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ABSTRACT

Measurement of the hydrogen ion consumed in the nitrite oxidation of azide is the basis for a simple and accurate method for determining azide ion in the range from 0.05 to 1.5 millimoles. The method is applicable to different procedures for obtaining soluble azide from insoluble metal azides, as illustrated by the analyses of silver, lead and palladium azides. The precision is comparable to that of other weak acid-strong base titrations.

Azide ion has been analyzed by a variety of reactions. Macro methods, both gravimetric (9) and volumetric (7,11), are based upon the low solubility of silver azide, and upon the quantitative oxidation of azide to nitrogen with cerate (1), permanganate (16), iodine (6) and nitrite (13,15) as titrants. Semimicro methods make use of the red complex FeN_3^{++} in a spectrophotometric determination (14) and of the Kjeldahl determination of nitrogen after thiosulfate reduction (12). A gas volumetric method involves the measurement of nitrogen liberated by cerate oxidation (3). These methods were developed for application to sodium azide and to primer components.

Silver precipitation methods usually give low results because of the appreciable solubility of silver azide. The various redox titrimetric methods use unstable titrants which must be standardized periodically, and oxygen must be excluded in one of these methods (15). The color of FeN_3^{++} is unstable, varies with the pH and is of no use in the presence of thiocyanate, a constituent of some primers. The Kjeldahl method is subject to positive errors; any ammonium ion or organic nitrogen present is counted as azide. The nitrogen volumetric method requires equipment and skills which may not be available for an occasional analysis of azide. A recent paper reported the analysis of palladium azide by a thermal decomposition technique in which the nitrogen evolved was measured (2). This method was not very satisfactory, as some samples were lost by explosion during analysis.

The method presented here was developed to overcome most of these difficulties and is based upon the measurement of the hydrogen ions stoichiometrically consumed in the following reaction (5):

$$2H^+ + N_3^- + NO_2^- = H_2O + N_2 + N_2O \quad .$$

This simple approach does not appear to have been used before, though it

offers some advantages. Large amounts of chloride and thiocyanate do not interfere under the conditions specified and the titrants, perchloric acid and sodium hydroxide, are stable. It is not necessary to standardize the unstable nitrite solution, as it is used in excess. As in some other methods, the azide must be in solution, and metal ions which hydrolyze at pH 8-9 must be absent; methods for meeting these conditions in the analyses of three insoluble azides are used and discussed. The precision for the final titration is the same as that for other weak acid-strong base titrations.

EXPERIMENTAL

Materials. Solutions of sodium nitrite, 1.0 M (fresh once a week), sodium thiocyanate, 1.0 M, and sodium chloride, 2.0 M, were prepared from reagent grade chemicals (Baker and Adamson). Carbonate-free, 0.1002 M sodium hydroxide (Acculute) was checked against weighed amounts of N.B.S. primary standard potassium acid phthalate, using the phenolphthalein end point. Perchloric acid, 0.1067 M, was obtained by dilution of the 70% acid (G. F. Smith Chemical Co.) and standardized against the sodium hydroxide, using phenolphthalein. One hundredth molar acid and base were prepared by dilution of the 0.1 M solutions. Sodium azide (Eastman-Practical) was homogenized by grinding and tumbling; titration with cerate (1) indicated a purity of 99.2 ± 0.1%. A 0.1001 M solution (later 0.1000 M) made by weighing the azide, was also checked by cerate titration. Shiny, spectroscopically pure palladium metal was dissolved in red fuming nitric acid and heated to fumes with perchloric acid to displace the nitrate. The solution was diluted to give 0.1000 M palladium perchlorate in about 0.2 M acid.

