Indirect Atomic Absorption Spectrophotometric Method For the Determination of Nitrate

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Summary: An indirect atomic absorption spectrophotometric method for the determination of 0.5 - 5 μmoles nitrate is described. The method is based on the formation of insoluble ternany complex, $[Ag(Phen)_2]NO_3$, by adding an excess of $[Ag(Phen)_2]^+$ solution in nitrate sample. Absorbance of unreacted silver ions has been measured in an air-acetylene flame. The effect of various ions has been investigated. The method is successfully employed for the determination of nitrate in fertilizer samples.

Introduction

Most of the methods reported for the determination of nitrate are based on reduction of nitrate in one form or another. In titrimetric procedures reduction may be carried out with iron(II) titanium(III) and tin(II) [1]. In another approach Devarda's alloy has been used to reduce nitrate to ammonia [2]. Spectrophotometric methods also either involve the reduction of nitrate to ammonia [3] or its convertion to a coloured nitrophenol [4]. All these methods have been employed for the determination of nitrate in various matrices but involve rather complicated procedures and strict control conditions.

Nitrate forms complexes with a few organic and organometallic reagents such as nitron [5], diphenylthallium (III) [6] and dicyclohexylthallium (III) [7] ions. Amperiometric and potentiometric titrations based on the reactions of nitrate with these reagents have also been applied for nitrate determination which too have their own problems.

On the other hand atomic absorption spectrophotometry has been far less used for the determination of anions as compared to metal ions. Some of the general indirect atomic absorption methods involve the formation of an insoluble compound and the determination of either the metal ions incorporated in the precipitate or the excess metal ions in the filtrate. These methods have been summarized in a review of the subject [8].

For nitrate estimation, only two methods, based on atomic absorption technique, are available in the literature. The first one involves the transformation of nitrate into the complex $[Cu(I)(neucuproin)_2]NO_3$ by reaction of copper(I) with nitrate in presence of neocuproin [9]. The complex is extracted into MIBK (Methyl isobutyl ketone) and sprayed into an air-acetylene flame. In the second procedure, cadmium metal is used to reduce nitrate to nitrite and absorbance of cadmium ions in solution is measured by atomic absorption spectrophotometry [10]. Both of these methods involve relatively tedious and time consuming steps like extraction of the copper complex in the former and reduction of nitrate under inert atmosphere in the latter method.

Nitrate forms insoluble ternary complex with silver in the presence of 1,10-phenanthroline [11]. In the present work, we exploited this complex formation for the determination of nitrate. The method is found quick, simple and adequately accurate especially for the analysis of nitrate in fertilizers.

Experimental

Apparatus:

A double beam Pye Unicam SP 2900 atomic absorption spectrophotometer equipped with an air-acetylene flame was used for measuring the silver absorbance at 328.1 n.m. Readout was on a chart recorder.

Reagents:

Silver-phenanthroline complex solution, 10^{-3}M, was prepared by dissolving 0.167 g of analytical reagent grade silver acetate and twice the equivalent molar quality of 1,10-phenanthroline in 1 litre with water. The solution was stored in an amber glass bottle.

For standard nitrate solution, analytical grade potassium nitrate was dried at 110°C to constant weight. To get 10^{-2}M solution, 1.01 g potassium nitrate was dissolved in water and diluted to 1 litre. This solution was further diluted ten times to get 10^{-3}M solution of nitrate.

Calibration:

1-5 ml aliquots of nitrate solution, containing 1-5 μ moles of nitrate, were transferred to 50 ml conical flasks. Each solution was diluted to 10 ml by adding the required volume of water. To maintain the pH between 4 to 4.5, 1 ml of 3M acetate buffer was added to each solution. The contents were thoroughly shaken for at least 10 minutes and then allowed the ppt. to settle down for another 15 minutes, in each flask.

The insoluble complex was filtered through a Wattman 41 filter paper. The ppt. was washed with 1:1 water-ethanol mixture. Filtrate and washings were collected in a 250 ml standard flask, and diluted to the mark with the water-ethanol mixture. This solution was aspirated into an air-acetylene flame using the water-ethanol mixture as a blank. Silver absorbance was measured in each filtrate and plotted against nitrate concentration.

Nitrate in fertilizer sample:

Fertilizer sample containing 20-40 μmoles of nitrate was dissolved in 100 ml of water. 10 ml of this solution were transferred into a conical flask and treated as described in the calibration. The absorbance of the filtrate obtained was measured under the same conditions as employed for the calibration.

