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Determination of nitrate by anion exchange with ultraviolet detection

by

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Determination of Nitrate by Anion Exchange with Ultraviolet Detection

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Abstract

A weak base anion exchange resin is synthesized by surface bonding 3-aminopropyltriethoxysilane to silica gel. This silylated silica gel is used to separate nitrate from interferences. The nitrate is then determined by measuring its absorbance at 220 nm. An interference study was performed and no anions commonly found in potable water interfers. A comparison of this method was made with the brucine method on real samples and satisfactory agreement was obtained between the two methods.

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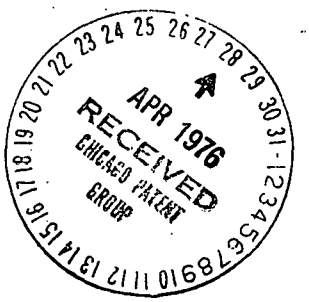

INTRODUCTION

Nitrate has for over half a century been considered in this country as one of the important substances to be determined in water because of its connection with pollution from sewage or manurial matter. The importance of the determination has been emphasized by the recognition that intake of well waters containing substantial amounts of nitrate causes methemoglobinemia in infants (1). In addition to the dangers of a continually high nitrate content in water, a sudden rise in its concentration indicates pollution, e. g. , from fertilizers, animal wastes or effluents (2).

In 1945, high concentrations of nitrates in well water in Minnesota were suspected as a cause of methemoglobinemia. The suspicions were realized when the 1947-1948 epidemic in Minnesota resulted in 139 cases, 14 of which were fatal. Although no case in the Minnesota epidemic was traced to a water containing less than 30 ppm nitrate nitrogen, 10 ppm was considered a significant concentration. Waring reported that "drinking waters containing high nitrate nitrogen--10-20 ppm or more--appear to be the cause of methemoglobinemia in infants . . . ", as quoted by Goldman and Jacobs (3).

Methemoglobinemia results from the oxidation of the iron (II) in hemoglobin by nitrite and, to a lesser extent nitrate. The methemoglobin formed cannot reversibly combine with oxygen or carbon dioxide. Death results from hypoxia in severe cases. Nitrate is not as toxic as nitrite, but it can be converted to nitrite by the intestinal bacteria Escherichia coli, and nitrate is much more prevalent in the environment than nitrite (4).

In light of these findings, an accurate means of determining nitrate is essential. Although a variety of methods is available for the determination of nitrate, the more accurate procedures are somewhat lengthy, and most have several interferences.

Because of the need for a rapid, convenient, and accurate method for the determination of nitrate, a chromatographic method was developed. A weak base anion exchange resin is used to separate nitrate from interferences. Advantage is taken of the ultraviolet absorbance of nitrate by using an ultraviolet spectrophotometer to determine the amount of nitrate in the effluent from the anion exchange column.

REVIEW OF COMMON METHODS

Although there have been numerous publications on the subject of nitrate ion analysis in recent years, little that is fundamentally new has been proposed. Most of the methods have been based either on nitration/oxidation of organic compounds or on reduction to nitrite ion for which the nearly specific diazotization-coupling reaction sequence is available. The latter has served as the basis for several differential methods for nitrate and nitrite.

One method that is frequently used for the determination of nitrate is the phenoldisulfonic acid method. This method appears to be one of the most accurate methods in the absence of interferences but is one of the most time consuming. It is based on the yellow color produced by the reaction between nitrate and phenoldisulfonic acid. This yellow color is measured at 410 nm for concentrations from 0.01 ppm to 2 ppm nitrate nitrogen and at 480 nm up to 12 ppm nitrate nitrogen.

Chloride above 10 ppm causes considerable interference which is a real problem because surface water often contains several hundred ppm chloride (5). Because of this, chloride has to be first determined, precipitated by silver sulfate, and the silver chloride filtered off. However, the silver sulfate used for this purpose presents problems with some water samples owing to incomplete precipitation of silver ion, which produces an off color or turbidity when the final color is developed. Nitrite levels in excess of 0.2 ppm nitrite nitrogen erratically increase the apparent nitrate concentration. Colored samples also interfere.

