

Once the relation of area to peak intensity had been established, greater accuracy would be obtained by counting for the full time at the peak of the line.

In the tantalum-columbium system, the  $TaL\beta$  plus  $CbK\beta$  doublet was determined by counting for 32 seconds at each of 11 points on the line and 11 points on the background. From Table I for the 0.5 atomic % tantalum specimen, the relative probable error was 0.75%. The probable error in the area under the  $CbK\alpha$  line was negligibly small compared to this. Therefore, the probable error in ratio  $A/B$  was about 1%. In Figure 4, at 0.5 % tantalum, ratio  $A/B$  was about 0.11. The probable error was 1% of this or 0.001. From the curve, it is seen that ratio  $A/B$  changes by 0.06 in going from 0 to 1% tantalum. Therefore, 0.001 represents 0.02% tantalum. The measured value for the tantalum content in this region has a statistical fluctuation of 0.02/0.5 or 4% of the amount present.

In the hafnium-zirconium system, the accuracy was not as great by Method A because of the lower counting rate with the long collimator. For the zirconium standard, the accuracy was between 5 and 10% of the amount present for counting times of

32 seconds. However, Method B should give the same accuracy for hafnium-zirconium as it did for tantalum-columbium.

The limit of the minimum amount of hafnium or tantalum detectable would depend on the length of the counting time, but considering the data above would probably be of the order of 0.1% for reasonable counting times.

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#### LITERATURE CITED

- (1) Cauchois, Y., and Mac Taggart, K., *Compt. rend.*, **12**, 1003 (1949).
- (2) Coster, D., and Hevesy, G., von, *Nature*, **111**, 79 (1932).
- (3) Feldman, C., *ANAL. CHEM.*, **21**, 1211 (1949).
- (4) Friedman, H., and Birks, L. S., *Rev. Sci. Instruments*, **19**, 323-30 (1948).
- (5) Zemany, P. D., Winslow, E. H., Poellnitz, G. S., and Liebafsky, H. A., *ANAL. CHEM.*, **21**, 493 (1949).

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# Phenoldisulfonic Acid Method of Determining Nitrate in Water

## Photometric Study

MICHAEL J. TARAS

*Department of Water Supply, Detroit, Mich.*

**Optimum conditions for nitrate analysis include absence of chloride ion and presence of a neutral or slightly alkaline medium during sample evaporation. Reproducible noninterference is possible at nitrite nitrogen levels below 0.2 p.p.m. All reagent volumes must be equalized in both visual colorimetric standards and samples. In many cases use of ammonium hydroxide for color development obviates necessity for final filtration.**

FOR many years, nitrate determination has been difficult in this laboratory. Scrupulous adherence to the standard procedure (1) yielded an off-color yellow which taxed the imagination when compared against standards prepared in the accepted manner. At first, it was thought that the fault lay in the synthesis of the phenoldisulfonic acid, and extreme care was exercised in preparation of the reagent. This precaution failed to improve the situation in any material way.

A search of the literature revealed the Detroit difficulty to be no isolated case. Burke's recommendation (3) that 1 ml. of phenoldisulfonic acid be added to the standards was found to produce a better match between the standards and sample.

However, the bulk of the studies (4-7) to date have centered on the nitrate range above 1.0 p.p.m. A thorough photometric investigation of the nitrate reaction disclosed that factors which could be overlooked in the higher nitrate ranges must be controlled very carefully in the lower ranges; doubly so, because phenoldisulfonic acid is one of the few reagents available for the determinations of the relatively small nitrate concentrations present in many municipal water supplies.

Several improvements suggested themselves during this period of trouble-shooting. It was found that the success of the visual determination depends on the equalization of all reagent volumes

in standards and samples alike, and that significant nitrate losses arise from the presence of chloride ion and the neutralization of the total alkalinity. Accordingly, a procedure embodying these findings was developed.

#### PHENOLDISULFONIC ACID REAGENT

The color of the phenoldisulfonic acid reagent depends on the initial color of the solid phenol and the acids used in the preparation. The whiter the crystals and solutions, the clearer and paler is the final reagent.

Oftentimes, the reagent possesses a faint color and reacts with strong alkalies to give a characteristic hue. This positive interference can be compensated for by the addition of identical volumes of reagent to samples and standards. This precaution nullifies the considerable error which may otherwise occur at the lower nitrate levels (under 0.5 p.p.m.), and also improves the visual color match where Nessler standards must be employed.

