3. The heat of reaction was calculated from the integrated van't Hoff equation and found to be 20,000 calories.

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Phenanthroline-Ferrous Ion: A Reversible Oxidation–Reduction Indicator of High Potential and its Use in Oxidimetric Titrations[1]

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The use of oxidimetry as an analytical tool would be greatly extended by the discovery of a mobile and truly reversible oxidation potential indicator suitable for use in titrations with solutions of ceric sulfate and potassium dichromate. Such an indicator must change color at a potential at least as high as 0.93 volt if iron is to be titrated in the absence of phosphoric acid and fluorides, and should preferably change at a potential as high as 1.26 volts if the widest possible use is to be made of ceric sulfate. In addition it should possess a color change both vivid and intense, it should be stable and non-reactive with other substances likely to be present during a titration, and it should not be destroyed by irreversible oxidation when the end-point is overstepped or when it is subjected to the action of local excesses of the titrating reagent.

The phenanthroline-ferrous ion[2] satisfies all these requirements and seems to be in this respect unique.

The following properties[3] are significant for the application of phenanthroline-ferrous ion as an oxidation–reduction indicator. The base orthophenanthroline dissolves easily in solutions of ferrous salts, three molecules combining with one ferrous ion. The complex ferrous ions are intensely red in color. At room temperature they are only very slowly decomposed by strong acids or by salts of other metals (Co^{++}, Cu^{++}, Ni^{++}, Zn^{++}, Cd^{++}) which form stable complexes with the base. They do not form or form only very slowly when ferrous ion is added to a strongly acid solution of the base or to a solution containing a complex of the base with another metallic ion. Such powerful oxidants as chlorine or potassium permanganate in acid solution oxidize the ferrous complex to a ferric one, blue in color, which is remarkably resistant to further action of these reagents. The red ferrous complex is regenerated by the addition of reduc-

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(1) This article is based upon a dissertation submitted by Ray P. Chapman to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1932.

(2) Walden, Hammett and Chapman, THIS JOURNAL, **53**, 3908 (1931).

(3) These have all been known since the original article of Blau [*Monatsh.*, **19**, 647 (1898)].

ing agents, and we have found that this oxidation–reduction reaction is truly reversible and mobile.[4]

Preparation of Phenanthroline.—Since the discovery of phenanthroline by Blau, who gave no detailed directions, its preparation has been discussed several times.[5] In our hands the yield has varied from a maximum of 30% of the theoretical to an occasional run with negligible yields. The following directions are the result of considerable study of the necessary conditions, but do not yet represent a complete control of all important variables.

To a freshly prepared mixture of 125 g. of glycerin, 125 g. of 100% sulfuric acid and 50 g. of As_2O_5, at a temperature of 115°, in a one-liter flask provided with thermometer, stirrer and reflux, add all at once 25 g. of *o*-phenylenediamine. The temperature will rise about ten degrees. Now heat carefully to 140° and maintain at that temperature for two hours, carefully avoiding any higher temperature. Pour the reaction mixture into water, make strongly alkaline, and allow to stand for at least one day. Separate the tarry product, wash, and dry it at 110° until hard and brittle. Powder, extract with benzene in a Soxhlet until the residue no longer gives a red color with ferrous sulfate. About ten to twenty hours is necessary.

The crude phenanthroline which crystallizes on evaporation of the benzene is best purified by dissolving in dilute acid, adding alkali until a small tarry precipitate forms, discarding the precipitate, and precipitating the base with excess alkali. This may be followed by recrystallization from water as the monohydrate[3] with decolorizing carbon.

Indicator Solution.—A 0.025 *M* solution of phenanthroline ferrous sulfate was found to be convenient for indicator purposes. It was prepared by dissolving the stoichiometric amount of phenanthroline monohydrate in a 0.025 molar solution of ferrous sulfate in water.[6] In all titrations one drop of this solution was used. Since this is equivalent to less than 0.01 cc. of 0.1 *N* oxidizing reagent, the indicator blank is negligible with standard solutions of this concentration and need only be determined when more dilute solutions are used. The solution suffers no detectable change within a year.

