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# A NEW ELECTRON TRANSFER REAGENT: IRON(II) IN ACETIC ACID MEDIUM AND IN PRESENCE OF PYROPHOSPHATE - DETERMINATION OF CHROMIUM(VI) AND THE SPECIATION OF IRON(III) – PYROPHOSPHATE IN THE MEDIUM THROUGH A COMPUTER PROGRAM

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## ABSTRACT

*Iron(II) in acetic acid medium and in presence of pyrophosphate is proposed as a new electron transfer reagent or reducing agent for the selective determination of chromium(VI) in presence of several other metal ions . The method consists in taking the chromium(VI) solution in about 1M acetic acid and 0.08M pyrophosphate medium and then titrating it against a standard solution of iron(II) either potentiometrically or using a thiazine dye as a redox indicator. The new method now developed is simple, accurate, and it has been extended to the estimation of chromium content present in metal ion mixtures as well in a steel tool sample. The formal redox potentials of chromium(VI)/ chromium(III) couple at different pyrophosphate and acetic acid concentrations have been measured. By comparing these potentials with those of iron(III)/ iron(II) couple available in literature, a possible explanation to the observed redox reaction has been offered. It is found that pyrophosphate binds iron(III) in the form of a complex causing to decrease the redox potential of iron system and thus enhances the reducing ability of iron(II)]. Therefore, the nature of the coordination species expected to be formed between iron(III) and pyrophosphate has been established using Miniquad-75 computer program.*

**Key Words** : Iron(II) reductant, Acetic acid, Pyrophosphate, Chromium(VI) determination, Miniquad-75 computer program.

## 1. Introduction

Chromium is one of the most useful transition metals. Its characteristics property of hardness and resistance to corrosion renders the metal to be employed in the preparation of hard and corrosion resistance and other alloys of steel which are used in the manufacture of heat resistance coils, surgical instruments, high speed tools etc. Further, it forms several stable chemical compounds (mostly with +3 and +6 oxidation stats) which find various applications in industry and in volumetric analysis. Potassium dichromate, a well known chromium(VI) compound serves as a primary standard reagent and as a powerful oxidizing agent, the standard redox potential of chromium (VI)/ chromium (III) couple being reported to be as high as 1.36V at $25^0$C [1]. Hence, chromium(VI) solutions find their usefulness in the determination of copious inorganic and organic compounds [1-15] either directly or indirectly using the solution as an oxidimetric titrant. Various redox indicators have been employed in the dichromate titrimetry [1-5,7, 13-16 ]. It is beyond the scope of the paper to describe these methods in brief, however, the references 1 to 16 cited in the paper throw light on these two aspects.

Though dichromate solutions are thus useful in innumerable determinations, surprisingly, only a handful of methods have so far been reported for the determination of dichromate. These methods utilize the reductants like iron(II) [1,2,13] , arsenic (III), iodide, ,tin(II) & vanadium(III) [17], titanium(III) [17,15], , uranium(IV) [2,17], hexacyanoferrate(II) , hydroquinone & molybdenum(V) [2], ascorbic acid (18) etc.

These methods are not free from drawbacks. For example, in the method using iron(II) as a reductant, either in sulphuric acid [1,2] or in phosphoric acid medium [13], several other metal ions interfere. Further, the high phosphoric acid required in the method makes the medium viscous and the method expensive. The procedure involving arsenic(III) as a reductant is an indirect one and needs the use of an expensive catalyst. The iodometric method is expensive, further, one has to keep the solution in darkness for about 10 minutes for completion of the reaction and the concentration of acid must be carefully controlled to prevent the formation of air sensitive hydroiodic acid. The reagents like tin(II), titanium(III), ascorbic acid are highly sensitive to atmospheric oxidation and hence they must be stored in a special apparatus or a stabilizer must be added (in the case of ascorbic acid) to the solutions to prevent aerial oxidation or decomposition. The preparation of reductant solutions such as vanadium(II), uranium(IV) and molybdenum(V) employed for the determination of chromium(VI) by means of the metal reductants is a tedious task. In the method using hexacyanoferrate (II) as a reductant the prussian blue colour which is likely to be formed by the combination of ferrate(II) & ferrate(III) in the reaction medium renders the detection of the end- point difficult.

Recent procedures reported in literature have been found to be mainly based on the expensive state of the art technology such as flow injection method [19], catalytic adsorptive stripping determination technique [20], or spectrophotometric determination methods [21-23] etc. Most of these methods [19,20] require highly sophisticated and expensive instrumentation while some of them [21-23] are tedious,time consuming and useful to determine only the micro or nano gram quantities of chromium.