Silver azide and lead azide samples were prepared by adding sodium azide solution to stoichiometric quantities of 0.1000 M solutions of the respective metal nitrates (B. and A. reagent). The analytical procedures were

tested on the resulting precipitates in the presence of the supernatant solutions because of the unstable nature of the dry metal azides. Palladium azide was similarly prepared from the palladium perchlorate solution and, in some cases, washed either with water to pH 4.0 or with 0.1 M perchloric acid, by centrifugation and decantation. The precipitate was analyzed in the final wash solution, the palladium gravimetrically as the dimethylglyoxamate (8).

General Method. Add 3 drops of phenolphthalein indicator to 50 ml. of solution free of all metal ions hydrolyzing at pH 8-9, and containing 0.5-1.5 millimoles of azide. Adjust the initial pH of the solution to the phenolphthalein end point with the acid or base, if necessary. While stirring, add 20 ml. of 0.1 M perchloric acid for every millimole of azide expected plus about 20% excess. Add 2.5 ml. of 1.0 M sodium nitrite from a graduated pipet and allow the reaction to proceed with stirring for 5-10 seconds. Titrate with 0.1 M sodium hydroxide, washing down the spray caused by gas evolution just before reaching the phenolphthalein end point. The titration should be completed without undue delay (3-4 min.) to prevent loss of nitrous acid by decomposition. Five hundredths to 0.15 millimoles of azide may be determined by using 0.01 M acid and base if the solution is stirred for 3 minutes after the addition of 2.5 ml. of 1.0 M sodium nitrite.

Silver Azide. Add 5 ml. of 2 M sodium thiocyanate to the sample containing 0.05-1.5 millimoles of azide in 50 ml. of water and stir for 2 minutes. Proceed as described in the general method, titrating in the presence of the silver thiocyanate precipitate.

Lead Azide. Add 30 ml. of water and one ml. of 70% perchloric acid to the sample in a 50 ml. distilling flask. Stopper immediately and distill the hydrazoic acid into 20 ml. of 0.1 M or 0.01 M sodium hydroxide, depending upon the amount of azide expected; take normal precautions to avoid excessive exposure to carbon dioxide in air. Recovery of hydrazoic acid is complete when

20 ml. of distillate has been collected. Proceed as described in the general method.

Palladium Azide. Add 5 ml. of 2.0 M sodium chloride and one ml. of 70% perchloric acid to the sample in 30 ml. of water. Proceed as with lead azide.

DISCUSSION

For rapid and complete oxidation of azide ion, it is necessary to have excess acid at a pH of less than 3.0 before addition of sodium nitrite, a large excess of nitrite ion and soluble azide. Nitrous acid is unstable in strongly acidic solutions, so it is better to add the sodium nitrite after acidification to avoid localized high acid concentrations. Hydrazoic acid is moderately volatile, boiling at 37° C.; however no losses were encountered when the initial volume was varied from 20 to 100 ml. or when the excess acid was varied from 0.1 to 3 millimoles, in 50 ml., while holding the sodium azide constant at 1.5 millimoles. In the case of silver azide an excess of 3 millimoles of acid cannot be tolerated. The thiocyanate, used for the metathesis of the sample, consumes nitrous acid to from nitrosylthiocyanate, which decomposes (10), leading to high results. The presence of 20% excess perchloric acid in the specified volume allows the azide-nitrite reaction to proceed without interference from the nitrosylthiocyanate side reaction.

The titration of a 1.5 millimole azide sample was followed potentiometrically. Upon the addition of sodium nitrite there was an immediate increase from the initial pH of 1.64, followed by a further increase to a constant pH of 2.85 after 5-10 seconds, indicating completion of the reaction. When all reactants except sodium nitrite were diluted tenfold, a reaction time of about 3 minutes was noted, but when the sodium nitrite was also diluted tenfold, the reaction was not completed within 3 minutes. The interrelated effects of azide, nitrite and hydrogen ion concentrations are not known, but the titration of 0.01 M azide appears to be about the limit of application of the method.

The final titration is for nitrous acid, equivalent in amount to the unreacted hydrogen ion added; hence, the pH before adding standard perchloric acid must be adjusted to the phenolphthalein end point to avoid low results from excess acid or high results from excess base.