The Oxidation Potential.—The molar oxidation potential of the indicator was determined by a titration method. The cell used is as follows

$$\mathrm{Au}\quad \begin{array}{l}\text{Quinhydrone, Satd.}\\ \\ H_2SO_4,\ 1\ M\end{array}\qquad \begin{array}{l}FeSO_4,\ 0.002\ M\\ Fe(C_{12}H_8N_2)_3SO_4,\ 0.002\ M\ \ \mathrm{Au}\\ H_2SO_4,\ 1\ M\end{array}$$

The quinhydrone–sulfuric acid solution was prepared by triturating quinhydrone with 1 *M* sulfuric acid immediately before use. The other solution was prepared by dissolving 0.06 g. of $FeSO_4{\cdot}7H_2O$ and 0.119 g. of $C_{12}H_8N_2{\cdot}H_2O$ in 50 cc. of water. To ensure the absence of ferric iron and excess ferrous iron in this solution, 1 g. of sodium carbonate was added and air drawn through for an hour. The resultant ferric hydroxide was removed by filtration. To this was added a solution containing 0.06 g. of $FeSO_4{\cdot}7H_2O$ in 1 *M* sulfuric acid which had been drawn through a Jones reductor. The combined solution was diluted to 200 cc. and made 1 *M* with sulfuric acid. It was connected to the

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[4] α,α-Dipyridyl ferrous ion [Blau, *Monatsh.*, **10**, 372 (1889); and Ref. 3] is an unsatisfactory indicator because its decomposition by acids is much more rapid than that of the phenanthroline-ferrous ion. Its oxidation potential though difficult to determine for this reason is certainly not very different from that of the phenanthroline compound.

[5] Hieber and Mühlbauer, *Ber.*, **61**, 2149 (1928); Smith, THIS JOURNAL, **52**, 397 (1930).

[6] Mr. Edmonds, in this Laboratory, has recently found that a satisfactory indicator solution can be prepared by boiling the crude alkaline precipitate with a 5% solution of ferrous sulfate and diluting the filtrate obtained after this treatment.

quinhydrone solution by means of a U-tube filled with 1 *M* sulfuric acid and closed by means of a coarsely ground glass plug. Because the concentration of sulfuric acid was the same throughout this cell and was large in comparison to the concentrations of other substances present, the liquid junction potential should be negligible. The titration was made with 0.01 *M* ceric sulfate in 1 *M* sulfuric acid. E. m. f. measurements were made at room temperature (24.8°) with a Leeds and Northrup Type K potentiometer. Results of one such titration are shown in Table I, and the curve obtained by plotting e. m. f. against titer is shown in Fig. 1.

TABLE I

POTENTIOMETRIC TITRATION OF A MIXTURE OF FERROUS SULFATE AND *o*-PHENANTHROLINE FERROUS SULFATE WITH CERIC SULFATE

Total $Ce(SO_4)_2$	E. m. f., volt	Total $Ce(SO_4)_2$	E. m. f., volt	Total $Ce(SO_4)_2$	E. m. f., volt	Total $Ce(SO_4)_2$	E. m. f., volt
0.0	−0.179	22.0	0.041	26.0	0.306	40.8	0.461
2.0	− .102	23.0	.056	29.0	.340	41.0	.477
4.0	− .073	24.0	.110	32.0	.360	41.2	.509
6.0	− .057	24.2	.154	35.0	.379	41.5	.518
10.0	− .033	24.4	.235	38.0	.403	43.0	.536
15.0	− .005	24.6	.254	40.0	.432	45.0	.555
20.0	+ .026	25.0	.278	40.5	.447	82.2	.655

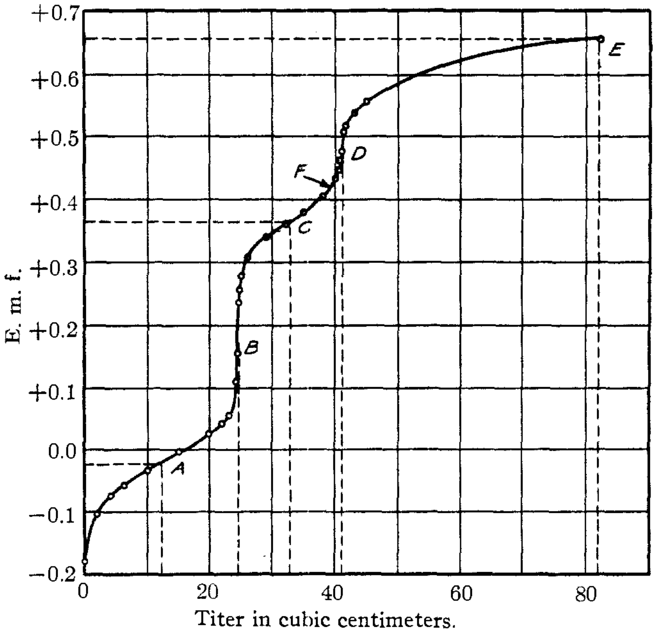

Fig. 1.—Titration of a solution of ferrous sulfate and ferrous phenanthroline sulfate in 1 *M* sulfuric acid with approximately 0.01 *M* ceric sulfate in 1 *M* sulfuric acid; quinhydrone in 1 *M* sulfuric acid used as a reference electrode.