The present paper describes a reductimetric titration method for determination of chromium(VI) with iron(II) in which the former is taken in a medium consisting of about 1M acetic acid and 0.08M pyrophosphate and titrated against the latter, detecting the end point either potentiometrically or using a thiazine group of dye as redox indictor. The new procedure now developed obviates all the disadvantages of the earlier methods. Further, several other metal ions [ Sb(V), As(V), Mo(VI), U(VI) etc.] which interfere in the earlier methods cited above, do not interfere in the present procedure and all the chemicals needed in the preparation of the reagent are inexpensive and readily available in a high state of purity. In combination with one of our earlier methods reported in phosphoric acid medium [24] , the new method now developed enables us to quantitatively analyze the metal ions present in some metal ion mixtures such as Cr(VI)-Mo(VI) ; Cr(VI)-U(VI) ; Cr(VI) – V(V) etc., and for the analysis of a steel tool sample for chromium and vanadium contents. Since it is expected and known that pyrophosphate binds iron(III) more strongly than iron(II) in the form of a complex causing to decrease the redox potential of iron system [thus enhance the reducing ability of iron(II) ], the authors have established the nature of the species expected to be formed between iron(III) and pyrophosphate through a Miniquad- 75 computer program.

## 2. Experimental

### 2.1 . *Preparation of Solutions :*

Iron(II) Solution: An approximately 0.1M solution of iron(II) [from an AR grade ammonium iron(II) sulfate hexahydrate ] was prepared in 0.2N sulphuric acid medium and the solution was standardized by titrating against a standard solution of dichromate [1] . From this solution a 0.05M and a 0.025M solutions of iron(II) were prepared by suitable dilution.

Chromium(VI) Solution : Stock solution of [0.05N or 0.0083M solution] of potassium dichromate has been prepared by dissolving an exactly required amount of AR grade salt in one liter of distilled water. The strength of the solution was checked by the iodometric method [17] . From this solution a 0.025N solution has been prepared by suitable dilution.

Chromium (III) Solution: A 0.05N solution of chromium (III) has been prepared from AR grade potassium chromium(III) sulphate dodecahydrate in one liter standard flask**.** The solution is standardized by the permanganate method [25].

Indicator Solutions**:-** Aqueous solutions [ 0.05%, 50mg dissolved in 100ml ] of thiazine dyes : Azure-B (AZ-B) , Azure- C (AZ-C ), Toluidine Blue (TLB), Methylene Blue (MLB ), New Methhylene Blue (NMB) ,Thionine (TON) and resorufine ( an oxazine group of dye ) have been prepared and utilized as a redox indicators in the procedures.

Sodium pyrophosphate Solution: A 0.2M solution (1L) of pyrophosphate has been prepared by dissolving the required amount of AR grade tetrasodium pyrophosphate dodecahydrate in distilled water.

Acetic Acid**:** Glacial acetic acid of AR grade has been utilized.

Apparatus: A digital potentiometer (pacific-Bombay) has been used for potential measurements. A bright platinum electrode and a saturated calomel electrode were used as indicator and reference electrodes respectively. The salt bridge consists of a U-tube with porous-end plates and filled with a saturated potassium chloride solution.

### 2.2 : *Recommended procedures:*

### ( A) Potentiometric Method:

To an aliquot (3-12ml) of chromium(VI) solution(0.05N) taken in a titration cell about 3ml of glacial acetic acid,(17M), 20ml of 0.2M pyrophosphate are added and the solution diluted to about 50ml [ overall concentration of acetic acid is about 1M and that of pyrophosphate is about 0.08M] . Purified nitrogen gas is passed through the reaction mixture for 2 to 3 minutes to expel any dissolved oxygen. The contents are now titrated against a standard solution of iron(II) (0.05N) potentiometrically while the solution being stirred on a magnetic stirrer. The break in potential at the equivalence point is found to be 70 to 80 mV for the addition of 0.05 ml of 0.05N iron (II) solution. Some of the typical results obtained by the method were furnished in Table-1.

### (B).Visual end - point method (indicator method):

The conditions for the visual end point method [overall concentration of acetic acid 1M acetic and that of pyrophosphate 0.08M ] are the same as those of the potentiometric method excepting that a 0.025 N solution of chromium (VI) (3-12 ml) have been titrated against a standard solution of iron(II) [ 0.025 N ] using some thiazine group of dyes [mentioned above] as redox indictors. The color transition of all the indicators at the end- point is from bluish violet to colorless [with very light green ting because of the presence of chromium(III)] and it is sharp and reversible.

