# Indirect Determination of Nitrate by Spectrophotometry

JAMIL ANWAR, MAHMOOD IQBAL FAROOQUI AND ZAIB-UN-NISA
*Institute of Chemistry, University of the Punjab, Lahore, Pakistan.*

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**Summary:** A relatively simple and sensitive method for the determination of nitrate has been developed. The method is based on the reduction of nitrate with mercury sulphuric acid mixture. Oxidized mercury is determined spectrophotometrically by dithizone method. Various parameters such as volume and concentration of sulphuric acid, effect of other anions and effect of time have been checked. The method is found equally useful for organic and inorganic nitrates.

## Introduction

Spectrophotometric methods for determining nitrate are based either on nitration or oxidation of an organic reagent to form some coloured compound or on reduction of nitrate to nitrite or ammonia. Various orgnic reagents such as xylenols [1], bianthronyl [2] and salicyclic acid [3] may be employed for the methods based on nitration and zinc [4], cadmium [5] and hydrazine [6] are used for reducing nitrate to nitrite. These methods generally involve complicated and time-consuming procedures and relatively strict control of conditions.

A few indirect spectrophotometric methods have also been reported for nitrate determination. Bloomfield [7] et al. have proposed an indirect procedure based on the interference of nitrate in the formation of rhenium -furildioxime complex. Recently another indirect method based on the formation of silver-phenanthroline-nitrate complex and spectrophotometeric determination of the excess phenanthroline with iron (II) has been developed in the author's laboratory [8].

This paper describe a relatively simple and sensitive method for nitrate determination. Mercury in the presence of sulphuric acid quantitatively reduces nitrate to nitric oxide [9]. The method described is based on this reduction. The nitrate sample is reduced with mercury-sulphuric acid mixture in nitrogen atomosphere and released mercury ions, in response, are determined by using dithizone as spectrophotometric reagent.

## Experimental

### *Reagents and Equipment*

Analytical grade reagents and doublly distilled water were used throughout this work. Mercury metal of 99.8% purity was washed successively with 5% nitric acid, water and ethanol and then dried.

A Pye Unicam SP8-400 UV/Vis spectrophotometer equipped with a digital readout system was used for absorption measurements.

*Stock solution of nitrate*

1000 $\mu gml^{-1}$ solution of nitrate was prepared by dissoliving 1.29g of AnalarR-grade ammonium nitrate in 1000 ml water. An aliquot of this solution was diluted ten times to get 100 $gml^{-1}$ of nitrate.

*Calibration*

An aliquot containing 10-50µg nitrate was transferred to a 50-ml conical flask with a ground glass neck and a side-arm with gas-bubbling tube. 3 ml of 96% sulphuric acid was added and nitrogen gas was passed for a few minutes. Then 3-4 drops of mercury was added and shaked the contents for 10 minutes. The liquid phase was poured off into a 100-ml separating funnel containing 10-20 ml water. The mercury residue was susscessively washed with 8-10 ml portions of water and washings were added to the funnel.

The mercury from the funnel solution was extracted with small aliquots of 0.001% dithizone solution in carbon-tetrachloride. The orange coloured extractions were collectd in a 50-ml measuring flask and the volume was made up to the mark with carbon tetrachloride. Absorbance of calibrating solutions was measured at 485 nm against the compensatory blank. Calibration graph was obtained by plotting the absorbance against nitrate concentration.

## Results and Discussion

*Effect of volume and concentration of sulphuric acid*

The effect of sulphuric acid volume was checked by using different volumes (1-7 ml) of 36N sulphuric to reduce 1 mg nitrate sample. As shown by fig. 1, relatively less mercury has been found in the samples which were reduced with smaller volumes, i.e. less than 3 ml, of sulphuric acid. This was probably due to the fact that less than 3 ml of sulphuric acid was not enough to complete the reduction process. However, little difference has been found in mercury absorbance when 3-7 ml acid was used for reduction.

