffer medium	Formal Redox Potentials, mV [N.H.E.] ± 5 mV .		
	Cr(VI)/Cr(III) Couple [chromium system]	Iron(III)/Iron(II) Couple [iron system]	Difference between chromium and iron systems.
4.00	414	111	303
4.30	419	106	313
4.46	422	101	321
4.63	426	98	328
4.78	433	94	339
5.00	436	88	348
5.22	442	86	356

N.H.E. = Normal Hydrogen Electrode

However, from these potentials data it may be seen that the difference in potential is found to be more than 300mV in the range 4.0-5.2 in presence of 0.06M sodium/potassium oxalate. This difference in potential is more than sufficient to bring rapid reduction of Cr(VI) by Fe(II). Thus, these potentials data neatly explain the conditions needed in the titration.
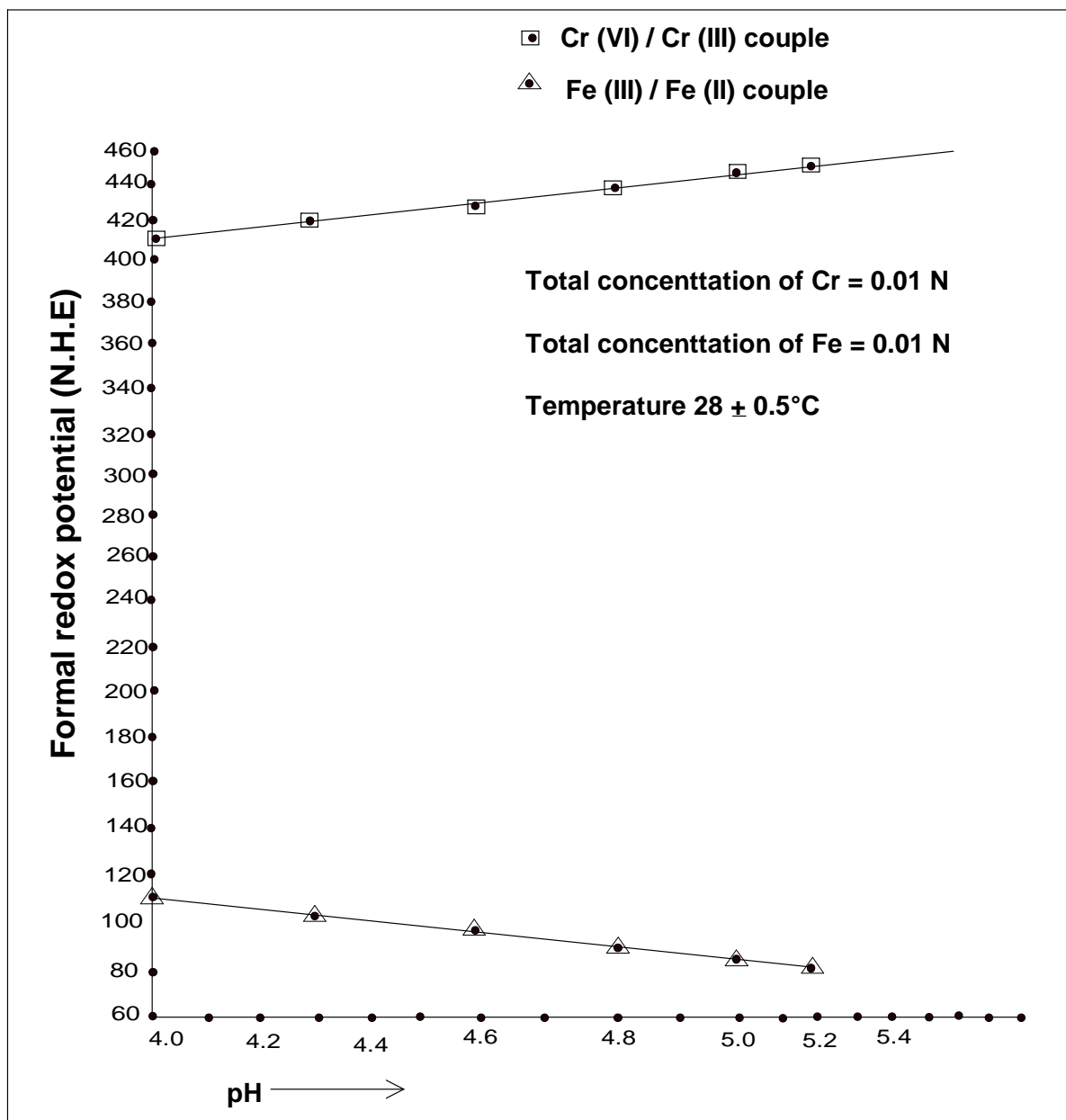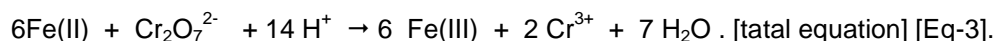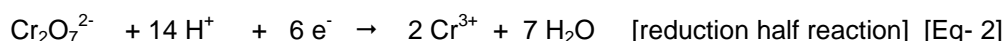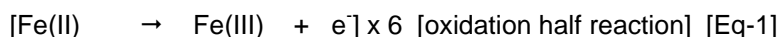