Table-1 :Potentiometric determination of chromium(VI) with iron(II) in acetic acid-
Pyrophosphate medium

| S.No. | Amount of chromium(VI) found, mg. | | Pooled Standard deviation (Sg) | $\frac{1.96\times sg}{\sqrt{n}}$ | 95% Confidence Levels $\overline{x}\pm\frac{1.96\times sg}{\sqrt{n}}$ |
|---|---|---|---|---|---|
| | Reference Method[17] | Author's Method* | | | |
| 1. | 3.983 | 4.002 | 0.013 | 0.010 | 3.992 to 4.012 |
| 2. | 5.022 | 4.998 | | | 4.988 to 5.008 |
| 3. | 6.148 | 6.172 | | | 6.162 to 6.182 |
| 4. | 7.187 | 7.165 | | | 7.155 to 7.175 |
| 5. | 8.313 | 8.301 | | | 8.291 to 9.311 |
| 6. | 9.352 | 9.370 | | | 9.360 to 9.380 |
| 7. | 10.48 | 10.46 | | | 10.45 to 10.47 |

*Average of six determinations.

Some of the results obtained have been given in Tables 2.

### 2.3 . *Sequential determination of metal ions presents in Cr(VI)-Mo(VI); Cr(VI)-U(VI) and Cr(VI)-V(V) in synthetic binary metal ion mixtures:*

Aqueous solutions of the above metal ion mixtures have been prepared by mixing 0.1N aqueous solutions of Cr(VI), Mo(VI), U(VI) and V(V) in various proportions in different 50 ml standard flasks and diluted to volume, such that the total concentration does not exceed 0.05N in a total volume of 50ml. The analysis is done by combining the present method [to get the chromium content] with another similar method [24] reported in 9.0M phosphoric acid medium [to get the total contents of the two metals ]. From the results of the two methods the content of each metal ion present in the mixture can be computed. The details are given in the following procedure.

Recommended Procedure:

From an above prepared metal ion mixture in 50ml flask, a 10 ml aliquot of a metal ion mixture is taken into acetic acid (1M) – pyrophosphate (0.08M) medium and titrated against iron(II) solution [0.05M] as per the recommended procedure described above using a thiazine dye as a redox indicator. The volume of iron(II) consumed is noted as titer- 1 [or $T_1$ ]. In this method Cr(VI) is reduced to Cr(III) and V(V) to V(IV) while Mo(VI) and U(VI) remain unaffected.

Table :-2 : Determination of chromium(VI) with iron(II) in acetic acid- pyrophosphate medium using redox indicators .

| Name of the indicator & its transition potential | Amount of chromium(VI) found, mg. | | Pooled standard deviation, **(Sg)** | $\frac{1.96 \times sg}{\sqrt{n}}$ | 95% Confidence Levels $\bar{x} \pm \frac{1.96 \times sg}{\sqrt{n}}$ |
|---|---|---|---|---|---|
| | Reference method [17] | Author 's method* $\bar{x}$ | | | |
| Methylene Blue ( 270mV )@ OR Thionine ( 260mV )@ | 1.732 | 1.743 | 0.008 | 0.006 | 1.737 to 1.749 |
| | 2.510 | 2.590 | | | 2.584 to 2.596 |
| | 3.466 | 3.478 | | | 3.472 to 3.484 |
| | 4.330 | 4.318 | | | 4.312 to 4.324 |
| | 5.196 | 5.210 | | | 5.204 to 5.216 |
| Toludine Blue ( 268mV )@ OR New Methylene Blue ( 255mV )@ | 1.689 | 1.679 | 0.009 | 0.007 | 1.672 to 1.686 |
| | 2.381 | 2.393 | | | 2.386 to 2.400 |
| | 3.248 | 3.325 | | | 3.318 to 3.332 |
| | 4.243 | 4.261 | | | 4.254 to 4.268 |
| | 5.110 | 5.120 | | | 5.113 to 5.217 |
| Azure –C ( 275mV )@ | 1.776 | 1.784 | 0.008 | 0.006 | 1.778 to 1.790 |
| | 2.815 | 2.798 | | | 2.783 to 2.804 |
| | 3.594 | 3.612 | | | 3.615 to 3.627 |
| | 4.417 | 4.404 | | | 4.398 to 4.410 |
| | 5.065 | 5.080 | | | 5.024 to 5.086 |
| Azure – B ( 265mV )@ | 1.949 | 1.960 | 0.009 | 0.007 | 1.953 to 1.967 |
| | 2.728 | 2.742 | | | 2.735 to 2.749 |
| | 3.637 | 3.623 | | | 3.616 to 3.630 |
| | 4.503 | 4.521 | | | 4.514 to 4.528 |
| | 5.150 | 5.135 | | | 5.128 to 5.142 |

*Average of six determinations. @ Transition potentials of the indicators with respect to normal hydrogen electrode.

