MERCUROUS NITRATE AS A REDUCTIMETRIC REAGENT

III. THE TITRATION OF VARIOUS OXIDISING AGENTS

by

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In the first paper of this series[1] it was suggested that mercurous nitrate might be used for titrating many oxidising agents besides ferric iron, by adding a small amount of a solution of ferrous iron to act as a carrier. When this reaction was tried, it was found that the re-oxidation of the reduced iron was too slow to be of practical value. However, when an excess of a ferrous solution was added, the oxidation took place instantaneously, and an amount of ferric iron equivalent to the original amount of oxidising agent was produced, and could be titrated with mercurous nitrate in the usual way.

It was found possible to determine dichromate, ceric sulphate, vanadate, permanganate, chlorate, hydrogen peroxide and persulphate in this way. Other oxidising agents which might react in the same way were not examined, e.g. nitrate[2]. The fact that dichromate may be titrated by this procedure is of importance, since it provides a ready means of standardising the mercurous nitrate solution. Otherwise, it is necessary to standardise by the calomel method, or against a ferric alum solution which has been standardised by some other means. Although some samples of ferric alum are sufficiently pure to be used directly as a standard, we have occasionally found other samples which were impure. Until the reaction with potassium dichromate was discovered it was always our practice to standardise the mercurous nitrate against a previously standardised ferric alum solution.

It is almost certain that the method might be extended to the indirect determination of lead and barium after precipitation as the chromates, and solution of the washed precipitates in acid, since neither barium nor lead interferes with the mercurous nitrate titration[3]. If barium can be determined in this way the method should also be applicable to the determination of sulphates by the conventional barium chromate method.

Finally by using mercurous nitrate in conjunction with a standard solution of ferric alum, it might be possible to determine reducing agents, such as hydroquinone, which reduce ferric iron, by adding excess of the standard ferric alum and back-titrating with mercurous nitrate.

RESULTS

Titration of various oxidising agents

Potassium Dichromate

ml of 0.1*N* Dichromate	ml of 0.1*N* $Hg_2(NO_3)_2$
25.00	25.00
25.00	25.02
20.00	20.00
20.00	19.98
20.00	20.00
15.00	15.00
15.00	15.00
10.00	10.02
5.00	5.00

Ceric Sulphate

ml of 0.1*N* Ceric Sulphate	ml of 0.1*N* $Hg_2(NO_3)_2$
25.00	25.00
25.00	25.00
20.00	20.00
20.00	20.02
20.00	20.02
15.00	15.00
10.00	10.00
10.00	10.00
5.00	5.02

Potassium Permanganate

ml of 0.1*N* Permanganate	ml of 0.1*N* $Hg_2(NO_3)_2$
25.00	24.98
25.00	25.00
25.00	25.00
20.00	20.00
20.00	20.00
15.00	15.02
10.00	9.98
10.00	10.00
5.00	5.02

Potassium Persulphate

ml of 0.1*N* Persulphate	ml of 0.1*N* $Hg_2(NO_3)_2$
25.00	25.00
25.00	24.98
20.00	20.02
20.00	19.98
15.00	15.00
15.00	15.00
10.00	10.00
10.00	9.98
5.00	5.00

Hydrogen Peroxide

ml of 0.1*N* Peroxide	ml of 0.1*N* $Hg_2(NO_3)_2$
25.00	24.96
20.00	20.00
20.00	19.98
20.00	20.00
15.00	15.02
15.00	15.00
10.00	10.00
10.00	10.00
5.00	4.98

Potassium Chlorate

ml of 0.1*N* Chlorate	ml of 0.1*N* $Hg_2(NO_3)_2$
25.00	25.00
25.00	25.00
20.00	20.00
20.00	20.00
20.00	19.96
15.00	15.00
15.00	14.98
10.00	10.00
5.00	4.98

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Sodium Vanadate

ml of 0.1*N* Vanadate	ml of 0.1*N* $Hg_2(NO_3)_2$
25.00	24.98
25.00	25.02
20.00	20.00
20.00	20.00
20.00	20.00
15.00	15.00
15.00	14.98
10.00	10.00
5.00	5.00

EXPERIMENTAL

0.1*M* Mercurous nitrate was prepared and standardised as described in a previous paper[5]. The ferrous iron solution was prepared by dissolving sufficient ferrous ammonium sulphate in 0.7*N* sulphuric acid to give an approximately 0.1*N* solution. If this solution is free from ferric iron, the amount added need not be measured exactly, but if traces of ferric iron are present, a carefully measured amount should be added, and a blank correction made.

