[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Volumetric Determination of Nitrates with Ferrous Sulfate as Reducing Agent

BY I. M. KOLTHOFF, E. B. SANDELL AND B. MOSKOVITZ

The only accurate method for the volumetric determination of nitrate is based on its reduction to ammonium or ammonia and distillation of the latter according to standard procedures. Other methods based on the quantitative determination of the oxidizing power of nitrate in strongly acid medium have been proposed in the literature,[1] but most of them require special apparatus, are time consuming, not very accurate and the results are seriously affected by the presence of air. In addition many reducing agents do not react in a simple stoichiometric way with nitric acid, but yield mixtures of oxides corresponding to various steps of oxidation of nitrogen. In the present work attempts were made to use hydrazine sulfate, arsenious oxide and antimony trichloride as reducing agents, but with unsuccessful results, the reaction mechanisms being very complicated and affected by slight changes in experimental conditions. The iodimetric method based on the quantitative reduction of nitric acid to nitric oxide by hydrogen iodide has been advocated repeatedly in the literature but cannot be recommended, since even traces of oxygen have a detrimental affect upon the results. Therefore it was decided to make a systematic study of the well-known reaction between nitric acid and ferrous iron, the latter being able to reduce the nitrate quantitatively to nitric oxide. The quantitative application of this reaction originated with Gossart,[2] who made it the basis of a direct titration using potassium ferricyanide as an outside indicator. The method yields only approximate results and has been modified by various authors. Recently L. Szebellédy[3] has shown that the appearance of the pink color of the ferrous–nitrogen oxide complex can be used as an indication of the end-point, but his procedure cannot be used for an accurate determination of nitrate. Pelouze[4] recommended the use of an excess of ferrous iron, titrating the latter back with permanganate. His method has been investigated and modified by various authors[5] but has not become a standard procedure, mainly for the following reasons: (a) the reaction between nitrate and ferrous iron

$$3Fe^{++} + NO_3^- + 4H^+ \longrightarrow 3Fe^{+++} + NO + 2H_2O$$

proceeds relatively slowly. Even in strongly acid medium in the presence of much hydrochloric acid a long period of boiling is required for the com-

---

[1] For a fairly complete review of the methods previous to 1913, see H. Beckurts, "Die Methoden der Maszanalyse," Verlag Fr. Vieweg- und Sohn, Braunschweig, 1913.

[2] Gossart, *Compt. rend.*, **24**, 21 (1847).

[3] L. Szebellédy, *Z. anal. Chem.*, **73**, 145 (1928); **74**, 232 (1928).

[4] Pelouze, *Ann. chim. phys.*, [3] **20**, 129 (1847).

[5] See Beckurts, Ref. 1, p. 522.

pletion of the reaction. (b) Nitric oxide is easily oxidized by oxygen and therefore precautions must be taken to exclude air during the reaction. (c) A strongly acid solution of ferrous iron is fairly rapidly oxidized by air.

In the following a simple procedure, based on the reaction between nitric acid and ferrous iron, has been developed which gives accurate and reproducible results.

Experimental

Reagents and Chemicals Used

Potassium nitrate C. P. twice recrystallized from water and dried at 120°.

0.18 *N* ferrous ammonium sulfate C. P. in 1 *N* sulfuric acid. A brief study of the influence of the acid concentration upon the stability (air oxidation) of ferrous iron solutions was made. Solutions of ferrous iron in 0.05, 0.1, 0.2, 0.5, 1 and 2 *N* sulfuric acid, respectively, were allowed to stand in partly filled glass-stoppered bottles. They were titrated at intervals of a week over a period of three to five weeks. It appeared that the solution in 1 *N* sulfuric acid was most stable. It is recommended, however, that the solution of ferrous ammonium sulfate be standardized each day before use. The use of 0.18 *N* ferrous iron is most convenient in working with quantities of potassium nitrate ranging from 0.080 to 0.22 g. when back titration is made with 0.1 *N* dichromate.

0.1 *N* potassium dichromate (a weighed amount of the pure salt made up to volume).

1% ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) in water.

1% solution of barium diphenylamine sulfonate in water as indicator in the titration of ferrous iron with dichromate. Diphenylamine and diphenylbenzidine can be used as well.

Sodium bicarbonate C. P. (tested for nitrate and other impurities which may have an oxidizing action).

C. p. hydrochloric acid, sulfuric acid and phosphoric acid.

In the first experiments mixtures of potassium nitrate with sulfuric acid or hydrochloric acid or both, from which the air had been removed, were boiled with excess ferrous sulfate in Erlenmeyer flasks, Bunsen valves being used to prevent entrance of air, until reduction was complete; after cooling and dilution with water, the ferrous iron remaining was titrated with dichromate. Solutions containing hydrochloric acid were reduced with greater speed than those containing sulfuric acid, but under all conditions boiling for more than half an hour was required to accomplish quantitative reduction of the nitrate. Therefore the effect of various substances on the rate of reaction was studied. It appeared that molybdate acts as a powerful catalyst in the reaction between nitrate and ferrous iron in strongly acid medium. Later it was found that Hac and Netuka[6] have made use of the same catalyst in the gasometric determination of nitrate with ferrous chloride as reducing agent.

After a systematic study the following volumetric procedure was developed.

Apparatus.—The apparatus adopted consisted of a 250-cc. Erlenmeyer flask fitted with a two-holed rubber stopper. A medicine dropper of 3 cc. capacity previously filled with ammonium molybdate solution was inserted in one of the holes and, in the other, a rubber tube leading to a saturated solution of sodium bicarbonate contained in a beaker. An Erlenmeyer flask with ground-glass stopper and dropping funnel can be used instead of the apparatus described.

The apparatus permits the addition of the catalyst after all the air has been expelled by boiling; the tube leading to the bicarbonate solution prevents the escape of irritating

---

(6) Hac and Netuka, *Coll. Czechoslov. Chem. Comm.*, **1**, 521 (1928). *Cf.* R. Hac, *Eighth Intern. Congress of Applied Chem.*, **1**, 207 (1912).

hydrochloric acid fumes into the atmosphere of the room during boiling and permits cooling the flask in a carbon dioxide atmosphere.

Procedure.—A 0.1- to 0.2-g. sample of nitrate is introduced into the 250-cc. Erlenmeyer flask; 25 or 50 cc. 0.18 *N* ferrous iron solution are added (an excess of approximately 50% of ferrous iron is recommended) and 70 cc. 12 *N* hydrochloric acid. Then 3 to 5 g. of solid sodium bicarbonate is added carefully in small portions to displace the air from the flask and immediately thereafter the flask is closed with the stopper, from which a rubber tube leads to a suspension of 50 g. of sodium bicarbonate in 100 cc. of water. The dropper fitted into the other hole of the stopper contains 3 cc. of 1% ammonium molybdate solution. The solution is heated and the catalyst added after two or three minutes' boiling. The boiling is continued for ten minutes, the sodium bicarbonate suspension then replaced with a fresh saturated solution, the flask removed from the flame and immersed in cold water. After cooling to room temperature the flask is unstoppered and 35 cc. of 6 *N* ammonium acetate for every 50 cc. of solution to be titrated and 3 to 5 cc. 85% phosphoric acid are added. The acetate reduces the concentration of the strong acid to between 1 and 2 *N*. The solution, which should have a volume of 100 to 150 cc., is slowly titrated with 0.1 *N* dichromate using 6 to 8 drops of diphenylamine sulfonate (or diphenylamine or diphenylbenzidine) as indicator. The ferrous iron solution is standardized under the same conditions as described above.

1 cc. of 0.1000 *N* iron is equivalent to 3.370 mg. of potassium nitrate or 2.067 mg. of NO_3.

The procedure gives results accurate to within 0.5% as may be inferred from data given in Table I.