In the similar way another 10 ml aliquot of same metal ion mixture is taken in a titration vessel and required volume of orthophosphoric acid and distilled water are added such that the concentration of the acid towards the equivalence is about 9.0M near the equivalence point [ in a total volume of about 50ml]. After passing purified nitrogen gas for about 2 minutes to expel any dissolved oxygen, 3 to 4 drops of the indicator [ resorufine ] [24] solution are added and the reaction mixture is titrated against iron(II) solution (0.05M) to a sharp color transition of the indictor from red to blue-green. The volume of iron(II) consumed in this case is noted as titer- 2 [or $T_2$ ] . In this procedure, Cr(VI) is reduced to Cr(III), Mo(VI) to Mo(V), U(VI) to U(IV) and V(V) is reduced to V(III), but not to V(IV) as in acetic acid – pyrophosphate medium. From the two titre values [$T_1$ and $T_2$ ] and the above stated experimental findings, the amount of each metal ion present in the above three binary metal ion mixtures can be computed as follows.

In the case of mixtures 1 & 2, $T_1$ corresponds to the amount of chromium (VI) present in a mixture while the difference between $T_2$ and $T_1$ corresponds to the amount of molybdenum(VI) and uranium (VI) present in the mixtures 1 and 2 respectively. Thus, the amount of each metal ion present in the mixtures 1&2 can be computed. In the case of mixture-3, since V(V) reacts in both titration 1 & 2 as mentioned above, it can be concluded that $T_2 – 2X [ T_2 – T_1 ]$ corresponds to the amount of chromium(VI) present in the mixture; while
$T_2 – T_1$ corresponds to the amount of vanadium(V) present in the mixture.

| (A). Chromium(VI) and Molybdenum(VI) mixture | | | | | |
|---|---|---|---|---|---|
| Amount of chromium(VI) found in 50 ml, mg | | | Amount of molybdenum(VI) found in 50 ml, mg | | |
| Reference method [24,26&27] | Present method* | R.S.D | Reference method [24,26&27] | Present method$^*$ | R.S.D. |
| 8.665 | 8.705 | 0.008 | 71.85 | 71.55 | 0.0613 |
| 10.40 | 10.34 | 0.009 | 62.35 | 62.55 | 0.052 |
| 12.13 | 12.18 | 0.010 | 52.75 | 52.55 | 0.041 |
| 13.87 | 13.82 | 0.011 | 43.18 | 43.30 | 0.033 |
| (B). Chromium(VI) and uranium(VI) mixture | | | | | |
| Amount of chromium(VI) found in 50 ml, mg | | | Amount of uranium(VI) found in 50 ml, mg. | | |
| 9.53 | 9.49 | 0.008 | 83.30 | 83.60 | 0.072 |
| 11.27 | 11.31 | 0.009 | 71.40 | 71.10 | 0.056 |
| 12.10 | 12.96 | 0.009 | 59.50 | 59.65 | 0.048 |
| 14.73 | 14.83 | 0.012 | 47.60 | 47.46 | 0.036 |

| ( C ). Chromium(VI) and vanadium(V) mixture | | | | | |
|---|---|---|---|---|---|
| Amount of chromium(VI) found in 50 ml, mg | | | Amount of vanadium(V) found in 50 ml, mg. | | |
| 7.80 | 7.83 | 0.007 | 22.95 | 23.04 | 0.019 |
| 7.80 | 8.65 | 0.007 | 20.40 | 20.36 | 0.016 |
| 9.53 | 9.49 | 0.008 | 17.85 | 20.32 | 0.014 |
| 10.40 | 10.37 | 0.003 | 15.30 | 15.26 | 0.012 |

*Average of six determinations.

Thus, the amount of metal ions present in the mixture can be found. Some of the typical results obtained by the procedure have been given shown in Table -3.

### *2.4 Determination of chromium and vanadium present in chrome vanadium steel:*

The methods now developed have been extended for the estimation of V and Cr cotents present in a steel sample which has been found to consists of Cr, V , Fe, in addition to C and Si.

Table : -3 : Sequential determination of metal ions present in some binary metal ion mixtures.

Recommended Procedure:

About 2.0 grams of the accurately weighed tool steel sample in the form of its drillings is taken into a Pyrex 100 ml beaker and treated with about 3.0 ml of concentrated sulphuric acid, 3.0 ml of orthophosphoric acid and 25 ml of water [28]. The contents are heated on a low flame to about half of its original volume . The solution is cooled to room temperature, diluted to about 40 ml and filtered to remove silica and other insolubles. The precipitate is washed thrice with a few ml of hot water and the washings are collected into the filtrate. To this solution a few drops of concentrated nitric acid are added to oxidize the ferrous iron and it is heated on a low flame until the fumes of nitrogen oxides are completely expelled. The solution is cooled to room temperature , and treated with about one gram of potassium bromate [to oxidize Cr and V to Cr(VI) and V(V)]], 3 ml syrupy phosphoric acid and about 0.3g of manganese(II) sulphate [which acts as a catalyst] and gently heated on a low flame for about ten minutes. To the solution, 2-3 ml of concentrated hydrochloric acid, 2-3 grams of ammonium sulphate are added and heated, to decompose the excess bromate, until the fumes no longer turns starch- iodide paper blue [28]. The solution is cooled to room temperature, the pH of the solution is adjusted to about 2 by drop-wise addition of [2 N] sodium hydroxide solution. The solution along with its washings is collected into a 100 ml standard flask, diluted to the mark with distilled water.

