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Titrimetric Determination of Iron(II), Molybdenum(V), and Thallium(I) with Potassium Chlorate Using Redox Indicators

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Accurate and convenient procedures have now been devised for the titrimetric determination of iron(II), molybdenum(V), and thallium(I) with potassium chlorate using visual indicators. These procedures are more advantageous than the procedures involving bromate. Further, chlorate is to be preferred as it is more inexpensive than bromate or iodate. Potassium chlorate is now obtainable at the purity required of a primary standard at a nominal cost. The chlorate titration procedure for iron(II) works satisfactorily even in the presence of organic materials such as oxalic acid, tartaric acid, and citric acid, so that it can be used for the determination of ferrous iron in pharmaceutical preparations or of ferric iron after reduction. It has been observed by us that oxygen of the air interferes in the titration of iron(II) in 6—7 M hydrochloric acid medium using naphthol blue black or methyl orange as a redox indicator but not in the titration of iron(II) in sulphuric acid medium using ferroin as an indicator. An inert atmosphere is not necessary for the titration of molybdenum(V) and thallium(I) in hydrochloric acid medium.

Although potassium chlorate is available at the purity required of a primary standard, it has not been very much used as a titrimetric reagent. Potassium chlorate may function in acid solution either as a five electron oxidant giving chlorine or as a six electron oxidant giving chloride as the end product. The calculated redox potentials for these two reactions are 1.47 and 1.45 V respectively, comparable to those of cerium(IV) sulphate and potassium permanganate. Inspite of these high redox potentials potassium chlorate is comparatively inert in dilute acid solution. Its comparative chemical inertness is explicable from kinetic considerations. The rates of reactions of potassium chlorate even with substances of very low redox potentials like tin(II) and titanium(III) are very slow. Recent studies on the kinetics of reactions involving chlorate have shown that the reaction rates increase with increasing hydrogen ion concentration. Since resonance stabilisation is large for oxyanions, it is necessary to overcome this stability in order that a chemical reaction takes place. On the addition of hydrogen ions at high concentration the oxyanions are converted into less stable forms which can easily react with other chemical species. Taking advantage of the kinetic results we have been able to establish conditions under which potassium chlorate can be used as an oxidimetric reagent for the direct titration of iron(II), molybdenum(V), and thallium(I) at room temperature using suitable redox indicators.

Experimental

Preparation of Solutions. A 0.1 N solution of potassium chlorate is prepared from "Pro Analysi" reagent supplied by E. Merck and its purity is checked by the method prescribed by Vogel.[1] The assayed purity agreed with the weight purity.

A 0.1 N solution of iron(II) was prepared from Analar reagent grade Mohr's salt supplied by British Drug Houses. The final concentration of sulphuric acid in the solution is 1.0 N. The solution is standardised against potassium dichromate.

A 0.1 N solution of molybdenum(V) was prepared from Analar reagent grade ammonium molybdate which was reduced in 3 M hydrochloric acid in a mercury reductor according to the instructions of Furman and Murray[2] and standardised against standard cerium(IV) sulphate by the procedure of Gopala Rao and Suryanarayana.[3]

A 0.1 N thallium(I) sulphate solution was prepared from Analar reagent grade thallous sulphate and standardised against potassium dichromate according to the procedure of Erdey, Vigh, and Buzas.[4]

All other chemicals used in the investigation are of chemically pure grade.

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[1] A. I. Vogel, "A Text book of Quantitative Inorganic Analysis," Longmans Green and Co. Ltd., London (1964) 3rd ed., p. 313.

[2] N. H. Furman and W. M. Murray, *J. Amer. Chem. Soc.*, **58**, 1689 (1936).

[3] G. Gopala Rao and M. Suryanarayana, *Z. Anal. Chem.*, **169**, 161 (1959).

[4] L. Erdey, K. Vigh, and I. Buzas, *Acta Chim. Acad. Sci. Hung.*, **26**, 85, 93 (1961).

Visual Titration of Iron(II) with Potassium Chlorate. From preliminary studies it was observed that ferroin is rapidly oxidised only in a medium containing sulphuric acid and phosphoric acid at final concentrations of 8—9 and 2M respectively. The oxidised indicator is, however, reduced rapidly by iron(II) under all conditions of acidity. In 9 and 10M sulphuric acid alone titrations cannot be conducted because ferroin decomposes as the end-point is approached. Phosphoric acid not only stabilises the indicator but also catalyses the oxidation of indicator by chlorate. In view of these considerations the following procedure is recommended for the titrimetric determination of iron(II) with potassium chlorate.