The problem of adapting the general method to heavy metal azides such as silver, lead and palladium azides, is basically one of determining hydrogen ion in the presence of easily hydrolyzable metal ions. The procedure may be applied directly if the insoluble metal azide can be metathesized or complexed with an anion which yields a metal ion activity much lower than that of the metal hydroxide, and which does not undergo oxidation or reduction with nitrite or azide. Thiocyanate rapidly and completely replaces azide from silver azide in the concentration applied and the product of metathesis, silver thiocyanate, has a solubility product about 10^{-4} that of silver hydroxide. Chloride can be used to metathesize silver azide, but the reddish-gray color, caused by light, interferes with detecting the phenolphthalein end point. If the proper conditions for metathesis or complexing cannot be obtained, the long-standing method of distillation of hydrazoic acid (4) may be used to separate an interfering metal ion such as lead. Large amounts of chloride, thiocyanate, nitrate and perchlorate do not interfere in any of these procedures; in this respect they are superior to the direct acid titration after distillation of hydrazoic acid (4).

The results given in Table I show little difference in precision for the determinations of sodium, lead and silver azides, though three somewhat different procedures are used.

Table I. Statistical Summary

No. of Samples	Millimoles of azide			Standard deviation	Relative std. dev., %
	Added	Ave. found	Range		
			Sodium Azide		
24	1.502	1.504	1.502-1.508	0.002	0.1
10	0.500(5)	0.500	0.499-0.502	0.001	0.2
10	0.1502	0.1503	0.1496-0.1510	0.0004	0.3
10	0.0500(5)	0.0502	0.0499-0.0505	0.0002	0.5
			Lead Azide		
5	1.502	1.499	1.495-1.502	0.003	0.2
5	0.500(5)	0.500	0.496-0.506	0.004	0.6
5	0.1502	0.1500	0.1497-0.1509	0.0005	0.3
5	0.0500(5)	0.0495	0.0486-0.0500	0.0005	1.0
			Silver Azide		
5	1.500	1.500	1.499-1.500	0.001	0.1
5	0.500	0.500	0.499-0.501	0.001	0.2
5	0.1500	0.1497	0.1489-0.1504	0.0006	0.4
5	0.0500	0.0504	0.0497-0.0512	0.0006	1.2

Palladium and azide evidently form strong complexes, as the azide is quantitatively distilled from palladium only with great difficulty unless a large excess of another strong complexing anion, such as chloride, is present. Chloride complexing is not strong enough, however, to prevent hydrolysis of palladium ion at pH 8-9, and so the azide must still be separated by distillation. Samples were prepared in the distilling flask with a $Pd^{++}:N_3^-$ ratio of exactly 1:2 and containing 16.81 mg. of azide. Distillation gave a recovery of about 5% when no chloride was added. When chloride was added as in the recommended procedure, 16.78 ± 0.16 mg. of azide was recovered. Identification of the unstable compound palladium azide has recently been reported (2), using analytical methods which gave a ratio for $Pd^{++}:N_3^-$ of 1:1.9 for a product which had been washed with water to a pH of 4.0 by centrifugation and decantation. When this product was analyzed for azide by the method given here, and for palladium by the gravimetric dimethylglyoxine method, the $Pd^{++}:N_3^-$ ratio was found to be 1:1.76 ± 0.04. The precipitate washed with water had either decomposed, with loss of nitrogen, or hydrolyzed, with loss of hydrazoic acid in the wash. Similar precipitates washed with 0.1 M perchloric acid gave a ratio of 1:1.80 ± 0.01. Finally, samples washed with either water or 0.1 M perchloric acid and allowed to stand, slowly liberated a gas, presumably nitrogen. The amount of nitrogen formed in an hour was enough to float the precipitate. It appears that the low results for azide are due, at least in part, to decomposition of palladium azide, though some hydrolysis in both water and 0.1 M acid may be a contributing factor.

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