The chromium and vanadium contents present in the solution were analyzed adopting the procedure described above for metal ion mixture-III and the results have been presented in table-

4. The values are found to be in good agreement with those obtained by the standard method described by Kolthoff and Belcher for the analysis of chrome vanadium sample [28].

Table- 4 : Analysis of a Tool Steel Sample for Chromium and Vanadium

| Amount of Chromium and Vanadium Found in a Tool Steel Sample, %* [Sample taken , 2 gm] | | |
|---|---|---|
| Method Employed | Chromium,% ± S.D | Vanadium, % ± S.D |
| (1). Reference Method[28]. | 3.994 ± 0.015 | 1.995 ± 0.006 |
| (2 ). Present Method Using Redox Indicators | | |
| (A). Methylene Blue or Thionine | 3.993 ± 0.017 | 1.983 ± 0.005 |
| (B). Toluidine Blue or New Methylene Blue | 3.995 ± 0.015 | 1.996 ± 0.007 |
| (C ). Azure- B | 3.996 ± 0.018 | 1.992 ± 0.003 |
| (D ). Azure- C | 3.991 ± 0.013 | 1.998 ± 0.006 |

*Average of six determinations    S.D = Standard Deviation.

## 3. RESULTS AND DISCUSSION

From the results presented in tables 1&2 of the experimental part, it may be seen that chromium(VI) has been determined in the range 4.00 to 11.00 mg by potentiometric method and in the range 2.00 – 5.00 mg by the indicator method. The accuracy of the methods is found to be ± 0.5 % and ± 0.7 % respectively. The precision of both the methods has been expressed in the form of pooled standard deviation and 95% confidence limits and the values have been incorporated in Tables 1 & 2. In the visual end point method, however, the detection of the end point is obscured by the deep green color of chromium(III) [formed by the reduction of chromium(VI) ] when the concentration of chromium (VI) taken in the 50 ml of the reaction medium exceeds about 6.00 mg. Hence, the amount of chromium(VI) up to only 5.00 mg has been determined by the method using 0.025N solutions of chromium(VI) and iron(II).

From the results presented in table 3, it may be seen that in combination with one of our earlier methods [24], the new method now developed has been extended for the analysis of the three binary metal ion mixtures : (1). (Cr(VI) + Mo(VI) ; (2). Cr(VI) + U(VI) and (3) Cr(VI) + V(V). The total content of each metal ion present in 50ml of the reaction mixture has been presented in the table -3. The accuracy of the method is found to be ± 0.7%. The precision of the method has been found by computing the relative standard deviation and it is incorporated in table-3. In table-4, the authors have given the results relating to the analysis of a steel tool sample for chromium and vanadium contents. The sample has been analyzed with an accuracy of ± 0.7% . The precision of the method is found by calculating the standard deviation and the values have been given in table-4 itself.

In the visual end point method described in the present paper, only six [mentioned in the experimental part ] out of several thiazine dyes tried found suitable as redox indicators . All the indicators impart blue color to the reaction medium and these are reduced to their colorless leuco- bases by iron(II) in a two electron reduction step at the end point [29] .

From the recommended procedure described above for the determination of chromium(VI) with iron(II) , it is evident that the reduction of the former by the latter is rapid and quantitative only when the concentration of acetic acid is 1M or above and that of pyrophosphate 0.08 M or above in the reaction medium. In order to explain the conditions needed in the present redox reaction based on the redox potentials data, the authors have measured the formal redox potentials of chromium (VI)/chromium(III) couple [ chromium or oxidant system] in 1M acetic acid medium and at different pyrophosphate concentration[ in the range 0.03- 0.14M] adopting the method of Gopal Rao and Dikshitulu [27] . These potentials of the oxidant system have been compared with those of the iron(III)/iron(II) couple [iron or reductant system ] which were earlier reported from our laboratories [30 ]. The potentials of both the systems have been presented in table-5 and depicted graphically in figure-1.

From the potentials data, it may be seen that, in 1M acetic acid medium, the difference in potential between two couples increases with increase in pyrophosphate concentration .

Table -5: formal redox Potentials of Chromium(VI)/Chromium(III) and Iron(III)/Iron(II) couples In 1M Acetic Acid Medium and at different Concentrations of Pyrophosphate, with respect to Normal Hydrogen Electrode [ N.H.E. ], mV ± 5 mV ; At 28$^0$C ± 0.1$^0$C

Concentration of Cr(VI) = Cr(III) = 0.005N. Total concentration of chromium = 0.01N in 50ml.