The practice of introducing equal volumes of all reagents into the blank and the visual and calibration standards is supported by the spectral transmittance curve obtained with a Beckman Model DU spectrophotometer. At wave length 410  $m\mu$ , the point of maximum absorption, the reagent blank records a

**Table I. Effect of Alkalinity Neutralization on Nitrate Recovery from Synthetic Solutions**

Nitrate Nitrogen Added P.p.m.	Total Alkalinity Added <sup>a</sup> P.p.m.	Nitrate Nitrogen Found		Loss Resulting from Neutralization %
		Unneutralized sample P.p.m.	Neutralized sample P.p.m.	
0.50	100	0.50	0.21	58
0.50	250	0.51	0.16	68
0.50	500	0.48	0.11	77
0.25	100	0.26	0.09	64
0.50	100	0.50	0.18	64
1.00	100	0.99	0.53	47
2.00	100	1.97	1.59	21
0.25	100 <sup>b</sup>	0.25	0.22	15
0.50	100 <sup>b</sup>	0.51	0.44	12
1.00	100 <sup>b</sup>	0.99	0.93	7
2.00	100 <sup>b</sup>	1.99	1.90	5

<sup>a</sup> Total alkalinity expressed as CaCO<sub>3</sub>. All alkalinities produced with Na<sub>2</sub>CO<sub>3</sub>.

<sup>b</sup> These alkalinities included 35 p.p.m. calcium as CaSO<sub>4</sub> and 10 p.p.m. magnesium as MgSO<sub>4</sub>.

measurable transmittancy when compared against distilled water in a 10-cm. cell path. The same effect is registered at a 1-cm. cell depth, but to a lesser extent.

#### COLOR DEVELOPMENT

The fundamental reaction of the analysis is the nitration of phenoldisulfonic acid in an anhydrous medium. Color development results from the conversion of the acid nitration product to the alkaline salt. For this reason, the color may be read immediately upon development. Visual standards prepared from high grade reagents are stable for at least a month. Occasionally, slight color develops after several hours' standing, owing to side reactions between reagent and alkali. This belated development is characteristic of reagent solutions containing considerable initial color. In this event, fresh preparation of visual Nessler standards is advisable.

The chromatic system is such that nitrate nitrogen can be determined accurately at a wave length of 410 m $\mu$  in the range from 0.01 to 2.0 p.p.m. with a 1-cm. cell. Conformity to Beer's law also extends to the higher wave lengths of 470 and 480 m $\mu$ , enabling measurements with the Beckman spectrophotometer up to 12 p.p.m. nitrogen.

#### NITRATE LOSS CAUSED BY ACIDIFICATION

A thorough investigation of the current standard procedure disclosed that an appreciable reduction of nitrate resulted from acidifying the total alkalinity of the sample. The loss averaged slightly more than 10% in natural waters, and exceeded that value in solutions corresponding to zeolite-softened effluents, where the alkalinity is predominantly due to sodium bicarbonate.

The results reported in Table I show that the nitrate loss in distilled water rises with an increase in neutralized sodium carbonate alkalinity, ranging from 58% at 100 p.p.m. neutralized total alkalinity to 77% at 500 p.p.m. neutralized total alkalinity. Table I also reveals the nitrate loss at various steps when the neutralized sodium carbonate alkalinity is held constant at 100 p.p.m. All alkalinity values are expressed in terms of calcium carbonate. On a percentage basis the neutralization loss reaches a maximum at low nitrate concentrations and declines with increasing nitrate content.

Except for zeolite-softened effluents, perhaps, natural waters boast a more diversified mineral composition than that represented by a dilute sodium carbonate solution. Accordingly, synthetic solutions containing 35 p.p.m. of calcium ion added as calcium sulfate, 10 p.p.m. of magnesium ion added as magnesium sulfate, and 100 p.p.m. of sodium carbonate alkalinity were prepared and the loss resulting upon neutralization was

noted at various nitrate nitrogen strengths. Table I shows the per cent loss to be considerably less than that occasioned in solutions composed of neutralized sodium carbonate alone, but on a level with that occurring in natural waters, as demonstrated in Table III. Thus, the mixed mineral salts present in a natural water reduce but fail to prevent entirely nitrate losses attendant upon the addition of dilute sulfuric acid. It is probable that neutralization of the sample to a pH below 5.0 introduces sufficient acid to release some nitric acid which might be volatilized during evaporation. As in the case of the neutralized sodium carbonate alone, the neutralization loss reaches a maximum at low nitrate strengths and declines with increasing nitrate concentration.

Although no acid natural waters were available for investigation, these findings suggest the advisability of raising the sample pH to the neutral or slightly alkaline region before evaporation is undertaken. Because most natural supplies are initially of a mildly alkaline reaction, such a step would be limited to a relatively few untreated samples.

#### EFFECT OF CHLORIDE ON NITRATE RECOVERY

Small amounts of chloride ion cause substantial reductions in the nitrate values of synthetic solutions. Table II reveals the extent of these losses in distilled water dosed with chloride ion. As little as 5 p.p.m. of chloride produce a 12% decrease in nitrate recovery, while higher chloride values cause correspondingly greater losses.

