

Spectrophotometric Determination of Nitrate Nitrogen with 2,6-Xylenol*

By

Mikio NAGASAWA

Faculty of Liberal Arts and Sciences

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Similar to the phenoldisulfonic acid and the chromotropic acid methods, nitrites and chlorides obstruct determination of nitrate nitrogen which is carried out by measuring the absorbance of 4-nitro-2,6-xylenol produced when 2,6-xylenol reacts with a nitrate. However, as the presence of chloride increases absorbance, quantitative analysis can be carried out with high precision by adding chloride together with the sample, using 1 ml of sample which contains a low concentration of nitrate nitrogen without removing the chloride.—(Method B).

Among the xylenol isomers, 3,4-xylenol and 2,4-xylenol have been studied up to the present as reagents for quantitative determination of nitrate. Asai¹⁾ found that, of the 6 isomers of xylenol, 2,6-xylenol is most suitable for this purpose. Montgomery and Dymock²⁾ improved the Hartley and Asai's method³⁾ and obtained high sensitivity in absorbance determination without removing the chloride by adding a fixed quantity of chloride. Hartley et al⁴⁾ used a solvent composition of 6:3:1 v./v. sulfuric acid-water-acetic acid and used 0.1 M of reagent in the case of 3:2:1.

Montgomery et al²⁾ made this 6:3.5:0.5 and diluted with water when determining absorbance. However, there are some problems in both of these regarding concentration of sample, stability of coloration and absorption of reagent blank. The author obtained good results by using a composition of 3:2:1 sulfuric acid-water-acetic acid.

Experimental

Apparatus.—Hitachi Model EPU-2A and Model 139 spectrophotometer with 1 cm quartz cell were used as the equipment.

Reagents.—2,6-Xylenol: Tokyo Kasei's Special Grade reagent was used. 1.2216 g of this was dissolved in 100 ml of acetic acid in a measuring flask and 10 ml of this was made up to 100 ml with acetic acid to make a 0.01 M reagent. This is stable for over 2 months when left standing at room temperature.

Sulfuric Acid: 1 part of water was added to 3 parts of Nippon Shiyaku's Special Grade sulfuric acid to make a 3:1 sulfuric acid.

Standard Nitrate Nitrogen Solution: 0.7218 g of JIS Special Grade reagent potassium nitrate was weighed accurately and dissolved and made up to 1 liter with water to prepare a stock solution containing 0.1 mg of nitrate nitrogen per ml.

Other Reagents and Pure Water: Special Grade reagents were used and water was used

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after distilling with hard glass distillation apparatus pure water obtained by ion exchange resin treatment.

Procedure.—8 ml of the 3:1 sulfuric acid was put using a burette into a 50 ml Erlenmeyer flask having a ground glass stopper, 2 ml of the aqueous sample solution was added, 0.01 M of the reagent added further, shaken quietly, cooled with water and absorbance determined at 319 $m\mu$ at room temperature using a reagent blank as the reference.—(Method A).

Results and Discussion

Absorption Spectra.—The absorption spectra is as shown in Fig. 1. The solid line shows absorption of the 10 ppm nitrate nitrogen and the broken line the absorbance of the reagent. Maximum absorption is between 310~320 $m\mu$.

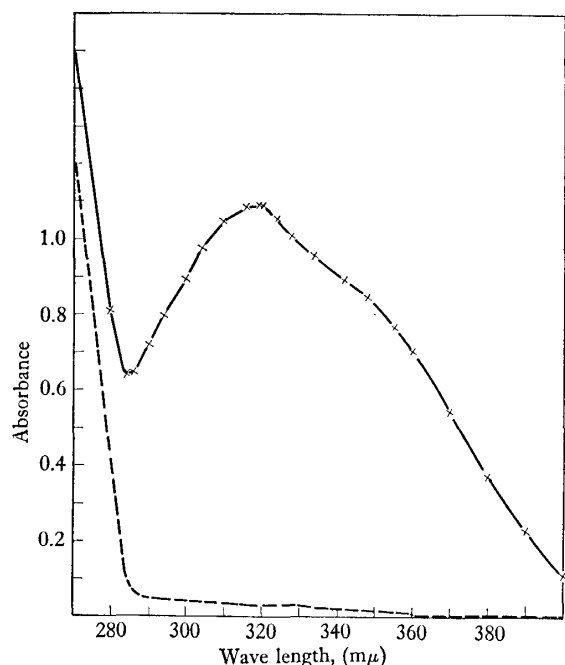
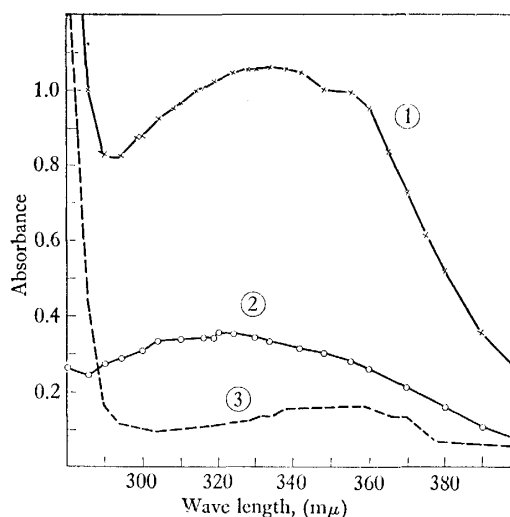