Concentration of Fe(III) = Fe(II) = 0.005N. Total concentration of iron = 0.01N in 50ml.

| Concentration of pyrophosphate M | Formal potentials of Cr(VI)/Cr(III) Couple,mV | Formal [30] potentials of Fe(III)/Fe(II) Couple,mV | Concentration of pyrophosphate M | Formal potentials of Cr(VI)/Cr(III) Couple,mV | Formal[30] potentials of Fe(III)/Fe(II) Couple, mV |
|---|---|---|---|---|---|
| 0.03 | 491 | 210 | 0.09 | 422 | 90 |
| 0.04 | 462 | 180 | 0.10 | 420 | 80 |
| 0.05 | 443 | 160 | 0.11 | 416 | 70 |
| 0.06 | 432 | 140 | 0.12 | 412 | 65 |
| 0.07 | 428 | 120 | 0.13 | 408 | 60 |
| 0.08 | 424 | 105 | 0.14 | 404 | 55 |

Further, it is evident that from a pyrophosphate concentration of about 0.07M onwards, the difference in potential between the two couples is found to be more than 300mv which is sufficient to bring rapid reduction of chromium(VI) by iron(II). In fact, the authors observed that the reduction of chromium(VI) by iron(II) is rapid and quantitative in about 1M acetic acid medium (or above ) and in presence of 0.08M pyrophosphate ( or above). Thus these potentials data neatly explain the conditions needed for rapid reduction of Cr(VI) by Fe(II).

Further, we have measured the potentials of the chromium system at different concentrations of acetic acid [range 0.5- 6.0M], keeping the concentration pyrophosphate fixed at 0.08M, adopting the method of Gopal Rao and Dikshitulu [27] and found that the potentials increase from about 413mV to 473mV with increase in acetic acid concentration from 0.5 to 6.0M, while those of iron system was reported [30 ] to increase from 60mV to 120mV with increase in acetic acid concentration from 0.5 to 6.0M. Thus, there is only a marginal increase in the redox potentials of the oxidant and reductant systems with increase in acid concentration. Hence, the concentration of acetic acid above 1M is not expected to have any influence on the redox behavior between chromium(VI) and iron(II). Therefore, the determination is recommend to be carried out in 1M acetic acid medium and in presence of 0.08M pyrophosphate.

In order to explain the suitability of the redox indicators in the new procedures, the authors have determined the transition potentials of the six thiazine dyes[which were used as indicators in the present procedure ] adopting the method of Belcher et.al [31] . The transition potentials of the indicators obtained have been shown in parenthesis at the name of each indicator in Table- 1 and they are found to be in the range of 255 -275 mV. From the data presented in table-5, the formal redox potentials of the chromium system [oxidant system] and iron system [reductant sytem] are found to be about 424mV and 105mV respectively under the optimum conditions of the titration [ i.e. in 1.0M acetic-0.08M pyrophosphate medium] at which the rapid reduction of Cr(VI) by Fe(II) takes place. The transition potentials obtained [255-275 mV] are found to be in the useful intermediate range between the formal potentials of the oxidant [ 424 mV ]and reductant[105 mV ]systems observed under the optimum titration conditions. Thus, the transition potentials data neatly explain the feasibility of the use of the six thiazine dyes as redox indicators in the present redox reaction.

From the potentials data presented in table-5 and in figure-1, it evident that the formal redox potentials of iron system decreases considerably with increase in the concentration of pyrophosphate, hence, iorn(II) acts as a powerful reducing agent in presence of pyrophosphate.

