

Assay of Sodium Nitrite

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The official U.S.P. assay for sodium nitrite which employs standard permanganate and standard oxalate solutions is compared with a new method using standard ceric sulfate solution. The proposed method is shown to be more accurate than the official method by comparison of the results with the absolute purity of the sodium nitrite determined by phase solubility analysis. The official N.F. XI method for sodium nitrite tablets involving determination of chloride produced by reduction of potassium chlorate is shown to give unacceptable precision.

THIS IS the second in a series designed to compare methods using standard permanganate solution with those employing standard ceric solution. The purpose of this series is to provide data to urge the adoption of standard ceric solution as the strong oxidizing agent of choice (1).

REAGENTS

Standard Sodium Oxalate.—A 6.5576-Gm. quantity of reagent sodium oxalate, previously dried to constant weight at 110°, was dissolved in enough water to make 1 L. This solution is 0.1591 *N*.

Standard Potassium Permanganate.—This was prepared and standardized according to directions given in U.S.P. XVI (2). Three replicate determinations of normality gave a value of 0.1070 *N*, S.D. 0.0001.

Standard Ceric Sulfate.—This was prepared and standardized against arsenic trioxide according to U.S.P. XVII (3). Three replicate determinations of normality gave a value of 0.0909 *N*, S.D. 0.0003.

Standard Silver Nitrate.—A 8.8974-Gm. quantity of reagent silver nitrate previously dried at 110° was dissolved in enough water to make 1 L. The calculated normality of this solution is 0.1112 *N*. Subsequent standardization in triplicate against sodium chloride of known purity gave a value of 0.1111 *N*, S.D. \pm 0.0001.

Standard Ammonium Thiocyanate.—This was prepared and standardized according to U.S.P. XVI (4). Three replicate determinations of normality gave a value of 0.1056 *N*, S.D. \pm 0.0001.

Potassium Chlorate Reagent U.S.P. XVI.—This also was utilized.

METHODS

A.—U.S.P. XVI Method for Sodium Nitrite (5).—This method, in which the standard oxalic acid solution was replaced with standard sodium oxalate, was employed. This involves reaction of a solution of the sodium nitrite sample with a known volume of

standard permanganate, addition of a known volume of standard oxalate, and titration of the excess oxalate with standard permanganate.

B.—Proposed Ceric Sulfate Method.—A weighed sample of sodium nitrite, about 500 mg., is dissolved in enough water to make 100.0 ml. This solution is titrated into 50.0 ml. of standard ceric sulfate solution. The end point is the disappearance of the yellow color of the ceric ion.

C.—N.F. XI Method for Sodium Nitrite Tablets (6).—This method involves reaction of an extract of a weighed sample of pulverized tablet containing about 350 mg. of sodium nitrite with a saturated potassium chlorate solution, determination of chloride by the Volhard method by addition of a known volume of standard silver nitrate to the nitric acid-acidified aliquot, and determination of excess silver ion by titration with standard thiocyanate solution using ferric ammonium sulfate T.S. (7) indicator. A weighed sample of sodium nitrite without excipients was used instead of the aliquot of tablet extract specified in the monograph.

D.—Phase Solubility Analysis.—This technique for determining absolute purity is described by Tarpley and Yudis (8). Absolute alcohol was the solvent used. Twenty-three points were fitted to a straight line by the method of least squares and the slope determined algebraically.

Table I shows a comparison of the four methods given above.

DISCUSSION

A single sample of "Baker analyzed" sodium nitrite, lot No. 2145, was used throughout the investigation. The value obtained in method *A* agrees well with the labeled assay of 98.7%. The official A.C.S. assay method is similar to method *A*, except that standard oxalate is replaced by standard ferrous ammonium sulfate (9).

Application of the *t* test to methods *A* and *B* shows that the difference is highly significant (99% confidence level). From this and the absolute value determined by method *D*, it is concluded that the proposed method *B* is superior to the official method *A*.

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TABLE I.—COMPARISON OF METHODS FOR THE DETERMINATION OF SODIUM NITRITE

	Method			
	A	B	C	D
Determinations, No.	9	6	15	...
Purity, %	98.5	100.4	98.7	99.97
S.D. \pm	0.6	0.1	1.5	...

In addition to superior accuracy and probably better reproducibility, the proposed method *B* makes use of one stable standard solution instead of two unstable standard solutions and requires less time for the performance of the assay. It can be adapted also to automatic equipment by use of a potentiometric end point indication with a platinum-camel electrode pair.

Preliminary investigations of method *B* failed to disclose any redox indicator which reacted rapidly enough to be useful in detection of the end point. No metallochrome indicators were tried. Potentiometric end point indication did not seem necessary in view of the high accuracy and reproducibility obtained with the visual end point.

The disbelief in the poor replication obtained in method *C* is shown by the large number of replicates which were done in groups of three on separate days. The high standard deviation for the complete series also held for each group of three. No reason could be found for the poor precision obtained. Blanks were 0.05 ml. of 0.1112 *N* silver nitrate.

The official method for sodium nitrite in tablets was adopted presumably because the official permanganate method for pure sodium nitrite gives high values for tablets containing sugar excipients, as permanganate oxidizes sugars. No such interference is anticipated for titration with ceric ion, since this agent, unlike permanganate, oxidizes neither sugars nor chloride ion.

A suggested procedure for sodium nitrite tablets is as follows: transfer a portion of pulverized tablets containing about 500 mg. of sodium nitrite to a 100-ml. volumetric flask. Add about 25 ml. of water, shake well, and add enough water to make 100 ml. Filter, rejecting the first 20 ml. of filtrate. Titrate the filtrate into 50.0 ml. of standard ceric sulfate solution.

This proposed method could not be tested, as no commercial source of sodium nitrite tablets could be found.

The high value for the standard deviation in method *C* prevents proper application of the *t* test to the averages obtained by methods *B* and *C*. If the *t* test is applied, however, the difference in averages is not significant at the 95% confidence level.

CONCLUSIONS

From the data presented, it is concluded that the proposed ceric sulfate method is more reliable and more accurate than the official methods. The proposed assay is easier to perform, requires less time, fewer reagents, and is capable of adaptation to automatic equipment. Briefly, it is superior in every way to the official methods.

REFERENCES

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