Potassium Dichromate. A solution of 0.1*N* potassium dichromate was transferred to a conical flask, and an amount of ferrous iron solution added equivalent to about double that of the dichromate. 10 ml of 40 per cent ammonium thiocyanate were added, and the ferric iron produced was titrated in the usual way. At the end-point the solution was pale green due to trivalent chromium. On standing for some time the colour intensified to a bright green.

Ceric Sulphate. The ceric sulphate solution was standardised against ferrous propylenediamine sulphate[4]. Measured quantities were treated with the ferrous iron solution, and the titration completed as described above.

Sodium Metavanadate. An approximately 0.1*N* solution of sodium metavanadate was prepared and standardised by reducing with sulphur dioxide, and titrating with standard permanganate.

Measured amounts of vanadate were determined by titration with standard mercurous nitrate using exactly the same procedure as before. The solution was pale blue at the end-point.

Potassium Permanganate. Potassium permanganate was standardised against ferrous propylenediamine sulphate.

Measured amounts were determined exactly as before using standard mercurous nitrate.

Hydrogen Peroxide. Hydrogen peroxide was standardised by titration against standard permanganate. Suitable amounts were then determined as before using mercurous nitrate.

Potassium persulphate. Potassium persulphate was standardised by adding a measured excess of standard ferrous ammonium sulphate, warming to 80° C., cooling, and back-titrating the excess ferrous ammonium sulphate with standard permanganate.

In the determination using mercurous nitrate, the solution, was warmed to 80° C. after the addition of the ferrous iron solution, rapidly cooled, ammonium thiocyanate added, and the titration completed as before.

Potassium Chlorate. The potassium chlorate solution was standardised gravimetrically by reducing to chloride and precipitating as silver chloride.

Suitable amounts were treated with the ferrous iron solution, heated just to the boiling-point, cooled rapidly to room temperature, and the titration continued in the usual way. When the solution was not brought just to the boiling-point (there is no need to boil longer) some of the chlorate was not reduced, and a shifting end-point was obtained due to the continued slow reduction of the chlorate by the residual ferrous ions. There is also some risk of the chlorate reacting with thiocyanate to form polymerised products. It is essential, therefore, to ensure that reduction of chlorate is complete before adding the thiocyanate.

SUMMARY

It has been found that when excess of a solution containing ferrous ions is added to certain oxidising agents, the equivalent amount of ferric iron produced can be titrated accurately with mercurous nitrate, enabling the original oxidant to be assessed. Oxidising agents which have been determined in this way are potassium permanganate, potassium persulphate, ceric sulphate, sodium vanadate, potassium chlorate, hydrogen peroxide and potassium dichromate. The last substance provides a convenient primary standard for the standardisation of mercurous nitrate solutions.

RÉSUMÉ

Lorsqu'on traite certains oxydants par une solution de fer(II) en excès, le fer (III) formé peut être titré avec précision au moyen de nitrate de mercure(I); ce qui permet de doser ces substances oxydantes. On peut analyser de cette façon les composés suivants: permanganate de potassium, persulfate de potassium, sulfate de cérium(IV), vanadate de sodium, chlorate de potassium, peroxyde d'hydrogène et dichromate de potassium. Ce dernier peut être utilisé comme substance de référence.

ZUSAMMENFASSUNG

Werden gewisse Oxydationsmittel mit einem Überschuss einer II-wertiges Eisen enthaltenden Lösung versetzt, so kann das gebildete III-wertige Eisen genau mit Mercuronitrat titriert werden; auf diese Weise können die oben erwähnten Oxydationsmittel bestimmt werden. Die folgenden Oxydationsmittel wurden analysiert: Kaliumpermanganat, Kaliumpersulphat, CerIV-sulphat, Natriumvanadat, Kaliumchlorat, Wasserstoffperoxyd und Kaliumbichromat. Die letztgenannte Substanz kann zum Einstellen der Mercuronitratlösung dienen.

REFERENCES

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