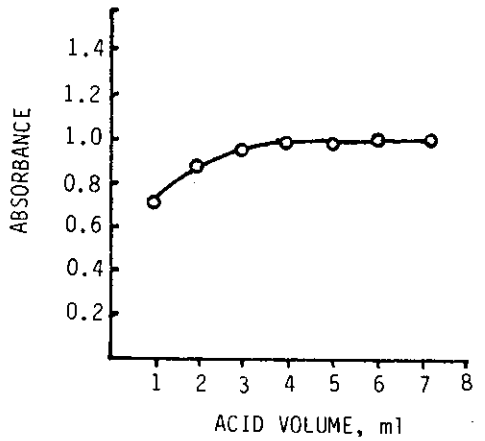


Fig.1: Effect of sulphuric acid volume on nitrate determination.

To check the of effect of concentration 5 ml aliquots of various concentrations of sulphuric acid have been added to 1 mg nitrate sample. As indicated by fig. 2, lower concentrations of sulphuric acid retarded the nitrate reduction significantly. It is also shown by the fig. 2 that 32 N is the minimum concentration for a fast enough and quantitative reduction of nitrate at room temperature. Effect of the concentration of sulphuric acid was more pronounced than the volume effect.

*Effect of shaking time and nitrogen atomsphere*

To obtain the minimum shaking period required to complete the reduction, nitrate sample was shaken with

mercury-sulpburic sulphuric acid mixture for different intervals of time. Fig. 3 shows the mercury absorbance obtained after different shaking intervals. As it is clear from the figure that ten minutes shaking of the contents was quite enough to complete the reaction and also that further shaking did not produced any considerable effect on results.

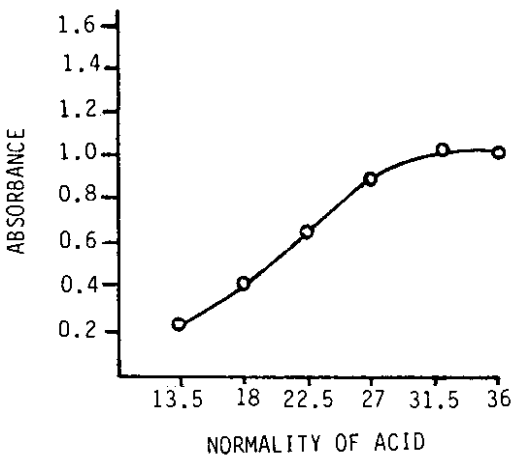


Fig.2: Effect of sulphuric acid concentration on nitrate determination.

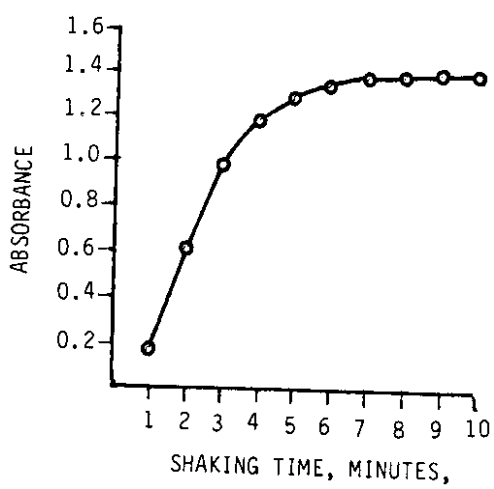


Fig.3: Effect of shaking time on nitrate determination.

To check the effect of atmospheric oxygen, reduction of nitrate was carried out with and without nitrogen atomsphere. In the presence of air random positive errors appeared, indicating some additional oxidation of mercury. Hence, to avoid this error, reduction process was carried out under nitrogen flow.

*Effect of temperature*

Two adverse effects have been noticed when reduction was carried out at high temperatures. First, the solubility of mercury in sulphuric acid became significantly high at elevated temperatures which increased the blank values and affected the results. Secondly, on warming, sulphuric acid decomposed the nitrate into nitirogen oxides and water. Therefore, room temperature ( 25°C) can only be recommended for the nitrate reduction.

*Effect of other anions*

The results of nitrate determination obtained in the presence of various other anions are shown in Table-1.

