

## INDIRECT DETERMINATION OF NITRATE BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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A new indirect atomic absorption spectrophotometric method for the determination of nitrate is described. The method is based on the reduction of nitrate with mercury-sulphuric acid mixture. Absorbance of released mercurous ions was measured in an air-acetylene flame.

**Key words.** Indirect determination of nitrate; indirect atomic absorption spectrophotometry; nitrate determination by AAS.

### INTRODUCTION

As compared to its use for metal analysis atomic absorption spectrophotometry has been far less employed for the determination of anions. For nitrates, only one method based on this technique has been extensively studied so far [1]. This involves the formation of an ion-association complex,  $[\text{Cu (I) (neocuproin)}_2] \text{NO}_3$ , by the reaction of nitrate with copper (I) in the presence of neocuproin. The resulting complex is extracted into MIBK (methyl isobutyl ketone) and sprayed into an air-acetylene flame for measuring copper absorbance. The method is relatively free from interferences as commented by several workers [2,3].

Another indirect method for nitrate determination based on atomic absorption spectrophotometry has been recently developed in the author's laboratory [4]. This procedure involves the transformation of the nitrate into a silver-phenanthroline-nitrate complex. The ternary complex is filtered off and the absorbance of excess silver ions in the filtrate is measured. A different approach has been employed by Hassan in which the nitrate is reduced with cadmium metal in the presence of hydrochloric acid under carbon dioxide atmosphere and the absorbance of oxidized cadmium is measured in an air-acetylene flame [5]. This method is relatively free from interferences but involves the rather tedious and time consuming procedure of nitrate reduction.

Literature reveals that mercury in the presence of sulphuric acid quantitatively reduces nitrate to nitric oxide [6,7]. In the present work a new method for nitrate determination based on this reduction is described. The nitrate sample is reduced with a mercury-sulphuric acid mixture and the absorbance of released mercurous ions is measured in an air-acetylene flame. The method has been

found equally useful for inorganic and organic nitrates.

### EXPERIMENTAL

**Reagents and apparatus.** Analar grade chemicals and doubly distilled water were used throughout this work. Mercury metal of purity not less than 99.8% was washed successively with 5 % nitric acid, water and ethanol and then dried.

A Varian-AA 1275 atomic absorption spectrophotometer equipped with a digital read out system and mercury hollow cathode lamp was used. The absorbance of mercury was measured at 253.7 nm.

**Standard procedure.** A fairly ground and dried sample containing 0.1-0.5 mg nitrate was transferred to a 50 ml conical flask with a ground glass neck and a side-arm with gas-bubbling tube. For smaller samples a suitable aliquot of nitrate solution was evaporated to complete dryness. 3 ml of 96% sulphuric acid were added and nitrogen gas was passed to displace air from the flask. 2-3 drops of mercury were added and the flask was shaken for 5-7 min. The liquid phase was decanted into a 100 ml standard flask containing 30-40 ml water. The mercury residue was, rinsed at least three times successively with 10-15 ml portions of water and the washings were added to the flask. The flask contents were diluted to the mark with water and aspirated into an air-acetylene flame. The absorbance at 253.7 nm was measured against a compensatory blank.

### RESULTS AND DISCUSSION

**Calibration curve.** A linear calibration, shown in Fig.1, was obtained over the concentration range of 0.1-0.5 mg nitrate. Calibration for a further lower range of con-

centration, 20-100  $\mu\text{g}$  of nitrate, could also be achieved but blank values became significantly high and calibration graph did not pass through the origin.

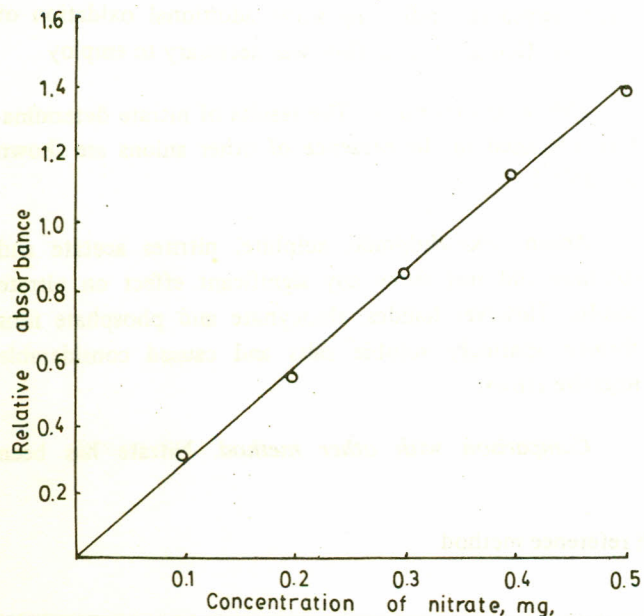


Fig. 1. Calibration graph for 0.1-0.5 mg nitrate.

