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**ESTIMATION OF NITRATES AND NITRITES  
IN BATTERY ACID**

BY

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# ESTIMATION OF NITRATES AND NITRITES IN BATTERY ACID

By L. B. Sefton

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## I. INTRODUCTION

### 1. OCCASION FOR THE INVESTIGATION

In connection with the testing of sulphuric acid to be used in storage batteries, it became apparent that the methods commonly used for the detection and estimation of small amounts of nitrates and nitrites in sulphuric acid differed not only in sensitiveness, but also in reliability. Since the usual specifications for battery acid do not allow more than a few thousandths of 1 per cent of nitrogen in any form, a high accuracy is required of the method used for its estimation. The determination of nitrogen as ammonia presented no difficulties. Many papers have been written about methods for the determination of small amounts of nitrates and nitrites in water, and a few of them can be used in a medium of sulphuric acid, but no comparison seems to have been made of methods directly applicable to battery acid.

This Bureau through the kindness of a number of manufacturers has obtained considerable information about the methods in commercial use at the present time. These methods differ

widely. For the most part they are qualitative methods by which an experienced operator may quickly decide whether or not the material is suitable for batteries. An increasing realization of the importance of the purity of battery acid makes quantitative methods desirable.

## 2. SCOPE OF THE WORK

Practical reasons render it necessary that the methods selected should combine reliability, accuracy, and sensitiveness with speed and simplicity. Elaborate apparatus and costly reagents are to be avoided as well as any preliminary treatment of the samples by evaporation or neutralization which tend to produce loss or contamination. It is also important that the reagents selected should not be affected by the other impurities likely to be present in battery acid. These restrictions make colorimetric methods alone applicable. A comparative study was made of methods used for the detection of nitrates and nitrites in sulphuric acid. The result of that study is embodied in this paper whose purpose is (1) to point out the methods proven to be most reliable and (2) to suggest the best conditions for using them.

One of the main facts brought out by the various experiments was that nitrates, as such, could not be estimated in the presence of nitrites, if the battery acid, either fresh or used, had been made up for more than three days. In view of that fact the methods selected for nitrates are those which will give the same results with nitrites under conditions above stated, so that the final results of analysis may be expressed in terms of nitrates and nitrites. The use of urea and hydrazine sulphate which has been suggested<sup>1</sup> to prevent the interference by nitrites of nitrate determinations was not satisfactory. Urea did not entirely prevent the interference and hydrazine sulphate prevented the formation of characteristic colors with nitrates as well as with nitrites.

For some reason not yet determined fresh battery acid and acid which had been used in batteries showed under the same given set of conditions appreciable differences in the depths of color given by the various reagents studied. These differences varied in amount and direction with the reagents, but were great enough in every case to make it necessary that the standards be made up

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<sup>1</sup> Niemczycki, Arch. Chem. Mikros, 4, p. 125 (C. A., 5, p. 2475; 1911). Sen and Dey, Z. anorg. Chem., 74, p. 52; 1912.

with used electrolyte (nitrate and nitrite free) when the sample of acid under examination has been used in a battery.

According to the specifications in current use, the impurities most often mentioned are nitrates, nitrites, ammonia, arsenic, chlorides, copper, and iron. Standard solutions of these substances were made up in a sulphuric-acid solution of specific gravity 1.28 and used in all experiments described in this paper.

## II. METHODS FOR THE DETERMINATION OF NITRATES

### 1. DIPHENYLAMINE METHOD <sup>2</sup>

Although the unreliability of this method has been pointed out by Caron <sup>2</sup> and others, it is desired to emphasize that unreliability in this paper, because of the common use of the method in the commercial testing of battery acid. Tests showed that the characteristic blue color given by the reagent with nitrates was given also by nitrites, iron, and arsenates, and by sulphuric acid itself, to such an extent as to render the method useless.

### 2. "HYDROSTRYCHNIQUE" METHOD

This method, first suggested by Deniges,<sup>3</sup> has been found to be satisfactory if used as follows: Prepare the reagent by dissolving 1 g of strychnine sulphate in 100 cc of water. Immediately before using, mix 5 cc of this solution with 5 cc of concentrated hydrochloric acid, and reduce by allowing to stand for 10 minutes with 4-5 g amalgamated zinc. Use the resultant "hydrostrychnique solution" for the tests.

To 10 cc of the battery acid (specific gravity about 1.28) to be tested, add 0.5 cc of the hydrostrychnique solution and mix well. Add 10 cc concentrated sulphuric acid (specific gravity 1.83) and mix. If nitrates or nitrites are present, a vivid pink color, permanent for several hours, will develop. Compare at the end of five minutes with nitrate standards similarly and simultaneously treated.