**Table II. Effect of Chloride on Recovery of 0.5 P.P.M. of Nitrate Nitrogen from Synthetic Solutions**

Chloride Added P.p.m.	Nitrate Nitrogen Recovery P.p.m.	Loss Resulting from Chloride %	Nitrate Nitrogen Recovery after Chloride Removal P.p.m.
0	0.50	0	0.50
5	0.44	12	0.49
10	0.40	20	0.50
25	0.35	30	0.51
50	0.33	34	0.51

These losses probably originate from the interaction of the hydrochloric and nitric acids liberated by the strongly acidic phenoldisulfonic acid reagent. For this reason, a minimum of chloride can be tolerated. Because most water supplies contain some chloride ion, it is important that the concentration be ascertained and the ion removed by the addition of standard silver sulfate solution before analysis is undertaken.

The application of silver ion invariably results in minute quantities of silver remaining in the solution finally made alkaline to develop the characteristic nitrate color. Alkalies such as sodium and potassium hydroxides peptize small amounts of silver hydroxide, imparting an off-color brownish hue to the solution and thereby making color matching difficult. Ammonium hydroxide, on the other hand, complexes the silver ion and enables an excellent visual match between color standards and samples. Another advantage of ammonium hydroxide is that filtration is unnecessary in the case of waters low in magnesium and iron.

The chloride ion in some waters can be removed by merely adding the equivalent amount of standard silver sulfate solution and centrifuging immediately for 15 to 30 minutes. Other waters require heat to coagulate the silver chloride, followed by filtration for best results. The Flat Rock samples, reported in Table III, were subjected to such treatment in order to precipitate all of the colloidal silver chloride and obtain a final yellow color which would visually match the Nessler standards.

Table III. Analysis of Natural Waters

Sample Source	Total Alkalinity Content <sup>a</sup> P.p.m.	Chloride Content P.p.m.	Nitrate Nitrogen Found in Untreated Sample P.p.m.	Nitrate Nitrogen Found in Sample after Chloride Removal	
				Total alkalinity neutralized P.p.m.	Total alkalinity unneutralized P.p.m.
Flat Rock raw 1	180	10	0.93	0.94	1.02
Flat Rock raw 2	153	7	0.60	0.62	0.65
Ypsilanti Township well	235	21	0.17	0.20	0.23
Ypsilanti well	245	18	0.12	0.13	0.16
Ann Arbor	188	11	0.50	0.53	0.62
Ann Arbor well	190	10	0.11	0.11	0.12
Willow Run village well	210	4	0.00	0.00	0.00
Detroit raw 1	79	7	0.12	0.14	0.17
Detroit tap 1	74	7	0.12	0.14	0.17
Detroit raw 2	79	8	0.12	0.15	0.19
Detroit tap 2	71	8	0.12	0.15	0.19
Detroit factory well	100	1000	0.00	0.68	0.77

<sup>a</sup> Total alkalinity expressed as CaCO<sub>3</sub>.

### NITRITE INTERFERENCE

By virtue of family resemblance and susceptibility to oxidation, considerable amounts of nitrite ion interfere with the nitrate determination. Concentrations below 0.2 p.p.m. of nitrite nitrogen exert no effect on the phenoldisulfonic acid reagent, but concentrations in excess of that amount yield erratic and unreproducible results. At 1.0 p.p.m. of nitrite nitrogen, the positive interference varied from 0.00 to 0.04 p.p.m. in terms of nitrate nitrogen; at 5.0 p.p.m., the amount of nitrate color developed varied from 0.04 to 0.75 p.p.m. No two runs gave identical or even closely similar values.

Because municipal supplies seldom contain 0.2 p.p.m. or more of nitrite nitrogen, interference from this quarter is not so general or serious as that deriving from the presence of chloride.

### APPARATUS AND REAGENTS

Beckman Model DU spectrophotometer with 10.005-cm. and 1.001-cm. Corex cells.

Cenco-Sheard-Sanford Photometer with blue filter near 410 m $\mu$ , and tubular cells with a 17-mm. light path (routine analysis).

Tall-form 100-ml. Nessler tubes for visual colorimetric investigations.

**Phenoldisulfonic Acid Reagent.** Dissolve 25 grams of c.p. phenol in 150 ml. of concentrated sulfuric acid, add 75 ml. of 15% fuming sulfuric acid, and heat for 2 hours on a hot water bath.

**Stock Nitrate Solution.** Dissolve 0.7216 gram of c.p. potassium nitrate in 1 liter of distilled water.

**Standard Nitrate Solution.** Evaporate 50.0 ml. of the stock nitrate solution to dryness on a water bath, dissolve the residue by rubbing with 2.0 ml. of phenoldisulfonic acid reagent, and dilute to 500 ml. with distilled water. The solution contains 10 p.p.m. of nitrate nitrogen. Prepare calibration curves and visual standards from this solution by taking the desired aliquots, adding 2.0 ml. of phenoldisulfonic acid reagent, and developing the color with ammonium hydroxide in accordance with the recommended procedure.