This has been observed that if before the addition of mercury, sample is shaken well with sulphuric acid, the anions like carbonate, sulphide, sulphite and nitrite are decomposed and do not interfere in the determination. A negligible difference in the nitrate results has been found in the case of these anions. However, halides and thiosulphate ions formed sparingly soluble salts and showed significant adverse effects on the results. Acetate and sulphate ions again did not show any appreciable effect.

*Comparison with reference method*

Nitrate has been determined in one organic and three inorganic compounds

Table-1: Effect of other anions on nitrate determination

| Anion, (X) | Added as | $[X]/[NO_3]$ | % error found |
|---|---|---|---|
| Carbonate | Ammonium | 5.00 | -0.55 |
| Acetate | " " | 2.5 | +0.35 |
| Sulphate | " " | 2.5 | +0.45 |
| Sulphite | Sodium | 2.5 | -0.60 |
| Thiosulphate | " " | 0.75 | -3.50 |
| Chloride | " " | 0.50 | -4.00 |
| Bromide | Potassium | 1.25 | -5.50 |
| Iodide | " " | 1.25 | -3.75 |
| Nitrate | Sodium | 2.5 | +0.60 |
| Sulphide | " " | 2.5 | +0.20 |

by the proposed method as well as by phenoldisulphonic acid method [10]. The results obtained in both cases are summarized in Table-2.

It is clear from the results obtained that the described method is equally useful for inorganic and organic compounds provided the matching standards are used for calibration. Relative standard deviation values obtained by the described method are comparable with those obtained by the reference method.

*Calibration and sensitivity*

Fig. 4 show a linear calibration obtained by plotting mercury-dithizonate absorbance against 10-50 µg concentrations of nitrate taken as ammonium nitrate. Calibration for lower concentrations of nitrate i.e., 2-10µg was also possible but blank values became significantly high and the calibration graph did not pass through the origin.

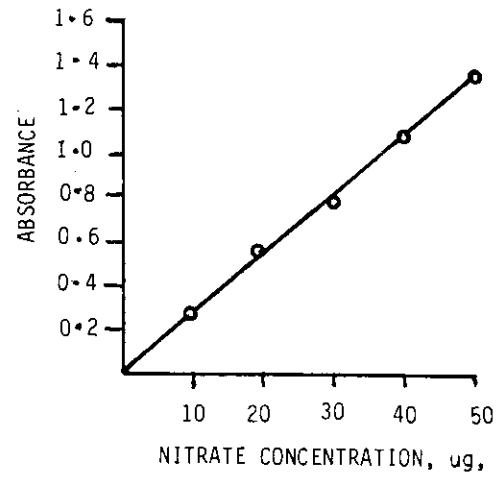


Fig.4: Calibration graph obtained for 10-50 g of nitrate.

Table-2: Comparison with phenoldisulphonic acid method

| Compound | Sample taken in, mg, | %Nitrate Calculated | Proposed method | Phenoldisulphonic acid method. |
|---|---|---|---|---|
| Ammonium nitrate | 1.00 | 77.5 | 77.20 | 77.60 |
| | 1.50 | | 77.00 | 77.25 |
| | 2.00 | | 77.15 | 77.45 |
| Potassium nitrate | 0.75 | 61.38 | 61.35 | 61.20 |
| | 1.50 | | 61.50 | 61.25 |
| | 2.00 | | 61.40 | 61.35 |
| Sodium nitrate | 1.00 | 72.94 | 72.80 | 72.70 |
| | 1.50 | | 73.05 | 73.50 |
| | 2.00 | | 72.80 | 72.90 |
| Urea nitrate | 1.00 | 50.40 | 50.48 | 50.42 |
| | 1.50 | | 50.40 | 50.55 |
| | 2.00 | | 50.45 | 50.45 |
| R.S.D. obtained for six Ammonium nitrate samples | | | 4.55% | 4.50% |
| R.S.D. obtained for six for five urea nitrate samples | | | 4.20% | 4.30% |

Nitrate samples of milligram level, 1-5 mg were also successfully analyzed when they were reduced according to the described procedure and volume of the oxidized mercury solution was made up to 100 ml. 1 or 2 ml of this solution were used to react with dithizone and absorbance of extracted mercury dithizonate was measured to prepare calibration graph.

## References

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