The reagent was found to be unaffected by solutions containing 0.005-0.010 per cent of ammonia, arsenic, copper, and chlorides. A solution containing 0.005 per cent of iron gave an orange color. If iron is present in a nitrate or nitrite sample, this orange color so changes the hue of the characteristic pink color as to render the method useless for the quantitative determination of nitrates and

<sup>2</sup> Caron, *Annal. Chim., anal.*, 16, p. 211; 1911.

<sup>3</sup> Deniges, *Bull. Soc. Chim.*, 9, p. 544; *Annal. Chim. anal.*, 19, p. 221; 1914.

nitrites. Nitrites, as has been implied, give with the reagent in solutions of acid which have been made up for more than three days a pink color practically identical in hue and depth with that given by equivalent amounts of nitrates. The method is sensitive under the conditions given to one part per 5 000 000 with fresh acid. Since the color that it gives is much more stable than that given by brucine, its use is recommended when the acid under examination contains no iron and when iron-free zinc can be obtained.

### 3. BRUCINE METHOD <sup>4</sup>

This method is in use in the commercial testing of battery acid and gives good results when the conditions stated below are rigidly adhered to both in samples and standards.

The reagent is prepared by dissolving 0.2 g brucine in 100 cc of pure concentrated sulphuric acid. It must be made up fresh each time it is used. The solution has a faint yellow color.

To a 10 cc sample of the battery acid to be tested add double its volume of pure concentrated sulphuric acid and cool to room temperature (about 25° C). Add 2 cc of the reagent and mix quickly and thoroughly. If nitrates or nitrites are present a rose-red color will develop; this changes quickly to a sulphur yellow and then more slowly to a golden yellow. When the sulphur yellow appears, compare with standards similarly and simultaneously treated. The sulphur-yellow color is chosen as the end point, because the rose-red color changes too rapidly to permit of a satisfactory comparison with the standard and the golden-yellow color is not sensitive enough to different amounts of nitrates or nitrites. The chief disadvantage of the method is the number and varying rates of these color changes.

**EFFECT OF IMPURITIES.**—The brucine test was unaffected by the presence of 0.005 to 0.025 per cent of iron, arsenates, arsenites, chlorides, copper, and ammonia. In solutions of acid density below 1.70, nitrites affect it to the same extent as nitrates. Nitrites in solutions of 1.83 specific gravity have no effect upon it.

**EFFECT OF ACID DENSITY.**—Since preliminary tests showed that the production and changes of color with the brucine reagent were accelerated by increasing acid density, it was desirable to select a density at which the development of colors would occur within a convenient length of time. To determine this, a series of tests was made on samples whose volumes, temperatures, and

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<sup>4</sup> Lunge and Lwoff, *Zeit. angew. Chem.*, 7, p. 345; 1894. *Analyst.*, 38, p. 450; 1913.

nitrate concentrations were identical, but whose acid densities varied from 1.835 to 1.605. The time required for the development of the sulphur-yellow color varied from one-half minute in the first to one hour in the last. In the samples in which the density was greater than 1.735 the change from sulphur to golden yellow was so rapid as to make comparison with standards difficult. In samples in which the acid density was below 1.635, the change was so slow as to make comparisons unreliable. The best acid density was found to be between 1.65 and 1.70.

**EFFECT OF NITRATE CONCENTRATION.**—A set of experiments was made on samples whose temperature, sulphuric-acid concentration, and absolute nitrate content were the same, but whose nitrate concentration, i. e., whose volumes varied. The colors developed very much more rapidly in the samples whose nitrate concentrations were high. This fact tends to decrease the value of the method as a quantitative one.

**EFFECT OF TEMPERATURE.**—An increase in temperature produces with this method an increase in the speed of color production and change. A sample at 23° C showed a sulphur-yellow color in about two minutes, while a similar sample at 70° C gave the same color within 10 seconds.

**EFFECT OF THE AGE OF THE REAGENT.**—A very great difference was observed among samples treated under similar conditions with brucine solutions which had been made up for varying lengths of time. With a reagent made up for less than 15 minutes, one part of nitrate in 5 000 000 was easily detected; but with a solution made up for a couple of hours not more than one part nitrate in 2 000 000 could be detected, and with solutions made up for several days, only one part in 500 000.

**SENSITIVENESS.**—In fresh electrolyte, the method is accurate to one part of nitrates or nitrites in 5 000 000; in used electrolyte, to one part in 400 000.

**MODIFICATION OF THE BRUCINE METHOD.**—The indifference of brucine to iron makes it so valuable as a reagent that efforts were made to render it more sensitive with used acid. The net results of these efforts is a reagent prepared in much the same way as the "hydrostrychnique" reagent. One g of the brucine was dissolved in 2 cc concentrated sulphuric acid and that solution mixed with 50 cc water immediately before using; 5 cc of this solution mixed with 10 drops of concentrated sulphuric acid were allowed to stand in contact with 4 or 5 g of amalga-

mated zinc for 5 or 10 minutes; 2 cc of the resultant solution was used for each test.