Results and Discussion

Effect of Silver to nitrate and silver to 1,10-phenanthroline ratio:

Calibration curves obtained by adding various quantities of silver complex to a fixed amount of nitrate are shown in Fig.1. The slope of the calibration line is found highly dependent upon the concentration of silver ions. The best working calibration 'A' was obtained by adding a slight excess of silver complex to the maximum concentrated standard solution of nitrate in which the ratio, Ag^{+}/NO_3' , was 1.33. Keeping this ratio constant the effect of Phen/Ag^{+} ratio was also noticed but no considerable change has been noticed on calibration by varying this ratio from 2.0 to 2.5. However, dilution of the silver complex and

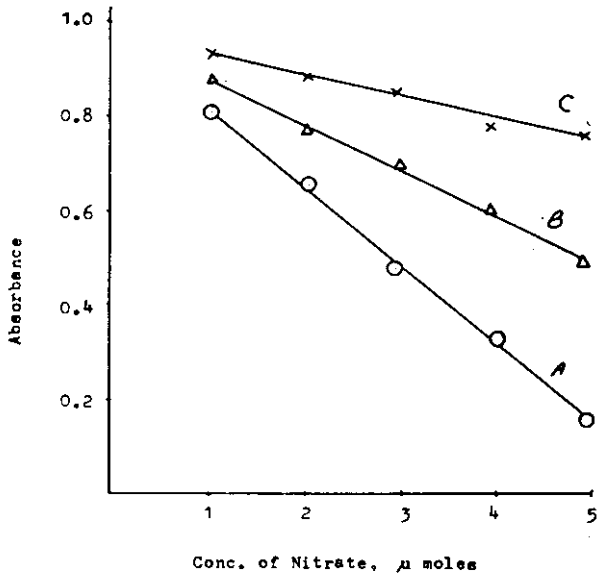

Fig.1: Calibration graphs with various Ag^+/Nitrate(Maximum) ratios

Ag^+/Nitrate(Maximum) ratio A:1.33, B:1.58, C:1.89

nitrate solutions affected the results significantly. Higher dilutions created a negative error in the final results of nitrate which suggests an incomplete precipitation of nitrate.

Effect of solvent:

In order to prepare a homogeneous solution of silver-phenanthroline complex, a mixed solvent was used. Ethanol, methanol, acetone and butanone in combination of water were tried. Butanone was excluded due to its limited solubility in water. Acetone affected the absorption by making the flame too reducing (yellowish), however smaller volumes 30% were tolerable. Methanol gave acceptable results but solubility of the reagents in this solvent was relatively poor. Ethanol-water mixture, 1:1, proved itself the best solvent for the method. Ethanol concentration less than 40% reduced the solubility of reagents and more than 50% disturbed the flame conditions.

Effect of pH:

Though the reaction between nitrate and silver-phenanthroline complex occurred in neutral solutions but it has been noticed that for quantitative work pH is a considerable factor. Complex formation was carried out at different pH values and most accurate and precise results of nitrate estimation were found at 4 - 4.5 pH which suggests that optimum complexation occurs in this range. To maintain this pH during complexation, 3M acetic acid/sodium acetate buffer was used.

Effect of other ions:

The effect of various ions has been investigated on estimation of nitrate. The percentage errors found in the case of different ions are summarized in Table 2.

Among the cations, ammonium, manganese, cobalt, nickel and zinc did not interfere much adversely but copper, iron and calcium significantly affect the nitrate results. Anions have been found relatively more effective than the cations. Halides affected the results in the order $Cl^- > Br^- > I^-$ which indicates the presence of electrostatic bonding between the silver-phenanthroline complex and the anion attached. Chlorate also behaved similar to chloride and caused a positive error. However sulphate, sulphite and fluoride did not leave any appreciable effect on nitrate results and fairly high amounts of these anions could be tolerated.

Comparison with reference method:

A number of nitrate fertilizer samples have been analysed by the described procedure as well as by nitron method. The results and standard deviations obtained in both cases are given in Table-2. The method has been found almost equally precise and

Table-1: Effect of various ions on nitrate estimation (Nitrate taken 62mg/l

$Ion_{(X)}$	Added as	$(X)_{/(NO3)}$	% error
Mn^{2+}	acetate	1.5	-0.6
Fe^{2+}	"	0.1	-1.8
Co^{2+}	"	0.5	-0.8
Ni^{2+}	"	1.00	-0.5
Cu^{2+}	"	0.1	-1.2
Zn^{2+}	"	0.8	-0.4
Ca^{2+}	"	0.1	-1.6
NH_4^+	"	2.5	+0.6
F^-	sodium salt	2.00	+0.2
Cl^-	"	0.01	+2.2
Br^-	potassium salt	0.01	+1.9
I^-	"	0.01	+1.5
ClO_4^-	"	0.01	+2.00
SO_4^{2-}	sodium salt	0.2	+0.3
SO_3^{2-}	"	0.2	+0.4

Table-2: Determination of nitrate in fertilizer sample

	% Nitrate	
	Indirect AAS method	Nitron method
	75.25	74.45
	75.46	76.20
	75.80	75.90
	76.10	75.35
	75.90	76.15
Mean	75.70	75.81
RSD	0.45%	0.51%

accurate with the standard nitron method.

In conclusion, the described method is quick, simple and adequately accurate for the estimation of nitrate at semimicro level. Though at present it seems that a number of other ions can interfere in the estimation but this problem can be solved by the prior removal of such ions. However, the method in its present form can be safely employed for the routine estimation of nitrate in fertilizer samples.

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