**Effect of temperature.** Two adverse effects have been observed when reduction of nitrate was carried out at high temperatures. First, the solubility of mercury in sulphuric acid became appreciably high at elevated temperatures and second, on warming, sulphuric acid decomposed the nitrate into nitrogen oxides and water.

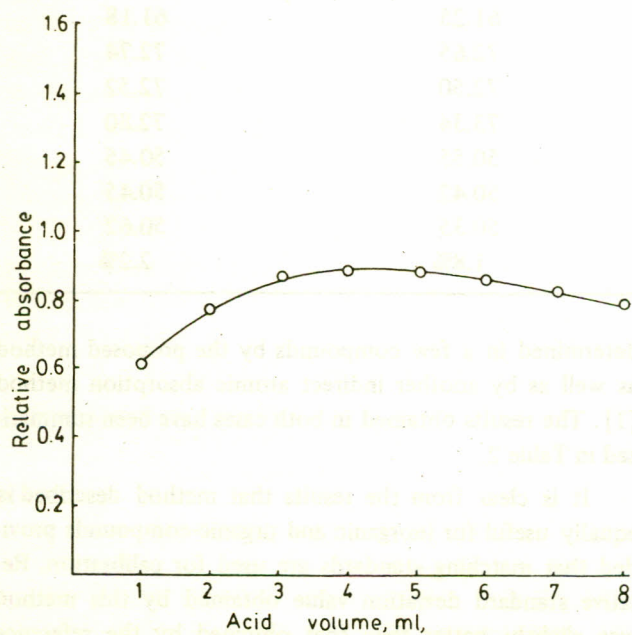


Fig. 2. Effect of sulphuric acid volume.

**Effect of sulphuric acid volume.** To check the effect of volume, different volumes of 36N sulphuric acid were used to reduce one mg nitrate sample. Fig-2 shows that less than 3 ml sulphuric acid was not enough to complete the reduction. However little difference was found in mercury absorbance when 3-8 ml acid was used.

**Effect of sulphuric acid concentration.** To check the effect of acid concentration 5 ml aliquots of various con-

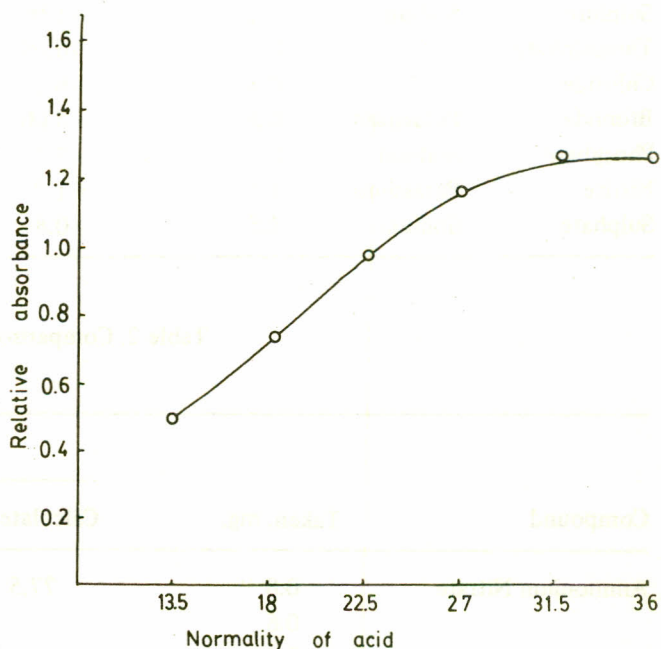


Fig. 3. Effect of sulphuric acid concentration.

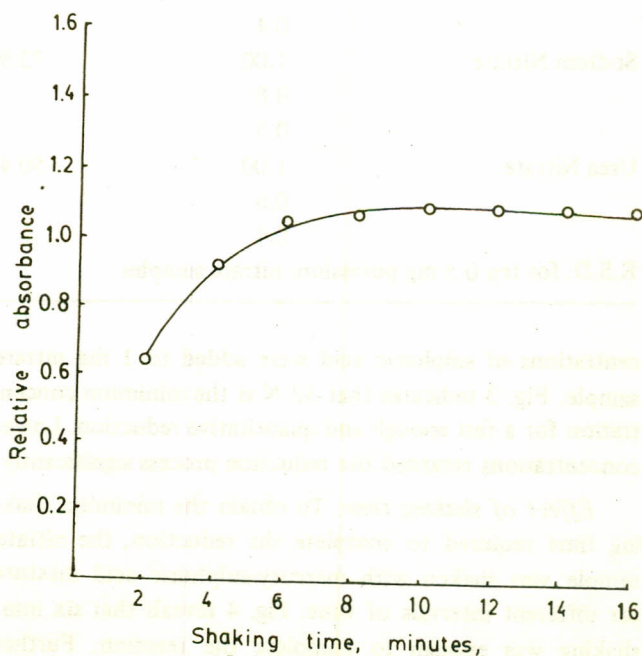


Fig. 4. Effect of shaking time.