Recommended Procedures for the Titration of Iron(II).

Procedure 1: A known volume of 12M sulphuric acid is taken in a 150 ml pyrex titration cell and enough distilled water added to give an overall acidity of 8—9M when diluted to 50 ml. The mixture is cooled to the room temperature and then an aliquot of iron(II) solution is added followed by 5 ml of 85% syrupy phosphoric acid. Stirring the mixture well, add 0.1 ml of 0.01M ferroin and titrate with 0.1N solution of potassium chlorate. The titration is to be made dropwise towards the end, giving a wait of 10 seconds between successive additions. At the end-point the colour change is from red to pale blue. The indicator correction is 0.07 ml of 0.1N chlorate solution to be deducted from the titer. The average relative error of determination of iron(II) is ±0.2%.

Procedure 2: The addition of 1—2 ml of 0.1N of vanadium(IV) sulphate in place of phosphoric acid also catalyses the reaction at overall acidity of 7—8M sulphuric acid using 0.1 ml ferroin as an indicator. The average relative error of determination of iron(II) is ±0.2%.

Procedure 3: Titrations of iron(II) with potassium chlorate have been found possible in 6—7M hydrochloric acid medium in an inert atmosphere, using 0.1 ml of 0.2% naphthol blue black or 0.1 ml of 0.1% methyl orange as a redox indicator. The colour changes at the end-point are from green to yellow with naphthol blue black and red to yellow with methyl orange. The indicator correction amounts to 0.06 ml of 0.1N potassium chlorate per 0.1 ml of any of the two indicator solutions, to be deducted from the experimental titre. For titrations of iron(II) in 6—7M hydrochloric acid medium an inert atmosphere is necessary, because iron(II) will be oxidised by oxygen of the air due to lowering of the iron(III)/iron(II) potential in hydrochloric acid medium.

Interferences: Five hundred milligram of oxalic acid, 75 mg of tartaric acid, 525 mg of citric acid, 41 mg of cobalt(II), 53 mg of nickel(II), 13 mg of chromium(III), and 15 mg of vanadium(IV) do not interfere in a volume of 50 ml. Glucose interferes. Representative results are presented in Tables 1 and 2.

TABLE 1. TITRATION OF IRON(II) WITH POTASSIUM CHLORATE

Indicator	Amount of iron(II) in mmol	
	Taken	Found
Ferroin	0.3960	0.3950
8—9 M H_2SO_4	0.4384	0.4390
+	0.5245	0.5234
2 M H_3PO_4	0.7091	0.7111
Ferroin	0.2567	0.2572
7—8 M H_2SO_4	0.5200	0.5190
+	0.6200	0.6182
1—2 ml of 0.1 M vanadium(IV)	0.7316	0.7335

TABLE 2. TITRATION OF IRON(II) WITH POTASSIUM CHLORATE

Indicator	Amount of iron(II) in mmol	
	Taken	Found
Naphthol blue black	0.3570	0.3651
6—7 M HCl	0.4039	0.4048
	0.4529	0.4536
	0.6806	0.6794
Methyl orange	0.3468	0.3476
6—7M HCl	0.4487	0.4478
	0.5665	0.5670
	0.7018	0.7037

Visual Titration of Molybdenum(V). Satisfactory visual titrations of molybdenum(V) with potassium chlorate can be made in 5—7M hydrochloric acid medium with the addition of 1 ml of 0.01M iron(III) as a catalyst per 50 ml using 0.1 ml of 0.1% methyl orange or methyl red as an indicator. While using 0.1 ml of 0.2% napthol blue black as an indicator it is necessary to add 3 ml of the iron(III) solution as a catalyst. The titration is carried out rapidly in the beginning and slowly towards the equivalence point allowing 20—25 sec, after each addition of a drop of the reagent; with methyl orange or methyl red the end-point is denoted by the disappearance of red colour. In the case of naphthol blue black the colour change is from bluish green to yellow. The indicator correction with 0.1N chlorate solution is 0.06 ml per 0.1 ml of any of these indicator solutions. These indicators do not work in sulphuric acid medium. The average relative error of determination is ±0.2%. Our observations showed that an inert atmosphere is not necessary for the titration of molybdenum(V).