The preliminary tests showed that this modified reagent was much more sensitive to nitrates and nitrites in used acid than the original brucine reagent. Unfortunately, however, it is affected by iron, though not to so great an extent as the "hydrostrychnique" reagent. The only advantage that it possesses over the latter reagent is the fact that it does not give any color with impurities other than iron.

### III. METHODS FOR THE DETERMINATION OF NITRITES

Nitrites are oxidized to nitrates in dilute sulphuric acid,<sup>5</sup> and it was further found that the rate of oxidation increased with the dilution of the acid. Experiments made on four solutions of equal initial nitrite concentration, but in acid of densities varying from 1.835 to 1.28 showed that the nitrites in the solution of 1.835 density had suffered no change after 10 days while that in the solution of 1.28 density was practically all changed to nitrates at the end of three days. Battery acid which has been made up for more than three days then is not likely to contain any nitrites, but since the methods in this paper are designed for the examination of any acid intended for battery purposes, three methods selected from a large number as those most likely to fulfill the requirements were studied.

#### 1. IODIDE METHOD <sup>6</sup>

It is desired to emphasize the unreliability of this method which although generally known to be unreliable in the presence of oxidizing agents—even in the presence of atmospheric oxygen<sup>7</sup>—continues to be used to some extent in the commercial testing of sulphuric acid. The modifications proposed<sup>7</sup> are not practicable with battery acid.

#### 2. INDOL METHOD <sup>8</sup>

This method was found to be a good qualitative one if used as follows: Prepare the reagent by dissolving 0.02 g of indol in 75 cc of 95 per cent ethyl alcohol. To 10 cc of the battery acid to be tested in a Nessler tube add 10 cc of concentrated sulphuric acid and 3 cc of the reagent and mix. If nitrites are present a

<sup>5</sup> Lunge, *Zeit. Angew. Chem.*, 15, p. 1; 1901.

<sup>6</sup> Blanc, *Annal. de Chim. Anal.*, 17, p. 216; 1912.

<sup>7</sup> Dienert, *Annal. Chim. Anal.*, 1, p. 4; 1919.

<sup>8</sup> M. Dane, *Bull. Soc. Chim.*, 9, p. 354; 1911.

permanent pink color appears. Unfortunately, however, a yellow color is also produced when only 0.001 to 0.002 per cent of ammonia, arsenates, arsenites, iron, chlorides, or copper are present. Although this yellow color affects the pink color to such a degree as to render the method useless for quantitative purposes, the interference is not so serious as to disqualify the method as a qualitative test for nitrites. The characteristic pink color was not affected by variations in acid density from 1.28 to 1.70, while above 1.70 the color tends toward yellow. When the nitrite content is below 0.001 per cent, and the acid density is above 1.35, the colors tend toward yellow. An acid density of 1.28 to 1.35 is recommended.

### 3. DIMETHYLANILINE METHOD <sup>9</sup>

This method was found to be the most satisfactory one for the detection of nitrites if used as follows: The reagent is prepared by dissolving 2 g of dimethylaniline in 3 cc concentrated hydrochloric acid and 25 cc of water. Three drops of the reagent are added to 25 or 30 cc of the battery acid to be tested and allowed to stand for 10 to 30 minutes. If nitrites are present, a yellow color appears. Compare with standards similarly and simultaneously treated. The test is unaffected by the presence of 0.005 to 0.010 per cent of any other impurities.

Unlike the indol, this method gives slightly but uniformly deeper colors with the fresh electrolyte than with the used electrolyte. Time is an important factor in the development of the color in very weak solutions of nitrite. The yellow color sometimes does not appear for 30 minutes. The gradation in color with varying amounts of nitrites is marked and thus renders it an excellent quantitative reagent. It will detect nitrites in amounts as low as one part in 1 000 000 (0.0001 per cent). In acid which has been used in a battery it will detect one part in 250 000 (0.0004 per cent).

## IV. CONCLUSIONS

1. The methods recommended in this paper have been selected from more than 50 methods mentioned in literature, as being the most suitable and reliable for battery purposes.

2. The methods recommended do not involve a complicated procedure or require elaborate apparatus. They are therefore available for quantitative determinations in an ordinary laboratory.

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<sup>9</sup> E. Holl Miller, *Analyst*, 37, p. 345; 1912.

3. Nitrates can not be estimated in the presence of nitrites, while nitrites can be estimated in the presence of nitrates.

4. The results from the "hydrostrychnique" and from the brucine methods may be expressed in terms of the total quantity of nitrates and nitrites.

5. The diphenylamine test for nitrates and the iodide test for nitrites are unreliable.

6. In the absence of iron, the "hydrostrychnique" or the modified brucine test is recommended for the determination of nitrates and nitrites.

7. In the presence of iron, only the original brucine test may be used for the determination of nitrates and nitrites.

8. The dimethylaniline test was found to be best for the determination of nitrites.

WASHINGTON, August 20, 1919.

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