After removing chloride and color, the sample is neutralized and evaporated to dryness. The residue is mixed with phenoldisulfide acid reagent, diluted with distilled water, and the sample is made alkaline. The resulting flocculent hydroxides have to be removed by filtration or addition of EDTA. The mixture is diluted to a standard volume and its absorbance is measured (6,7).

Accuracy of the order of $\pm$ 0.1 ppm nitrate nitrogen can be obtained only by the proper treatment of the chloride and nitrite interference. A synthetic unknown sample containing 1.0 ppm nitrate nitrogen, 10 ppm chloride, 0.20 ppm ammonia nitrogen, 1.5 ppm organic nitrogen, 10.0 ppm phosphate, and 5.0 ppm silica in distilled water was determined by the phenoldisulfonic acid method, with a relative standard deviation of 74.4% and a relative error of 38.0% in 46 laboratories (6).

A second method for the determination of nitrate, and the one recommended by the American Society for Testing Materials, is the brucine method. In this method, the reaction between nitrate and brucine produces a yellow color which is used for the colorimetric estimation of nitrate. The intensity of the color is measured at 410 nm. The calibration curve of concentration vs. absorbance is not a straight line, thus the relationship doesn't follow Beer's Law. This method is recommended for the approximate range of 0.1-2 ppm nitrate nitrogen.

All strong oxidizing or reducing agents interfere. The interference by residual chlorine may be eliminated by the addition of sodium arsenite, provided that the residual chlorine does not exceed 5 ppm. Ferrous and ferric iron and quadravalent manganese in concentrations above 1 ppm give slight positive interferences. The interference due to nitrite up to 0.5 ppm nitrite nitrogen is eliminated by the use of sulfanilic acid. Chloride interference is masked by the addition of excess sodium chloride. High concentrations of organic matter will usually interfere.

After pretreatment of the sample to eliminate interference, a strong solution of sulfuric acid is added to the solution. After mixing, the brucine-sulfanilic acid reagent is added to the sample. The reaction rate between brucine and nitrate ion is affected significantly by the amount of heat generated during the test. Thus the procedure seeks heat control by reagent addition sequence and incubation of the reaction mixture for a precise interval of time at a known constant temperature.

In the absence of interfering substances, an accuracy of 0. 5 ppm nitrate can be obtained. Several synthetic unknown samples containing nitrate and other constituents dissolved in distilled water were analyzed by the brucine method. For a sample containing 0. 5 ppm nitrate nitrogen, a relative standard deviation of 14. 4% and a relative error of 0. 6% were obtained. For a sample containing 5. 0 ppm nitrate nitrogen, a relative standard deviation of 15. 4% and a relative error of 4. 5% were obtained. Both samples were analyzed by 50 laboratories (6, 8).

There are several reduction methods for the determination of nitrate. In these methods the nitrate is reduced to nitrite which is determined by diazotizing to form a highly colored azo dye that is measured colorimetrically (9). In one such method powdered zinc is added to the sample to reduce the nitrate. The amount of zinc and the contact period for reduction are critical. The reaction is temperature dependent, and all samples must be run at a temperature near that at which the calibration curve is prepared. Nitrite originally present is destroyed by sodium azide in acid solution. Strong oxidizing and reducing substances interfere. Antimonous, auric, bismuth, chloroplatinate, ferric, lead, mercurous, metavanadate, cupric, and silver ions interfere. With a 2 cm light path, the minimum detectable concentration is 10 ug/l nitrogen, and the color system obeys Beer's Law to about 1. 4 mg/l nitrogen. On undiluted samples and in the absence of interference, precision is estimated to be $\pm$ 20 ug/l nitrogen and accuracy is estimated to be 20 ug/l nitrogen (6, 10).

Orion Research, Inc., has recently made commercially available a nitrate ion selective electrode which incorporates a liquid water-immiscible ion exchanger. The response is greater to perchlorate, chlorate, and iodide ions than to nitrate and somewhat less to bromide and sulfide ions. The nitrate ion selective electrode is not very selective and many ions interfere when they are present in higher quantities than the nitrate ion. The consequence of this and other difficulties is that the nitrate electrode is not suitable for the

measurement of small quantities of nitrate in unknown samples. It is, however, very suitable for the routine analysis of samples whose approximate composition is well known and not subject to large variations. The effective range is 0.6-6000 ppm in solutions of pH 2-12 (5,9,11).