Fig. 3.1 Formal Redox potentials of Cr (VI) / Cr (III) and Fe (III) / Fe (II) couples in Buffer media of varying pH at fixed oxalate ion concentration of 0.06M.

The author could not measure formal potentials of chromium system below pH 4.0 because, it was observed in the potentiometric method [2.2.1], oxalate ion [above 0.04M] slowly reduces the chromium(VI) in the lower pH range of 1.0- .3.5. The authors have also measured the formal potentials of both chromium and iron systems at different oxalate ion concentrations in the range 0.03- 0.10M, keeping the pH of the buffer medium fixed at about 4.5 and found that the potentials both chromium and iron systems decrease with increase in the concentration of oxalate: from about 450 to 400 mV in the case of former and from 125 to 85 mV in the case of latter. The decrease in potential is most likely due to the increase in complex formation between oxalate and chromium(VI) as well as between oxalate and iron(III) with increase in oxalate ion concentration.

It is also interesting to note while the determination of chromium(VI) by iron(II), in presence of oxalate, is found feasible in the pH range 4.0-5.2, the reverse process which involves the determination of iron(II) with chromium(VI) is found satisfactory in pH range 1.5- 2.5. The difference in formal potentials between chromium and iron systems under the experimental conditions may be sufficiently high [300 mV] for the reaction to go to completion. But, this could not be verified experimentally based on the formal potentials data as above, since, the potentials of chromium system could not be determined accurately in buffer medium of low pH and in presence of oxalate. This is because, as per the standard procedure [17] adopted for measurements of formal potentials, in this case,

the chromium(VI) solution [0.05N] must be taken into a buffer medium of low pH [1-3] containing oxalate [0.05-1.0M]. It already been stated above that under these conditions [low pH/higher oxalate ion/Cr(VI) concentrations], chromium(VI) will be slowly reduced by oxalate ion, thus impairing the potential measurements.

However, a satisfactory explanation to the fact that the determination of iron(II) by chromium(VI) is feasible in a buffer medium of low pH may be offered by considering the stoichiometric chemical equations 1 to 3 given below, representing the redox reactions which take place in the method .

$$[Fe(II) \quad \rightarrow \quad Fe(III) \quad + \quad e^-] \times 6 \quad [\text{oxidation half reaction}] \quad [\text{Eq-1}]$$

$$Cr_2O_7^{2-} \quad + 14\ H^+ \quad + \ 6\ e^- \ \rightarrow \ 2\ Cr^{3+} + \ 7\ H_2O \quad [\text{reduction half reaction}] \ [\text{Eq- 2}]$$

$$6Fe(II) + \ Cr_2O_7^{2-} \ + 14\ H^+ \rightarrow 6\ Fe(III) + \ 2\ Cr^{3+} + \ 7\ H_2O \ . \ [\text{tatal equation}] \ [\text{Eq-3}].$$

