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Volumetric Determination of Iron by Reduction with Hypophosphite.

By

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Although hypophosphites are powerful reducing agents capable of reducing the cations to metallic or lower valency states, their use in analytical procedures has been rather limited. EVANS[1] found that hypophosphites reduce acid solutions of tin (IV) quantitatively to tin (II) when traces of mercury salts are present. He developed a volumetric method for the determination of tin based on this reaction. The same author[2] used hypophosphite for separation of arsenic as metal from antimony. IVANOV-EMIN[3] estimated germanium iodometrically after reduction of germanium (IV) to germanium (II) with sodium hypophosphite.

We have now carried out experiments to see whether hypophosphites can be employed for reduction of Iron (III) to Iron (II) in acid solutions. SIEVERTS and MAJOR[5] long ago observed that iron solutions are reduced on treatment with hypophosphite at the temperature of boiling water bath. But the Iron (II) so formed could not be titrated against potassium permanganate since the phosphorous acid which was also present in the mixture is readily oxidized by this oxidant. MITCHELL[4] observed that considerable error is caused by the presence of hypophosphite when ferrous salts are titrated by potassium dichromate. This is evidently due to a secondary reaction between potassium dichromate and hypophosphite induced by the primary fast reaction between potassium dichromate and ferrous iron. We have now observed that ceric sulphate and sodium vanadate solutions give accurate results when ferrous iron solutions are titrated in presence of hypophosphite or phosphite or both. Having established the advantage of these two reagents over potassium permanganate and potassium dichromate, we examined whether the reduction of Iron (III) to Iron (II) with hypophosphite is quantitative.

Experimental.

A known volume of ferric alum solution is treated with an excess of a 5 per cent solution of hypophosphite and hydrochloric acid to keep the acidity to the required level. (Sulphuric acid could not be substituted for hydrochloric acid since the reaction was found to be slow.) The mixture is then boiled for different lengths

of time, cooled under the tap and the ferrous iron formed is titrated with a standard solution of ceric sulphate using n-phenyl anthranilic acid as indicator. The ferric alum solution is standardized by reduction with stannous chloride and titration against standard ceric sulphate. The results of one of the several estimations carried out are recorded in Table 1.

Table 1.

Iron taken = 1.0520 millimols; Acid concentration = 2 N HCl.

Time of reaction (minutes)	Iron found (millimols)	Time of reaction (minutes)	Iron found (millimols)
5	1.0160	20	1.0500
10	1.0400	30	1.0500
15	1.0500		

Results in the above table show that the reaction is complete in 15—20 min. The influence of the acid concentration has also been studied and it was found that quantitative reduction of iron (III) was affected by hypophosphite at an acid concentration of 2—3 N, the time of the reaction being 15—20 min. At higher or lower acid concentrations the reduction was found to be incomplete during this time.

The method outlined above has been adopted for estimations of iron over a wide range of concentrations and the results obtained were in good agreement with the standard method. Some results are given in table 2. The titration of the ferrous iron can be carried out either with ceric sulphate or sodium vanadate (Table 2).

Table 2.

Iron taken (millimols)	Iron found (millimols)	Iron taken (millimols)	Iron found (millimols)
1.7010	1.6995	0.3520	0.3510
1.1340	1.1320	0.2539	0.2535
0.9320	0.9310	0.1720	0.1710
0.7040	0.7020	0.0847	0.0847

Summary.

A new method for the reduction of Iron (III) to Iron (II) with hypophosphite is suggested. The iron solution is treated with an excess of sodium hypophosphite and hydrochloric acid (overall concentration 2 N) and the mixture boiled for 15—20 min. After cooling, the ferrous iron formed is titrated with standard ceric sulphate or sodium vanadate.

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References.

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Über die Anwendbarkeit einer colorimetrischen Platinbestimmung in Platforming-Katalysatoren.

Von

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Bei der Bestimmung des Platins in den Platforming-Katalysatoren ergeben sich nach den bisher angewandten Methoden häufig Schwierigkeiten. Die Katalysatoren bestehen aus dem die Spalt- und Isomerierungsfunktion ausübenden Träger (Al_2O_3) und etwa 0,5% Platin, das meist metallisch vorliegt. Es ist schwer, Träger und Platin gleichzeitig vollständig aufzuschließen. Man verwendet dazu hauptsächlich einen Schmelzaufschluß nach dem Kupellationsverfahren. Das isolierte Platin wird anschließend gewogen oder auf nassem Wege gravimetrisch bestimmt. Beide Arten der Bestimmung sind zeitraubend.

Sowohl der Aufschluß des Katalysators als auch die Bestimmung des Platins können jedoch ohne Einbuße an Genauigkeit wesentlich vereinfacht und beschleunigt werden, wenn der Aufschluß auf nassem Wege erfolgt und das Platin in der verdünnten Katalysatorlösung nach dem von G. H. AYRES u. A. S. MEYER[1] in allen Einzelheiten untersuchten spektrophotometrischen Zinn(II)-chloridverfahren bestimmt wird[2]. An Stelle des Spektrophotometers kann auch ein einfaches lichtelektrisches Colorimeter verwendet werden (z. B. das Colorimeter von Dr. B. LANGE, Modell 6). Bei vorhandener Eichkurve wird für eine Doppelbestimmung ausgehend von der feingemahlenen Durchschnittsprobe, eine Zeit von etwa 1½—2 Std benötigt.

Der Katalysatorträger zieht besonders während des Vermahlens begierig Wasser an. Es ist daher unbedingt notwendig, von dem zur Einwaage vorbereiteten gemahlenen Katalysator gleichzeitig mit der Platinanalyse in einer gesonderten Einwaage den Glühverlust zu bestimmen und den ermittelten Platingehalt auf diese geglühte Substanz zu beziehen. Die Glühtemperatur muß so hoch gewählt werden, daß das