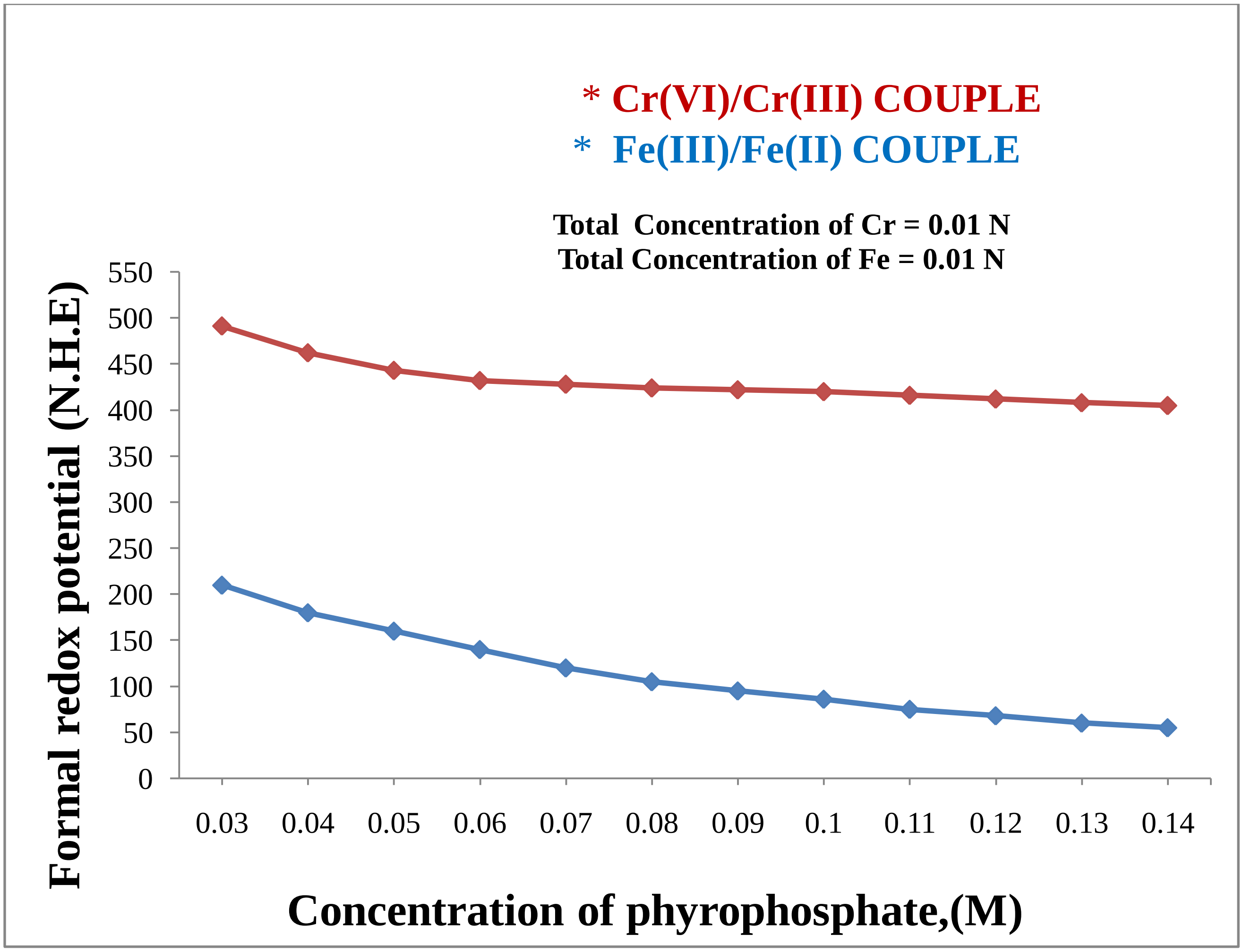

**Figure.1 :** Formal Redox potentials of Cr(VI)/Cr(III) and Fe(III)/Fe(II) couples in Acetic Acid (fixed at 1 M) medium and at different pyrophosphate concentrations.

The decrease in potential of iron system is no doubt due to the complex formation between iron(III) and pyrophospahate. However, the nature of these complexes formed at different pH values has not so far been established. Therefore, the authors have made an attempt to establish the nature of the species using Miniquad-75 computer program and presented below the results of our investigations.

Potentiometric technique using CALVIN – Wilson [32,33] method was employed to determine the number and nature of the species present in the solution. The pH metric titrations were carried out in a double walled tip less glass vessel of 100cm$^3$ capacity to carry out the titration under inert atmosphere at a required temperature. Requisite quantities of sodium chloride solution [to give an overall ionic strength of 0.10 mole dm$^{-3}$], water, pyrophosphate [0.005 – 0.015 mole dm$^3$ in various experiments], mineral acid in a total volume of 50 cm$^3$ were taken and them titrated against a standard solution of sodium hydroxide [ ~ 0.2 M ] solution both in the presence and absence of iron(III) [overall concentration 0.002M ]. After addition of each aliquot (0.1ml ) of the alkali, the pH meter dial reading was recorded at regular intervals until the two successive readings did not differ by 0.02 pH units.

The titration data obtained in different experiments with various initial concentration of the ligand and metal ion were analysed by Miniquad -75 computer program [34] , while the initial estimates of the parameters required by this program were obtained using the classical methods. However, the data obtained by the best fit model have been shown graphically in Figure 2., by depicting the pH versus the percentage distribution of the species. From the Figure it may be seen that various types of species such as $ML_2H_2$ or $[Fe(HP_2O_7)_2]^{3-}$; $ML_2H$ or $[Fe(P_2O_7)_2H]^{4-}$ ; and $ML_2$ or $[Fe(P_2O_7)_2]^{5-}$ have been formed between iron(III) and pyrophosphate in the pH region of about 3.0 – 7.0. Here, M stands for $Fe^{3+}$ , L stands for $P_2O_7^{4-}$. The stability constants of $ML_2H_2$ , $ML_2H$ and $ML_2$ have been found to be 17.21 ; 23.44 ; 27.02 respectively. However, most of the redox reactions using iron(II) as a reducing agent in acetic acid medium and in presence of pyrophosphate have been found feasible in the pH range 4.0 – 5.0. From **figure -2**, it may be seen that in this pH range, the predominant species are $ML_2H$ or $[[Fe(P_2O_7)_2H]^{4-}$. In fact, the pH of the reaction medium consisting of an overall concentration of about 1M acetic acid and 0.08M pyrophosphate, in presence of 3-10 ml of potassium dichromate solution (0.05M) is found to be about 4.2 ± 0.2 pH units. Therefore, it may be concluded that the species $ML_2H$ or $[FeH(P_2O_7)_2]^{4-}$ are stabilized in the pH region of our interest i.e.pH 4.0 – 5.0, in which the chromium(VI) is rapidly and quantitatively reduced to chromium(III) by iron(II).