Fig. 1. Absorption spectra of 4-nitro-2,6-xylenol formed with 10 mg./l. of nitrate nitrogen and 10^{-2} M 2,6-xylenol. (Light path 1 cm.; reference: water.) ---- Reagent blank, reference: water.



① 10^{-1} M 2,6-xylenol (reference: water)
② 10^{-3} M 2,6-xylenol (reference: water)
③ 10^{-1} M 2,6-xylenol reagent blank
(reference: water)

Fig. 2. Absorption spectra of 4-nitro-2,6-xylenol formed with 10 mg./l. of nitrate nitrogen and 10^{-1} M 2,6-xylenol or 10^{-3} M 2,6-xylenol.

Reagent Concentration.—The absorption curves when 10 ppm of nitrate nitrogen is treated with 10^{-1} M and 10^{-3} M respectively, and absorption of the reagent are shown in Fig. 2. Hence 10^{-2} M was used.

Stability of Coloration.—The stability of coloration for different sulfuric acid: water: acetic acid ratios was investigated.

No.	Sulfuric acid : Water : Acetic acid (3:1)
②	2 : 1 : 1
③	3 : 1 : 1
④	4 : 1 : 1
⑤	5 : 1 : 1

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⑥	6	:	1	:	1
⑧	8	:	1	:	1
⑩	10	:	1	:	1

Absorption of 7 different ratios of 0.1 M reagent and 10 ppm nitrate nitrogen are shown in Fig. 3. ② indicated poor coloration, absorption was large in case of ③ but a considerable

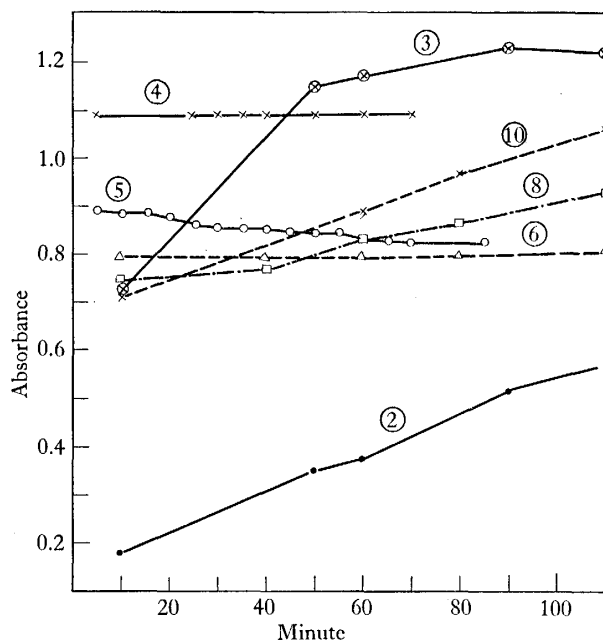


Fig. 3. Effect of standing times of 4-nitro-2,6-xylenol in various solvents.

time was required until the maximum was reached, concentration increased with time and the same is true in the case of ⑧ and ⑩ also. ⑥ was stable and absorbance was large in the case of ④. Consequently, ④, that is a ratio of sulfuric acid (3:1): water: acetic acid of 4:1:1, was used.

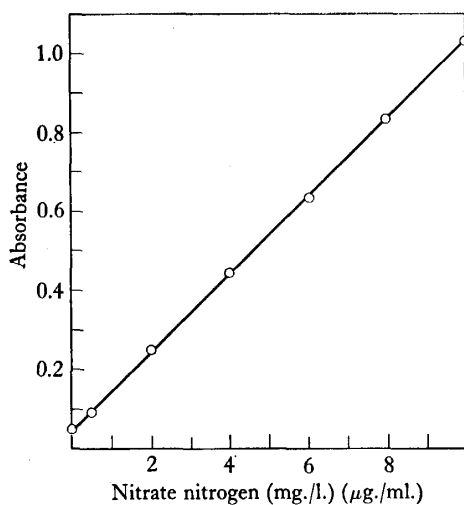


Fig. 4. Calibration curve.