TABLE I

VOLUMETRIC DETERMINATION OF NITRATE

Potassium nitrate Taken, g.	Potassium nitrate Found, g.	Error, %	Potassium nitrate Taken, g.	Potassium nitrate Found, g.	Error, %
0.2528	0.2526	−0.1	0.1015	0.1012	−0.3
.2030	.2026	− .2	.1011	.1010	− .1
.2021	.2021	.0	.1011	.1008	− .3
.2021	.2021	.0	.1011	.1011	.0
.2276	.2277	+ .05	.0910	.0909	− .1
.1539	.1534	− .3	.0811	.0810	− .1
.1210	.1212	+ .2	.0506	.0505	− .2
.1320	.1318	− .15	.0203	.0202	− .5
.1015	.1015	.0	.0202	.0202	.0

Notes.—1. The titer of the ferrous iron solution is determined in a blank under the same conditions as in the presence of nitrate. The titer is the same as found by direct titration, if air does not gain access to the solution. It may be mentioned that the air sensitivity of the ferrous iron is increased in the presence of molybdate.

2. Indication that the reduction is complete is obtained from the color of the solution during boiling. Upon addition of molybdate the solution becomes dark brown owing to the formation of the ferrous sulfate-nitric oxide complex; after two or three minutes' boiling, during which the NO is expelled, the color brightens to a reddish-orange. The orange color lightens to yellow upon cooling to room temperature.

3. Even less than the recommended amount of molybdate gives quantitative reduction within ten minutes. Experiments were made with 100 mg. of potassium nitrate in the presence of 5, 10, 20 and 30 mg. of molybdate, respectively. In all cases quantitative results were found.

4. Ions which are readily reduced by ferrous iron, such as chlorate, bromate and iodate, interfere with the nitrate determination. However, in most cases it will be

possible to develop a procedure by which the oxidizing agents can be titrated without interference by nitrate, whereas the sum of nitrate and other oxidizing agent can be determined by the procedure described above. Small amounts of perchlorate do not affect the results; however, with large amounts of perchlorate slightly high results are found. With 150 mg. of potassium nitrate and 800 mg. of ammonium perchlorate the results were 1 to 1.5% high. It may be mentioned that manganous ion and phosphoric acid do not interfere with the determination.

The procedure described can also be applied to the determination of small quantities of nitrate between 20 and 2 mg. In the determination of very small amounts of nitrate the solutions of dichromate and ferrous iron used were four to six times more dilute than recommended in the standard procedure. The further manipulations were carried out as described above with the exception that the solution was boiled at a rate which resulted in a final volume of approximately 50 cc. After cooling, 20 cc. of 6 *N* ammonium acetate and 10 cc. of phosphoric acid were added. The solution was diluted to a volume of 100 to 150 cc. and 4 drops of indicator added for each 50 cc. of solution. The blanks were made in the same way as the determinations. With these dilute solutions the blanks should be run under the experimental conditions since a slight oxidation of the ferrous iron during the procedure results in a relatively large error.

The figures in Table II show that the results are accurate to within 3% with quantities of nitrate between 12 and 2 mg.

TABLE II

DETERMINATION OF SMALL AMOUNTS OF NITRATE

Nitrate in mg. NO_3		Error, %	Nitrate in mg. NO_3		Error, %
Taken	Found		Taken	Found	
12.27	12.10	−1.4	4.91	4.86	−1.0
11.86	11.70	−1.3	2.45	2.40	−2.0
11.86	11.70	−1.3	2.45	2.38	−2.8
4.91	5.04	+2.6	2.45	2.38	−2.8
4.91	4.82	−1.8			

Summary

A procedure has been described for the volumetric determination of nitrates, in which ferrous sulfate is used as reducing agent in strong hydrochloric acid medium with molybdate as catalyst. With the aid of this procedure a nitrate determination can be made in twenty minutes. With quantities of nitrate greater than 20 mg. the maximum error is 0.5%, the error decreasing as the size of the sample increases. Amounts of nitrate of the order of a few milligrams can be determined with an accuracy of about 2%.

MINNEAPOLIS, MINNESOTA

RECEIVED NOVEMBER 17, 1932
PUBLISHED APRIL 6, 1933