It may be seen from the reduction half reaction [Eq-2] and total equation [Eq- 3] that the reaction between Fe(II) and Cr(VI) is favoured in a buffer medium of low pH or high H^+ ion concentration. Moreover, in this method iron(II) solution is taken into a buffer medium and chromium(VI) solution into the burette and the former is titrated against the latter. Obviously under these conditions, since dichromate solution is added from the burette, its concentration in the reaction medium would be too low under these conditions and to make the reaction proceed in the forward direction, high acidity [high H^+ ion] or low pH is required as per these two equations. Thus the titration of iron(II) against dichromate or Cr(VI) is favoured in the low pH region of the buffer.

In order to explain the suitability of redox indicators employed in the two indicator methods : determination of chromium(VI) with iron(II) and iron(II) with chromium(VI) ; the authors have measured the transition potentials of the thiazine dyes employed as redox indicators in these determinations, adopting the method of Belcher et.al [34]. The values have been shown in parenthesis under the name of each indicator in tables-2.2 and 2.4. The transition potentials of the four thiazine dyes employed in former method [table 2.2] are found to be in the range of 253 -264 mV. The formal redox potentials of chromium system and iron system under the conditions [pH ~ 5.0 and 0.06M oxalate] at which the titration is carried out are found to be about 436 mV and 88 mV respectively. The transition potentials recorded [253- 264mV] are found to be in the useful intermediate range between the formal potentials of the chromium [436 mV] and iron [88 mV] systems observed under the optimum/actual titration conditions. Thus the transition potentials data neatly explain the suitability of the four

thiazine dyes as redox indicators in the determination of chromium(VI) with iron(II). The transition potentials of three thiazine dyes used as redox indicators in the latter method [determination of iron(II) with chromium(VI)] are found to be in the range of 260 - 273mV . But we could not explain the suitability of the indicators as above, because the titration of Fe(II) against Cr(VI) is favoured under low pH conditions and as per the reasons stated earlier, the formal potentials of the chromium system could not be measured accurately in a buffer medium of low pH and in presence of oxalate.

Conclusions

Iron(II) in buffer medium and in presence of oxalate has been found to be an advantageous electron transfer reagent or reducing agent for the selective determination of chromium(VI). Thus, chromium(VI) [3-11mg] has been selectively determined in presence of several other metal ions like Mo(VI), U(VI), V(IV), Sb(V), As(V), etc. by taking chromium(VI) solution in a buffer medium of pH 4.0-5.2 containing 0.04- 0.10M potassium oxalate and titrating it against a standard solution of iron(II). By reversing the above redox process, iron(II) [9-30mg] has also been selectively determined in presence of the above mentioned metal ions by taking iron(II) solution into a buffer medium of pH 1.5-2.5 containing 0.04- 0.10M oxalate and titrating it against a standard solution of chromium(VI). In these methods, the end-point has been detected either potentiometrically or using a thiazine dye as redox indicator. In combination with one of our earlier methods developed using iron(II) as a reducing agent in phosphoric acid medium, the method now proposed for the determination of chromium(VI) has been successfully employed for the quantitative analysis of

30

some binary metal ion mixtures like Cr(VI) - Mo(VI) ;(2). Cr(VI) -U(VI); and (3). Cr(VI)- V(V). Similarly in combination with the stannous chloride method available in literature for the determination of iron(III) , the method now developed for the determination of iron(II) has been applied for the quantitative analysis of iron(III) and iron(II) present in a synthetic mixture and for analysis of an iron ore for iron content. From the study of the above redox procedures it has been inferred that in buffer –oxalate medium, low pH [1-3] and higher oxalate ion concentrations [above 0.04M] favours the reduction of chromium(VI) to chromium(III) . This study is very important and significant in mitigating the ground water pollution due to chromium(VI) which is more toxic than chromium(III). This is because chromium(VI) solutions are generally leached into ground water from industries like corrosion inhibition and electroplating and the pollution due to them are often controlled by the reduction of chromium(VI) to chromium(III) using a variety of organic compounds including oxalic acid.

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