MERCUROUS NITRATE AS A REDUCTIMETRIC REAGENT

II. THE INTERFERENCE OF THE MORE COMMON CATIONS AND ANIONS IN THE DETERMINATION OF IRON

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The only information hitherto available regarding the interference of other ions in the titration of ferric iron with mercurous nitrate is that divalent manganese has no effect, and hydrochloric acid in concentrations above 0.1*N* causes high results[1]. PUGH[2], using mercurous perchlorate as the titrant, noted that sulphuric and nitric acids above 5 ml per 100-200 ml caused high results. The present paper describes our studies of the effect of increasing the acidity and of many of the more common ions on the reaction.

When the concentration of nitric acid rose much above 2.5*N*, the colour of ferric thiocyanate returned very rapidly after the titration was completed. At an acidity of 2*N* in nitric acid a period of 15 min. was required. The speed of the colour return increased with increasing acidity, until a point was reached where an end-point could not be obtained. Presumably at these high acidities the ferrous iron was rapidly re-oxidised by the nitric acid. The maximum acidity permissible was found to be 2.5*N*. Hydrochloric acid interfered at lower concentrations, but the maximum permissible amount (0.8*N*) was much higher than that reported by BRADBURY AND EDWARDS and by PUGH. As will be seen later, this is probably because more thiocyanate is used in our standard procedure. PUGH states that the interference can be eliminated by partial neutralisation, but it is obviously the chloride ion and not the hydrogen ion which causes the interference, and it is difficult to see what effect neutralisation can achieve. When partial neutralisation was tried we were unable to note any diminution in the interference. Similarly when sodium chloride was added in place of hydrochloric acid, the interference was of the same order as when equivalent amounts of hydrochloric acid were present. It was thought that the interference of chloride might be overcome by dissolving mercuric oxide in the acid solution to bind chloride ion as the feebly ionised mercuric chloride, but no such effect was noted. It was found, however, that the interference was eliminated by increasing the amount of thiocyanate present. For example, when the acidity was 2*N* in hydrochloric acid, double the usual amount of thiocyanate prevented the interference.

The interference of cations

Silver gave a white precipitate of the thiocyanate when present in moderate amounts, and at the end-point the precipitate had a violet colour. However, when sufficient thiocyanate was added to dissolve the precipitate, the titration was unaffected. Lead gave a white precipitate of the insoluble thiocyanate which was not soluble in excess of thiocyanate. There was also a small amount of lead sulphate formed by interaction with the ferric ammonium sulphate, but the end-point was quite distinct in the turbid solution. Zinc gave a white precipitate of zinc mercuric thiocyanate during the course of the titration, but it did not interfere with the end-point.

TABLE I

INTERFERING EFFECT OF CATIONS IN TITRATION WITH MERCUROUS NITRATE

Cation	Effect	Cation	Effect
Silver	None	Cadmium	None
Mercury (II)	None	Aluminium	None
Tin (IV)	None	Chromium (III)	None
Iron (II)	None	Nickel	None
Manganese (II)	None	Beryllium	None
Zinc	None	Zirconium	None
Calcium	None	Bismuth	Interferes above 50 mg
Barium	None	Cobalt	Interferes above 200 mg
Strontium	None	Copper	Interferes at all concns.
Titanium (IV)	None	Thallium (II)	,, ,, ,, ,,
Thorium	None	Titanium (III)	,, ,, ,, ,,
Uranium (VI)	None	Tin (II)	,, ,, ,, ,,
Lead	None	Cerium (IV)	,, ,, ,, ,,

Copper caused high results. At first this was thought to be due to its catalysing the re-oxidation of ferrous iron, but it was noted that the increase in titre was always proportional to the amount of copper present. This effect has since been studied more fully, and will form the subject matter of a further communication. As would be expected, tin (II) interfered by reducing the ferric iron present, and cerium (IV) by oxidising the ferrous iron. Bismuth interfered owing to the formation of a fairly intense yellow colour with thiocyanate. Thallium (II) gave a dense black precipitate at the end-point which interfered seriously. Cobalt in moderate amounts gave the insoluble blue thiocyanate which masked the end-points. Small amounts did not interfere.

The effect of the more common cations on the titration is summarised in Table I.

The interference of anions

Orthophosphate slowed down the reaction, but did not interfere. Bromate and iodate reacted violently with thiocyanate. Bromine and iodine were liberated from bromides and iodides, and fluoride bleached the colour of the ferric thiocyanate complex. Pyrophosphate and oxalate behaved similarly. As would be expected sulphite and thiosulphate reacted with the ferric iron. Molybdate interfered because of the formation of the characteristic blood-red colour with thiocyanate which masked the end-point of the titration. Nitrite, even in very small amounts interfered, because of the formation of nitrosyl thiocyanate. The effect of various anions is summarised in Table II.