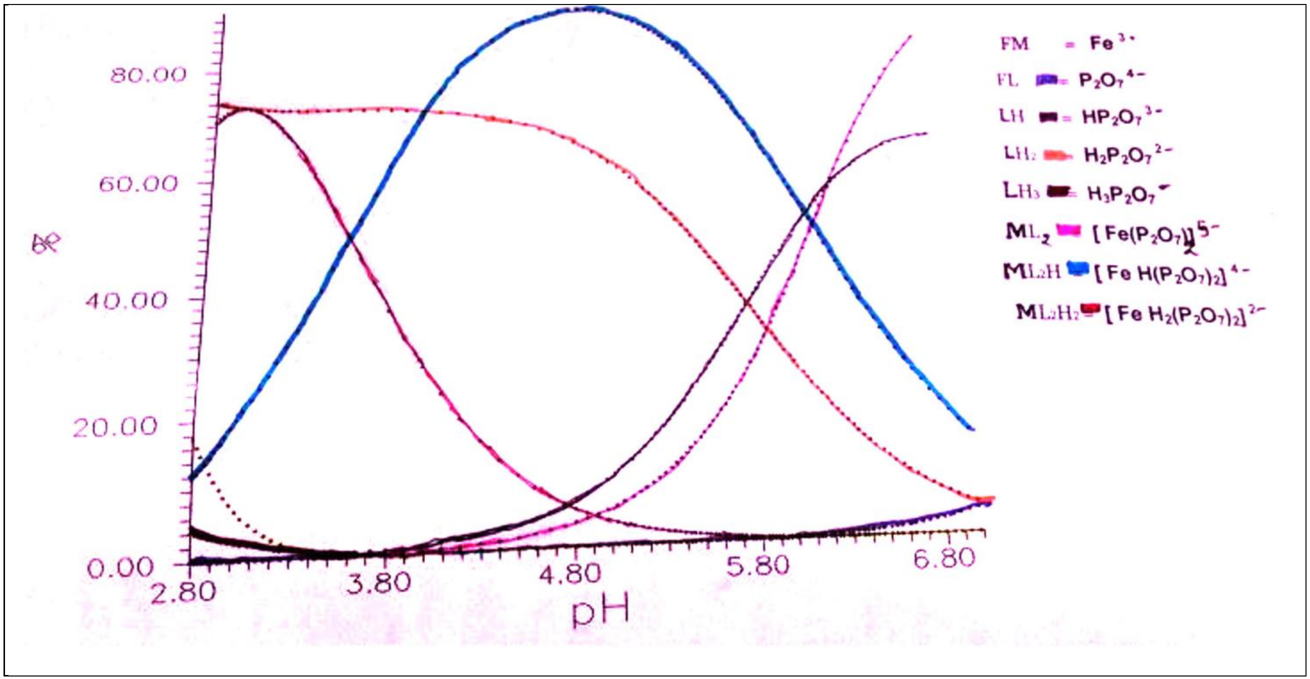

**Figure 2. :** Percentage distribution of species

## 4. Conclusions

Chromium can be selectively determined in presence of several other transition metal ions using iron(II) as a reducing agent in acetic acid medium [1M or above ] and in presence of pyrophosphate [0.08M or above ] employing both potentiometric and visual end-point techniques . The method developed is accurate and involves the use of inexpensive reagents. In combination with of one of our earlier methods reported, the new method now developed can be confidently applied for the analysis of binary metal ion mixtures consisting of Cr(VI)- Mo(VI) ; Cr(VI)- U(VI) and Cr(VI)- V(V) ; and for the analysis of a steel tool sample for chromium and vanadium contents. The formal redox potentials of chromium system and that of iron system are found to decrease with increase in the concentration of pyrophosphate. But, the decrease is found to be more pronounced in the case of iron system, because of the fact that iron(III) is bound by pyrophosphate in the form of a complex. Using the Miniquad -75 computer program, the coordinate species $[[Fe(P_2O_7)_2H]^{4-}$ are found predominant in the pH region 4.0-5.0 where most of the redox reactions are found feasible.

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