Davenport and Johnson have recently reported an anion exchange method for nitrate and nitrite that employs electrochemical detection (4,12). Nitrate and nitrite are reduced at a cadmium tubular electrode. The resulting current is amplified and a trace of current versus time is made with a strip chart recorder, giving the familiar chromatographic peaks. The amount of nitrate and nitrite in the sample is determined from the area under the peaks. Since cations such as iron (II) and copper (II) are electroactive, all cations are removed from the eluent by a cation exchange column. An anion exchange column is used to separate nitrate, nitrite, and oxygen, as oxygen is also electroactive. Severe interference resulted from bromate and bisulfite as these are eluted simultaneously with nitrite and are electrochemically reduced. An error that is produced by iodide increased with successive injections of iodide-containing sample. Over a five-day period the relative standard deviation of peak areas is 10%. By bracketing the unknown sample with injections of standard solutions, the relative standard deviation is reduced to 2%. The detection limit is reported to be 0.1 ppm nitrogen.

The ultraviolet spectroscopy method takes advantage of the ultraviolet absorbance of nitrate at 210 or 220 nm. It offers a rapid means of determining nitrate in potable water (1,3,6,13,14,15,16). The absorbance due to alkalinity is removed by acidifying the sample. Filtration of the sample is required if turbid. Dissolved organic matter, nitrite, chromium (VI), iron (III), and iodide interfere. Organic matter can cause a positive but variable interference, the degree depending on the nature and concentration of the organic matter. To correct for organic interferences, the absorbance of the sample is measured at 275 nm where nitrate does not absorb. The absorbance at 275 nm is multiplied

by a factor and subtracted from the absorbance of 220 nm to give the corrected nitrate absorbance. This factor is reported to be 2, 2.5, and 4 by references 6, 3, and 2 respectively. Nitrite, iron (III) and chromium (VI) can be determined and their absorbance subtracted. Nitrite, chromium (VI), and iodide are often of insignificant concentration in potable water to cause interference.

Bastian et al. suggested the removal of iron (III) and other interfering cations by a cation exchange column (13). Navone used a zinc-copper couple to reduce the nitrate in the sample to ammonia and used this solution as a blank to subtract the absorbance of interfering species (14). The minimum detectable concentration is reported to be 0.040 ppm nitrate nitrogen, with the nitrate calibration curve following Beer's Law up to 11 ppm nitrogen (6).

EXPERIMENTAL

Apparatus

Anion Exchange Column

The anion exchange column used is shown in Figure 1. Air pressure is used to force eluent and sample through the anion exchange resin. Pressure ranging from 2-10 psi is applied to obtain the desired flow rate. The flow rate is determined by measuring the time necessary to collect a given volume of effluent. By closing the valve the rubber stopper can be removed and eluent or sample added to the column without changing the regulator setting. A stopcock is necessary at the bottom of the column to prevent the liquid level from going below the top of the resin, which causes air entrapment in the resin and inefficient elution. The inside diameter of the glass tip below the stopcock should be small to keep mixing to a minimum. The effluent from the column is collected in 5 ml volumetric flasks.

Spectrophotometer

Detection is accomplished by transferring the effluent from the 5 ml volumetric flasks to a spectrophotometric cell with a path length of 1 cm and which is suitable for use at 220 nm. The cell is placed into a spectrophotometer and the absorbance is measured versus distilled water. The spectrophotometer used was a Cary Model 16. A Cary Model 14 recording spectrophotometer was used for recording all spectra.

pH Measurements

A Corning Model 7 pH meter was used for all pH measurements, except in capacity determinations, where Hydrion pH Papers were used.