**Standard Silver Sulfate Solution.** Dissolve 4.397 grams of the c.p. salt in 1 liter of distilled water. One milliliter of this solution is equivalent to 1.0 mg. of chloride ion.

Concentrated ammonium hydroxide solution (density 0.90), c.p.

### RECOMMENDED PROCEDURE

Determine the chloride content of the water (2) and treat 100 ml. of the sample with an equivalent amount of standard silver sulfate solution. Remove the precipitated chloride either by centrifugation or by filtration, coagulating the silver chloride by heat if necessary. Transfer the clarified sample to a casserole and evaporate to dryness over a hot water bath. Rub the residue thoroughly with 2.0 ml. of phenoldisulfonic acid reagent to ensure solution of all solids. If need be, heat mildly on the hot water bath a short time to dissolve the entire residue. Dilute with 20 ml. of distilled water and add concentrated ammonium hydroxide solution (about 6 to 7 ml.) until maximum color is developed. Filter any resulting flocculent hydroxides from the

colored solution into a 100-ml. volumetric flask or Nessler tube, dilute to the mark, and mix thoroughly.

Make photometric readings in cells of appropriate light path (1-cm. cells are suitable) against a blank prepared from the same volumes of phenoldisulfonic acid reagent and ammonium hydroxide used in the determination. Measure transmittancy at a wave length of 410 m $\mu$  or in conjunction with a blue filter exhibiting maximum absorption in the range from 400 to 425 m $\mu$ .

Add 2.0 ml. of phenoldisulfonic acid reagent to all color standards if visual comparison is employed.

### ANALYSIS OF NATURAL WATERS

The chloride content of the natural waters investigated in this study ranged from 4 to 1000 p.p.m. while the total alkalinity varied between 71 and 247 p.p.m. Three sets of parallel experiments were conducted on each sample. In the first set, the sample was evaporated over a boiling water bath without any pretreatment. In the other two sets the chloride was first precipitated with the required amount of standard silver sulfate solution; then the total alkalinity of one 100-ml. portion was neutralized with 0.02 N sulfuric acid and evaporated to dryness on a water bath, parallel with a second 100-ml. portion in which the alkalinity was left unneutralized.

Coincident with the findings obtained on the synthetic solutions, the maximum nitrate values for each natural water resulted in the samples from which the chloride was removed and the total alkalinity was left unneutralized. The lowest values occurred when the chloride was allowed to remain and the total alkalinity was neutralized. Slight improvement was noted when the sample was left untreated. Still greater improvement was evident when the chloride was eliminated but the neutralization was retained.

Only two of the waters, Detroit and Flat Rock, had measurable quantities of nitrite. The highest nitrite content of the Flat Rock samples was 0.04 p.p.m. of nitrogen, whereas both Detroit raw samples had 0.001 p.p.m. of nitrite nitrogen.

With the exception of the Detroit and Flat Rock supplies, which are of surface origin, all samples were drawn from ground water sources. All except Detroit water had a total alkalinity and hardness in excess of 100 p.p.m., as calcium carbonate.

### DISCUSSION

The data suggest the advisability of retaining the alkalinity normally present in most natural supplies as a means of minimizing the nitrogen losses attendant upon the neutralization currently recommended in the phenoldisulfonic acid method of nitrate analysis. The need is also indicated for removing as much chloride ion as possible, because of a natural incompatibility with nitrate in the highly acid medium required for the dominant reaction. Studies on synthetic and natural samples corroborate the importance of the losses occurring at low nitrate concentrations in the absence of these precautionary steps. The method is accurate to  $\pm 0.01$  p.p.m. on known nitrate concentrations in the region below 1.00 p.p.m. of nitrogen. An average reproducibility of 0.01 p.p.m. has been achieved on typical routine natural water samples in this laboratory.

### LITERATURE CITED

- (1) Am. Public Health Assoc., New York, "Standard Methods for Examination of Water and Sewage," 9th ed., pp. 69-70, 1946.
- (2) *Ibid.*, pp. 73-4.
- (3) Burke, G. W., *J. Am. Water Works Assoc.*, 15, 169-70 (1926).
- (4) Chamot, E. M., and Pratt, D. S., *J. Am. Chem. Soc.*, 31, 922-8 (1909).
- (5) *Ibid.*, 32, 630-7 (1910).
- (6) Chamot, E. M., Pratt, D. S., and Redfield, H. W., *Ibid.*, 33, 366-84 (1911).
- (7) Welcher, F. J., "Organic Analytical Reagents," Vol. I, pp. 254-61, New York, D. Van Nostrand Co., 1947.

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