Table 1. Effect of other anions on nitrate determination

anion, X	Added as	[X]/ [NO <sub>3</sub> ]	% error found
Carbonate	Ammonium	4.5	+ 0.6
Acetate	"	4.00	+ 0.2
Sulphide	Sodium	3.00	+ 0.5
Sulphite	Sodium	2.00	-1.00
Thiosulphate	"	0.5	16.00
Chloride	"	0.5	-6.5
Bromide	Potassium	0.5	-5.00
Phosphate	Sodium	0.5	-7.5
Nitrite	Potassium	1.5	+ 1.2
Sulphate	Sodium	2.5	-0.8

*Effect of atmospheric oxygen.* To check the effect of atmospheric oxygen the reduction was carried out with and without nitrogen flow. In the presence of air random errors appeared, indicating some additional oxidation of mercury. Hence nitrogen flow was necessary to employ.

*Effect of other ions.* The results of nitrate determination obtained in the presence of other anions are shown in Table 1.

Anions like sulphide, sulphite, nitrites acetate and sulphate did not show any significant effect on nitrate results. However halides, thiocyanate and phosphate ions formed sparingly soluble salts and caused considerable negative errors.

*Comparison with other method.* Nitrate has been

Table 2. Comparison with reference method

Compound	Taken, mg,	Calculated	% Nitrate	
			Proposed method	Reference [1] method
Ammonium Nitrate	0.8	77.5	77.20	77.30
	0.6		77.00	77.52
	0.4		76.80	77.40
Potassium Nitrate	0.8	61.38	61.50	61.64
	0.5		61.40	61.37
	0.4		61.25	61.18
Sodium Nitrate	1.00	72.94	72.65	72.74
	0.8		72.50	72.52
	0.5		73.34	72.80
Urea Nitrate	1.00	50.40	50.55	50.45
	0.6		50.42	50.45
	0.4		50.35	50.62
R.S.D. for ten 0.5 mg potassium nitrate samples			1.8%	2.2%

concentrations of sulphuric acid were added to 1 mg nitrate sample. Fig. 3 indicates that 32 N is the minimum concentration for a fast enough and quantitative reduction. Lower concentrations retarded the reduction process significantly.

*Effect of shaking time.* To obtain the minimum shaking time required to complete the reduction, the nitrate sample was shaken with mercury-sulphuric acid mixture for different intervals of time. Fig. 4 reveals that six min. shaking was enough to complete the reaction. Further shaking did not produce any considerable effect on results.

determined in a few compounds by the proposed method as well as by another indirect atomic absorption method [1]. The results obtained in both cases have been summarized in Table 2.

It is clear from the results that method described is equally useful for inorganic and organic compounds provided that matching standards are used for calibration. Relative standard deviation value obtained by this method was slightly better than that obtained by the reference method.

CONCLUSION

A simple and sensitive indirect atomic absorption spectrophotometric method for the determination of nitrate is established. The method is based on the reduction of nitrate with mercury-sulphuric acid mixture. The absorbance of oxidized mercury ions in air-acetylene flame is used as a measure for nitrate ions. The method has been found equally useful for inorganic and organic nitrates. Anions such as halides, thiocyanate and phosphate interfered with the determination. The relative standard deviation for ten determinations of 0.5 mg nitrate was 1.8%.

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Table 1. Conversion of 2-quinoline using cobalt. Conditions as catalyst.

Run	Time period (hr)	Temperature (°C)	Rate of flow of oxygen (l/min)	Yield (%)
1	30	128	0.3	98
2	30	130	0.3	98
3	30	132	0.3	98
4	40	130	0.3	98
5	40	132	0.3	98
6	50	130	0.3	98
7	50	132	0.3	98

Table 2. Reduction of 2-quinoline using manganese. Conditions as catalyst.

Run	Time period (hr)	Temperature (°C)	Rate of flow of oxygen (l/min)	Yield (%)
1	30	128	0.3	98
2	30	130	0.3	98
3	30	132	0.3	98
4	40	130	0.3	98
5	40	132	0.3	98
6	50	130	0.3	98
7	50	132	0.3	98

The present authors have reported the reduction of nitrate with mercury-sulphuric acid mixture in air-acetylene flame and the absorbance of oxidized mercury ions in air-acetylene flame is used as a measure for nitrate ions. The method has been found equally useful for inorganic and organic nitrates. Anions such as halides, thiocyanate and phosphate interfered with the determination. The relative standard deviation for ten determinations of 0.5 mg nitrate was 1.8%.

RESULTS AND DISCUSSION

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