Calibration Curve.—The calibration curve of 1–10 ppm nitrate nitrogen is shown in

Fig. 4. A straight line is obtained.

Interference.—Chloride: The case when standard chloride sample is added was investigated. The result is shown in Table 1. In case the chloride content is below 80 ppm, the sample can be used as it is but if the concentration is more than the above stated, about 0.2 g of silver sulfate is added to 25 ml of the sample and the precipitate is removed by filtering.

Table 1. Effect of Chloride on Nitrate Recovery

Nitrate nitrogen ppm	Chloride added ppm	Total nitrate nitrogen found by- ppm
5.00	10	4.98
5.00	20	5.00
5.00	30	5.04
5.00	40	5.02
3.00	50	3.02
5.00	60	5.06
5.00	80	5.02
5.00	100	5.60
5.00	750	6.80
4.00	800	5.32

Nitrite: Nitrites of all levels indicate obstruction. This can be decomposed completely by adding about 20 mg of sulfamic acid to 20 ml of the sample, and in this treatment, nitrite will not have any effect on the subsequent determination. The result is shown in Table 2.

Table 2. Sulfamic Acid Elimination of Nitrite Interference

Nitrate nitrogen ppm	Nitrite nitrogen added ppm	Total nitrate nitrogen found by- ppm
5.00	1.00	4.94
5.00	3.00	4.92
5.00	5.00	5.08

Iron: Iron (II) of below 2 ppm does not obstruct. The result is shown in Table 3. All levels of Iron (III) increase absorption. There are cases in which obstruction can be prevented considerably by adding Fe^{3+} to the reagent blank but it is necessary to remove this by adding alkali. Also, it is reported that Ca^{2+} , Mg^{2+} , Mn^{2+} , SO_4^{2-} , PO_4^{3-} and acetic acid do not obstruct.

Table 3. Effect of Iron (II) on Nitrate Recovery

Nitrate nitrogen ppm	Fe^{2+} added ppm	Total Nitrate nitrogen found by- ppm
5.00	0.50	5.00
5.00	1.00	5.00
5.00	2.00	5.00
5.00	5.00	5.22

Application.—The results of investigation of drinking water from private piping system, shallow well water, river water and swimming pool water are shown in Table 4. Shallow

well water and swimming pool water contained nitrite nitrogen and therefore these were treated with sulfamic acid. Recovery of nitrate of drinking water from private piping system added by 5 ppm was $99.8\% \pm 1.4$, well water added by 2 ppm was 100.8 ± 2.2 , river water to which 5 ppm was added was 104.2 ± 0.1 , pool water to which 2.0 ppm was added was 99.5 ± 1.5 and pool water to which 5 ppm was added was 100.8 ± 0.8 .

Table 4. Application of the Method A to Natural Waters

Sample	Nitrate nitrogen added ppm	Total nitrate nitrogen found by- ppm	Added nitrate nitrogen found by- ppm
Drinking water		1.58	
" 1/2	5.00	5.70	4.91
" ×2		2.78	
" 1/2	5.00	6.33	4.94
Shallow well water		2.88	
" 1/2	0.25	1.70	0.26
" 1/2	2.00	3.46	2.02
" 1/2	5.00	6.66	5.22
River water		1.41	
" 1/2	5.00	5.68	4.98
Swimming pool water		2.30	
" 1/2	2.00	3.20	2.05
" 1/2	5.00	6.11	4.96

When Quantitative Analysis is carried out without Removing Chloride

Procedure of Quantitative Analysis: 8 ml of 3:1 sulfuric acid is taken in a 50 ml Erlenmeyer flask having a ground glass stopper, 1 ml of the aqueous sample solution and 1 ml of 24% ammonium chloride solution are added, 2 ml of 0.01 M reagent is added and shaken quietly, cooled with water and absorbance determined at $304 m\mu$ with reagent blank as the reference at room temperature—(Method B).

Absorption Spectra: The absorption spectra is shown in Fig. 5. The maximum absorption shifts toward the short wavelength side due to formation of nitroso compound and sensitivity increases about 2 times.

Calibration Curve: The calibration curve for 1–5 ppm nitrate nitrogen is shown in Fig. 6. A straight line is obtained.

Coexisting Substances.—Chloride: The case of chloride addition is shown in Table 5.