The point of inflection B is the stoichiometric point for the reaction

$$Fe^{++} \rightleftharpoons Fe^{+++} + 1e \qquad (1)$$

The point of inflection *D* is the stoichiometric point for the reaction

$$\mathrm{Fe(C_{12}H_8N_2)_3^{++}} \rightleftharpoons \mathrm{Fe(C_{12}H_8N_2)_3^{+++}} + 1e \qquad (2)$$

Since both of these reactions are simple electronic oxidations requiring 1 faraday per mole, the potentials at the mid-points *A* and *C* are the molar oxidation potentials of reactions 1 and 2, respectively. At point *E* the titer is double that at *D*, and the potential is the molar oxidation potential for the ceric–cerous reaction. Previous investigators have found the molar oxidation potentials of the ferrous–ferric reaction[7] and the cerous–ceric reaction[8] to be 0.75 and 1.44 volts, respectively. The oxidation potential of the indicator may thus be obtained by finding the potential at *C* relative to either *A* or *E*. The average of the values for the molar potential of the indicator obtained in both ways from two closely agreeing titrations is 1.14 volts.

Because of the relatively low color intensity of the oxidized form this is effectively a one color indicator. The point of visible color change (red to colorless) corresponds to 90% oxidation of the indicator when this is present at the concentration used in our titrations, and to a potential, therefore, of 1.20 volts, the point marked F in Fig. 1. For titrations with ceric sulfate this potential is reached with a 0.01% excess of oxidant. The indicator may therefore be expected to function correctly with this valuable reagent for all simple titrations in the presence of the usual concentrations of strong acids. The behavior of an indicator when potassium dichromate or potassium permanganate is used as titrating reagent cannot be predicted from consideration of oxidation potentials. We shall show experimentally that this indicator does function precisely with these reagents when ferrous sulfate is the substance titrated.

Application to Titrations.—To illustrate the utility and precision attainable in titrations with this indicator we give in Table II the results of three different methods of standardization of a solution of ceric sulfate. In two of these the primary standard was Bureau of Standards sodium oxalate, in the other it was potassium dichromate purified according to the

TABLE II

STANDARDIZATION OF $\mathrm{Ce(SO_4)_2}$ SOLUTIONS

	By $\mathrm{K_2Cr_2O_7}$ through $\mathrm{FeSO_4}$				By $\mathrm{Na_2C_2O_4}$, excess $\mathrm{Ce(SO_4)_2}$ titrated with $\mathrm{FeSO_4}$				By $\mathrm{Na_2C_2O_4}$ through $\mathrm{KMnO_4}$ and $\mathrm{FeSO_4}$			
Soln.	Obs.	Mol. of $\mathrm{Ce(SO_4)_2}$	Av. dev., parts per 1000	Ext. dev., parts per 1000	Obs.	Mol. of $\mathrm{Ce(SO_4)_2}$	Av. dev., parts per 1000	Ext. dev., parts per 1000	Obs.	Mol. of $\mathrm{Ce(SO_4)_2}$	Av. dev., parts per 1000	Ext. dev., parts per 1000
1	4	0.09857	0.4	1.0	14	0.09847	0.7	2.9				
2	18	.09994	.3	1.5	9	.09986	.6	2.2	4	0.09994	0.4	1.0
3	18	.09815	.5	2.1	6	.09819	.6	1.8	2	.09824	.1	0.2
4	4	.09751	.3	0.8	10	.09751	.9	3.0				
5	7	.09779	.5	1.6	8	.09783	.7	2.4				
6	5	.09678	.5	1.5	12	.09685	.5	1.6				

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(7) Popoff and Kunz, THIS JOURNAL, **51**, 3822 (1929).

(8) Kunz, *ibid.*, **53**, 98 (1931).

recommendations of Vosburgh.[9] These are the two most available precise primary oxidimetric standards.

In the standardization against potassium dichromate, the ceric sulfate was titrated with approximately 0.1 *M* ferrous sulfate in a volume of 200 cc. and at a sulfuric acid concentration of 1 molar. Other experiments have shown that any volume from 100 to 300 cc. and any acid concentration from 0.5 to 3 molar gave identical results. The reverse titration is equally satisfactory, and in this case either hydrochloric or sulfuric acid may be used. Only actual experience can bring out the high degree of precision of this titration and the vividness and sharpness of the end-point. Weighed portions of the purified dichromate were dissolved in 200 cc. of 2 molar hydrochloric acid, and titrated after addition of one drop of indicator with the same ferrous sulfate solution.