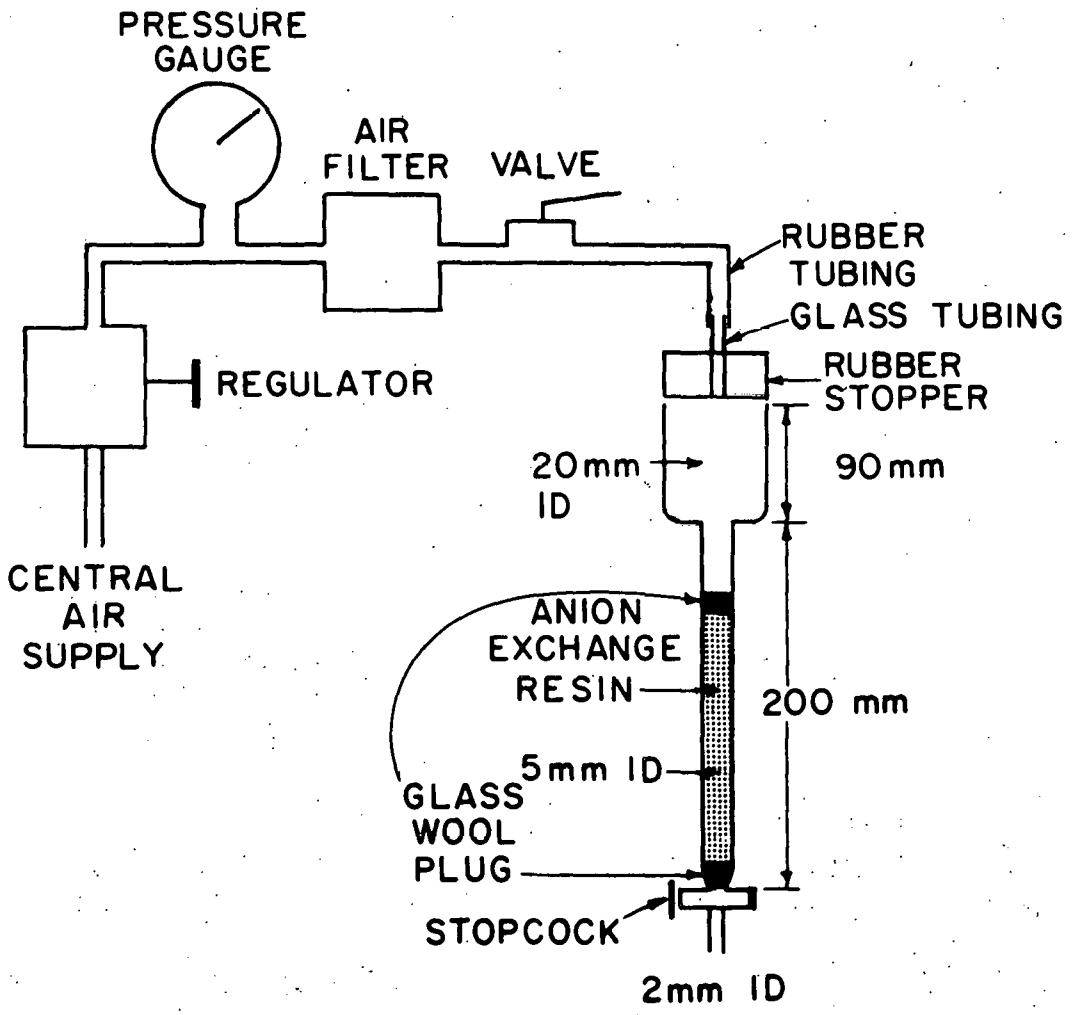

Figure 1. Anion exchange column with connections for supplying air pressure for forced flow.

Reagents

All water used was distilled water. Standard nitrate solutions were prepared from Fisher Certified Reagent primary standard potassium nitrate, which was dried at 120° overnight. Compounds used in the interference study were all reagent grade and were not dried before use. Solutions for use in the brucine method determinations of nitrate were prepared as described in Standard Methods of Chemical Analysis (17). The various eluents were prepared by diluting Fisher Scientific Company Reagent ACS 70% perchloric acid with distilled water.

Anion Exchange Resin

The weak base anion exchange resin is prepared by surface bonding 3-aminopropyltriethoxysilane (Aldrich Chemical Company) to silica gel (Supelco Company). Twenty milliliters of distilled water and 3 ml of 3-aminopropyltriethoxysilane are added to a 100 ml beaker and the pH of the solution is adjusted to 4 by dropwise addition of concentrated perchloric acid. Four grams of silica gel (100-120 mesh) is added to the solution. The mixture is stirred for 15 min with a magnetic stirrer. The liquid is poured off and the resin is dried overnight at 80° (18,19).