Table 5. Effect of Chloride on Nitrate Recovery

Nitrate nitrogen ppm	Chloride added ppm	Total nitrate nitrogen found by- ppm
2.50	375	2.45
2.00	400	1.90

Quantitative analysis can be carried out without removing the chloride. Nitrite: Similar to the previous case, all levels obstruct but this can be removed by sulfamic acid treatment. The result is shown in Table 6. Iron: The presence of a small quantity (1.25 ppm) of

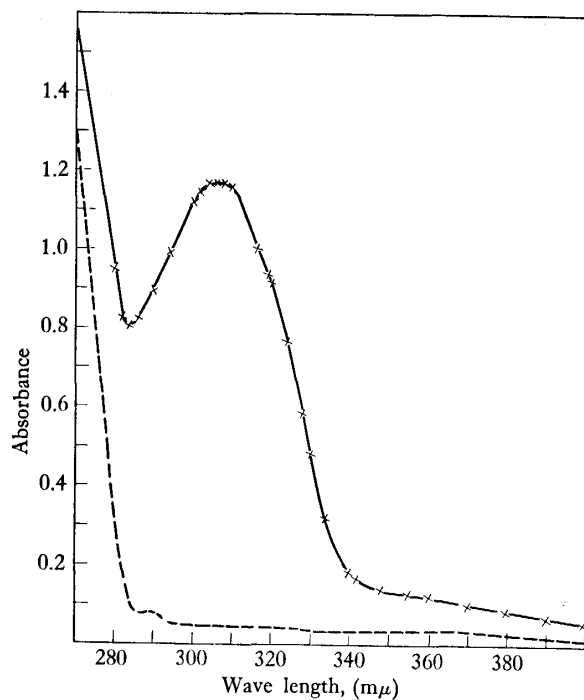


Fig. 5. Absorption spectra of the reaction mixture. To a cooled 8 ml. portion of 3:1 sulfuric acid, in order, 1 ml. of sample and 1 ml. 24% ammonium chloride and 2 ml. of $10^{-2}M$ 2,6-xyleneol in glacial acetic acid. ---- Reagent blank, reference: water.

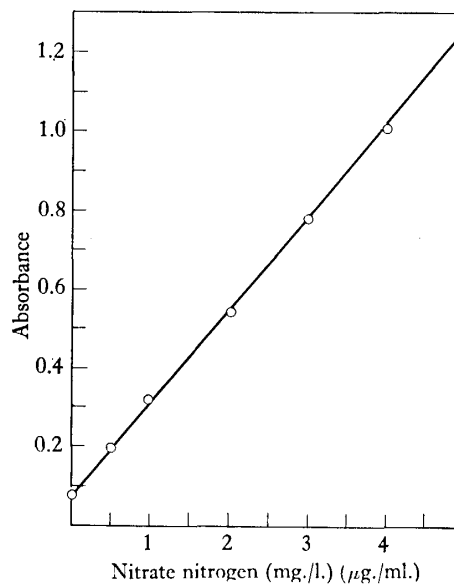


Fig. 6. Calibration curve.

Iron (II) does not obstruct. The result is shown in Table 7. All levels of Iron (III) obstruct. It is necessary to remove this.

Table 6. Sulfamic Acid Elimination of Nitrite Interference

Nitrate nitrogen ppm	Nitrite nitrogen added ppm	Total nitrate nitrogen found by-ppm
2.50	0.50	2.50
2.50	1.50	2.50
2.50	2.50	2.50

Table 7. Effect of Iron (II) on Nitrate Recovery

Nitrate nitrogen ppm	Fe ²⁺ added ppm	Total nitrate nitrogen found by-ppm
2.50	0.25	2.48
2.50	0.50	2.48
2.50	1.25	2.50
2.50	2.50	2.57

Applications.—An example of analysis is shown in Table 8. The estuarial water contained 14.5 g/liter of chloride and creek water contained 729 mg/liter of chloride.

Table 8. Comparison of Results by Method A and Method B

Sample	Nitrate nitrogen added ppm	Total nitrate nitrogen found by-		Added nitrate nitrogen found by-	
		Method A ppm	Method B ppm	Method A ppm	Method B ppm
Estuarial water		1.21			
" 1/2	5.00	9.77		9.17	
" 1/2			0.63		
" 1/4	2.50		2.82		2.51
Creek water		2.06			
" 1/2	5.00	5.88		4.85	
" 1/2			0.99		
" 1/4	2.50		2.92		2.43

Conclusion

Quantitative analysis of 1–10 ppm is possible with 2 ml sample by the A method and 1–5 ppm with 1 ml sample without removing chloride by the B method.

One sample can be analyzed in 10 minutes without going through the procedure of evaporation and drying, distillation or dilution.

References

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