Interferences: Twenty six milligram of chromium(III) and 44 mg of vanadium(IV) do not interfere.

Some typical results are given in Table 3.

TABLE 3. TITRATION OF MOLYBDENUM(V) WITH POTASSIUM CHLORATE

Indicator	Amount of molybdenum(V) in mmol	
	Taken	Found
Methyl orange	0.2357	0.2352
5—7M HCl	0.3593	0.3600
+	0.4428	0.4424
1 ml of 0.01M iron(III)	0.5036	0.5024
Methyl red	0.2332	0.2327
5—7M HCl	0.4715	0.4706
+	0.5977	0.5966
1 ml of 0.01 M iron(III)	0.6585	0.6600
Naphthol blue black	0.2642	0.2636
5—7M HCl	0.3807	0.3814
+	0.4592	0.4584
3 ml of 0.01M iron(III)	0.5452	0.5439

Visual Titration of Thallium(I). Accurate visual titrations of thallium(I) are possible with potassium chlorate in 6—8M hydrochloric acid using 0.1 ml of 0.1% methyl orange or methyl red or neutral red or phenosafranine and 0.1 ml of 0.2% naphthol blue black as indicators. The titration with potassium chlorate is made rapidly in the beginning and dropwise towards the end giving a wait of 20—25 sec between drops. The indicator corrections are 0.1 ml in the

Table 4. Titration of thallium(I) with potassium chlorate

Indicator	Amount of thallium(I) in mmol	
	Taken	Found
Methyl orange	0.2168	0.2174
6—8M HCl	0.2423	0.2430
	0.4354	0.4346
	0.4782	0.4770
Methyl red	0.2104	0.2108
6—8M HCl	0.2265	0.2272
	0.3443	0.3433
	0.4948	0.4940
Neutral red	0.2533	0.2528
6—8M HCl	0.3663	0.3675
	0.4055	0.4045
	0.4827	0.4840
Phenosafranine	0.2435	0.2440
6—8M HCl	0.2622	0.2626
	0.3376	0.3366
	0.4386	0.4373
Naphthol blue black	0.2022	0.2026
6—8M HCl	0.3175	0.3185
	0.3632	0.3621
	0.3936	0.3944

case of methyl orange and methyl red, 0.06 m*l* in the case of phenosafranine and neutral red and 0.04 m*l* in the case of naphthol blue black. The average relative error of determination is found to be ±0.25%. Methyl red and methyl orange turn from red to yellow, naphthol blue black turns from blue to light pink at the end-point. Phenosafranine changes color from blue violet to colorless through pink, while neutral red gives a transition of violet to colorless through pink. It has been observed by us that titrations of thallium(I) gave identical results both in air and an inert atmosphere. This shows that thallium(I) is not oxidised by oxygen inspite of the lowering of the thallium(III)/thallium(I) potential.

Some typical results are given in Table 4.

Discussion

The procedure now developed for the determination of iron(II) with potassium chlorate is much more simple and convenient than the procedure with potassium bromate. Moreover potassium chlorate is more inexpensive than potassium bromate. Kolthoff and Belcher[5] state that in the titration of ferrous iron with bromate using methyl red or methyl orange as an indicator, the colour of the indicator disappears long before the equivalence point is reached, due to the slowness of the reaction between iron(II) and bromate. Smith and Bliss[6] recommended the addition of a copper salt as a catalyst. However, as the copper also catalyses the atmospheric oxidation of the ferrous iron, arsenate is proposed to be added. They also recommended the addition of phosphoric acid to lower the oxidation potential of the system.

It is noteworthy that in the potassium chlorate method now developed for the determination of iron(II), various organic materials such as oxalic acid, tartaric acid, and citric acid do not show any interference; whereas the permanganate and dichromate methods cannot be used in their presence. The chlorate method, therefore, holds out great promise for the determination of iron(II) in pharmaceutical preparations.

The titration method for thallium(I) now developed by us is also more advantageous than the bromate procedure as the latter requires heating to 50—60°C.

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[5] I.M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience Publishers, Inc., New York, (1957), p. 521.

[6] G.F. Smith and H.H. Bliss, *J. Amer. Chem. Soc.*, **53**, 4291 (1931).