TABLE II

INTERFERING EFFECT OF ANIONS IN TITRATIONS WITH MERCUROUS NITRATE

Anion	Effect	Anion	Effect
Tungstate	None	Bromate	Interferes at all concns.
Arsenate	None	Thiosulphate	,, ,, ,, ,,
Arsenite	None	Iodate	,, ,, ,, ,,
Perchlorate	None	Nitrite	,, ,, ,, ,,
Borate	None	Sulphite	,, ,, ,, ,,
Orthophosphate	None	Selenate	,, ,, ,, ,,
Citrate	None	Permanganate	,, ,, ,, ,,
Formate	None	Vanadate	,, ,, ,, ,,
Phthalate	None	Chlorate	,, ,, ,, ,,
Benzoate	None	Periodate	,, ,, ,, ,,
Molybdate	Interferes at all concns.	Bromide	Interferes above 200 mg
Selenite	Interferes at all concns.	Iodide	,, ,, 200 ,,
Dichromate	Interferes at all concns.	Fluoride	Interferes, but effect can be overcome up to 500mg
Ferricyanide	Interferes at all concns.	Oxalate	Interferes, but effect can be overcome up to 500mg
Ferrocyanide	Interferes at all concns.	Pyrophosphate	Interferes, but effect can be overcome up to 500mg
Persulphate	Interferes at all concns.		

Attempts were made without success to overcome the interference of copper by adding tartrate, citrate, acetate, orthophosphate, glycine and thiourea. Fluoride interference could not be masked by the addition of thorium or aluminium ions. However, it was found that up to 500 mg could be tolerated by raising the acidity of the solution with nitric acid. Care must be taken not to exceed an acidity of 2.5M. The effect of pyrophosphate and oxalate was overcome in the same way. In all these cases the end-point was much more sluggish than in the normal procedure. Fluoride was used in an attempt to overcome the interference of vanadate and molybdate, but no masking effect could be observed. Nitrite interference was readily overcome by treating the solution with a slight excess of sulphamic acid, warming and then cooling before the titration.

EXPERIMENTAL

Mercurous nitrate and ammonium thiocyanate were prepared as described in the previous paper in this series.[3]

The interference of the various cations and anions was examined by adding amounts of the appropriate salt so that 500 mg of the particular ion being examined were present. If no interference was noted, further amounts were not investigated since in practice it would be unlikely for larger amounts to be present. When interference was found, amounts of the ion ranging from 0.1 mg upwards were added until significant interference occurred. In these tests the interferences were only checked for titres ranging between 5 and 25 ml of 0.1*M* mercurous nitrate. A fair estimation of the interferences at other concentrations should however be possible from these results.

SUMMARY

The interfering effect of most of the more common cations and anions on the titration of ferric iron with mercurous nitrate has been examined. As would be expected, ions capable of oxidising ferrous iron interfere. Certain other cations and anions interfere, but in several cases this effect can be eliminated. Copper and thallium must be completely absent, and ions which give coloured products with thiocyanate ions, *e.g.*, molybdenum.

RÉSUMÉ

Les auteurs ont étudié l'effet de la plupart des cations et anions courants sur la titration des ions ferriques, par le nitrate de mercure (I). Il est évident que tous les ions pouvant oxyder le fer (II) gênent. D'autres cations et anions peuvent gêner, mais il est souvent possible d'éviter leur action perturbatrice. Le cuivre et le thallium doivent être absents, de même que les ions donnant des colorations avec l'ion thiocyanique, par exemple le molybdène.

ZUSAMMENFASSUNG

Der Einfluss der meisten gewöhnlichen Kationen und Anionen auf die Titration des dreiwertigen Eisens mit Mercuronitrat wurde untersucht. Wie zu erwarten war, stören alle diejenigen Ionen, die zweiwertiges Eisen zu oxydieren vermögen. Gewisse andere Kationen und Anionen können auch stören, doch kann diese Wirkung in vielen Fällen ausgeschaltet werden. Kupfer und Thallium dürfen nicht anwesend sein, ebenso wie Ionen, die mit Thiocyanat gefärbte Reaktionsprodukte geben, wie z.B. Molybdän.

REFERENCES

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[2] W. Pugh, *J. Chem. Soc.*, (1945) 588.
[3] R. Belcher and T. S. West, *Anal. chim. Acta*, 5 (1951) 260.

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