The color of the chromic salt and, in the case of the hydrochloric acid solutions used here, of the ferric chloride modifies the color change at the end-point, but does not decrease the certainty with which it may be recognized, or the precision of the results. In the case of both hydrochloric acid solutions and sulfuric acid solutions the color change at the end-point is instantaneous when ferrous sulfate is titrated into a dichromate solution, but requires a little time when the titration is in the reverse direction. In the latter case it is therefore necessary to approach the end-point cautiously, waiting for a few seconds after each addition of titrating solution.

For the direct standardization against sodium oxalate,[10] the following method was used. Fifty cc. of ceric sulfate solution was measured in 150–200 cc. of 1 molar sulfuric acid. A weighed amount of sodium oxalate was dissolved without heating in this solution which was then warmed to 40–50°, and allowed to stand until cool. The temperature is not critical and may be estimated closely enough by touch. The heating may be omitted entirely if the solution is allowed to stand for one hour at room temperature. The excess of ceric sulfate was then titrated, using the phenanthroline-ferrous indicator, with ferrous sulfate for which a titer ratio with the ceric sulfate used had been freshly determined.

In the standardization through potassium permanganate the ceric sulfate was titrated with ferrous sulfate by means of the indicator, and this ferrous sulfate was then titrated with 0.1 *N* potassium permanganate which had been carefully standardized against Bureau of Standards sodium oxalate.

The results of weight titrations with two solutions of ceric sulfate given in Table III still further emphasize the precision of this titration. For this work it was found necessary to store the ferrous sulfate solution under an atmosphere of carbon dioxide to prevent oxidation by the air. In Series

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(9) Vosburgh, THIS JOURNAL, **44,** 2120 (1922).

(10) The direct standardization of ceric sulfate solutions against sodium oxalate by electrometric titration has been shown to be possible by Willard and Young [THIS JOURNAL, **50,** 1322 (1928)] and by Furman [*ibid.*, **50,** 755 (1928)]. The titration must be made in a hot solution in which the new indicator cannot be used because of the rapid decomposition of the complex by the acid necessarily present.

1, 18–26 g. of ceric sulfate solution were run into 200 cc. of one molar sulfuric acid and titrated with ferrous sulfate using one drop of indicator. In Series 2 the ferrous sulfate was added rapidly until the end-point was overstepped and the titration was completed by adding from a volume buret ceric sulfate diluted ten times.

TABLE III

WEIGHT TITRATIONS

Series	No. of obs.	Mean ratio $\frac{Ce(SO_4)_2}{FeSO_4}$	Av. devn., parts per 10,000	Extreme devn., parts per 10,000
1	6	1.0991	1	3
2	4	1.0963	1	3

Table IV illustrates the precision attainable with 0.01 *N* reagents. In series 1 20–40 cc. of 0.01 *M* ferrous sulfate in 200 cc. of 1 *M* sulfuric acid were titrated with 0.01 *M* ceric sulfate. In series 2 potassium permanganate in conjunction with the indicator was used and in the third series the same potassium permanganate without the indicator.

TABLE IV

TITRATIONS WITH 0.01 *N* REAGENTS

Series	Oxidant	No. of obs.	Blank corr., cc.	Mean ratio	Av. devn., parts per 1000	Extreme devn., parts per 1000
1	$Ce(SO_4)_2$	8	0.08	0.9610	0.6	2
2	$KMnO_4$	6	.10	1.071	0.5	2
3	$KMnO_4$	6	.26	1.074	1	5

In these cases also the use of the indicator gives concordant results whether ceric sulfate or potassium permanganate is the oxidant. Comparison of the results in series 2 and 3 shows that the well-known difficulty of using 0.01 *N* potassium permanganate is largely overcome when the end-point is obtained through the agency of this indicator.

Summary

1. It has been shown that the *o*-phenanthroline ferrous ion has the properties of an ideal indicator for use with powerful oxidants. It has a high molar oxidation potential (1.14 volts), it is reversible and mobile and it undergoes a vivid and intense color change.

2. When it is used as the indicator in titrations of ferrous sulfate with either potassium dichromate or ceric sulfate or the reverse titrations, a high degree of precision is possible.

3. Three methods of standardizing ceric sulfate solutions with the aid of this indicator give identical results.

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