One molar perchloric acid is added to the resin in the beaker and the fines are decanted by swirling, letting the larger particles settle, and carefully pouring off the liquid containing suspended, fine particles. This is repeated several times to ensure complete removal of fine particles, which plug up the column and pass through the glass wool causing interference. Washing with 1 M perchloric acid also removes unreacted silylating agent and any impurities on the surface of the resin that may cause interference. The column is filled with water. A piece of glass wool is wetted and

forced to the bottom of the column with stiff wire, being careful to exclude air. The resin is slurried in water and poured into the column to a height of approximately 12 cm. This requires 1.5-2 g of resin. A second piece of glass wool is wetted and forced to the top of the resin, being careful to exclude air. Liquid should be kept above this second piece of glass wool at all times to prevent air entrapment in the resin and glass wool.

Resin capacities were determined by acid-base titrations. After resin preparation and decanting the fines, the resin is allowed to air dry. The resin is weighed, slurried in water, and poured into the column. A weak solution of ammonium hydroxide (0.1 M) is passed through the resin until the effluent is basic to pH test paper. The resin is washed with distilled water until the effluent is neutral to pH test paper. A known volume of standard acid is passed through the resin and the effluent is collected. This is followed by two 5 ml portions of distilled water, which are also collected in the same container. The standard acid effluent and the last two 5 ml portions of distilled water are titrated with standard base. The milliequivalents of standard acid added minus the milliequivalents of standard base required for the titration equal the milliequivalents of reaction sites on the resin. And knowing the grams of resin added, milliequivalents per gram of resin can be calculated.

Procedure for Nitrate Determination

After the column has been prepared, 25 ml of 1 M perchloric acid is passed through the column followed by 15 ml of distilled water. The pH of 75-100 ml of the sample is adjusted to 3-3.5 by dropwise addition of concentrated perchloric acid. An aliquot of the sample is transferred to the column with a pipet and is drained to the top of the upper glass wool

plug. Five milliliters of pH 3-3.5 perchloric acid is added to the column and drained to the top of the upper glass wool plug. Twenty milliliters of 0.02 M perchloric acid is added to the column and drained to the top of the upper glass wool plug. Fifteen milliliters of 1 M perchloric acid is passed through the column. This 15 ml of effluent are collected in three 5 ml volumetric flasks. The absorbance of the contents of each flask is measured at 220 nm. The concentration of nitrate in each flask is determined from a calibration curve and the concentration of the sample is calculated. Twenty-five milliliters of 1 M perchloric acid is added to the column and drained to the top of the upper glass wool plug. Fifteen milliliters of distilled water is passed through the column, and the column is ready for the next sample. A blank should be ran periodically and subtracted from the absorbance of the sample to compensate for the absorbance of the perchloric acid and any column bleeding that may occur.

RESULTS AND DISCUSSION

Anion Exchange Resin

The method of resin synthesis described previously under EXPERIMENTAL gives resin capacities of 0.25-0.27 meq/g. This resin gives satisfactory results for the separation of nitrate from interferences and the nitrate is eluted easily with 1 M perchloric acid. This silylation reaction is both fast and simple. The reaction is shown in Figure 2. The curing by heating is to ensure complete bond formation between the silica gel matrix and the silane as implied in Figure 2. No problems were encountered in executing the reaction. There was no evidence of chemical degradation except when the resin was heated overnight at 110°, which causes the amine resin to become yellow, indicating oxidation and probable formation of some type of bound nitrogen oxide. Oxidation problems could also occur if the resins were placed in solutions containing appreciable amounts of very strong oxidizing agents.

Sodium hydroxide and strong hydrogen fluoride solutions appear to break down the resin. Exposure of the resin to strongly acidic or basic solutions for long periods of time will cause the silyl bonds to hydrolyze slowly. For this reason the resin should be rinsed with distilled water before storage. Periodic replacement of the resin may be necessary. The immobilized amine resin is air stable and may be stored at room temperature (18,19).

To convert the resin to the anion exchange form, perchloric acid is reacted with the resin. This reaction is shown in Figure 3. Perchloric acid was chosen because of its low absorbance at 220 nm and its good eluting ability. As shown in Figure 3, the resin can act as an anion exchanger after treatment with perchloric acid.

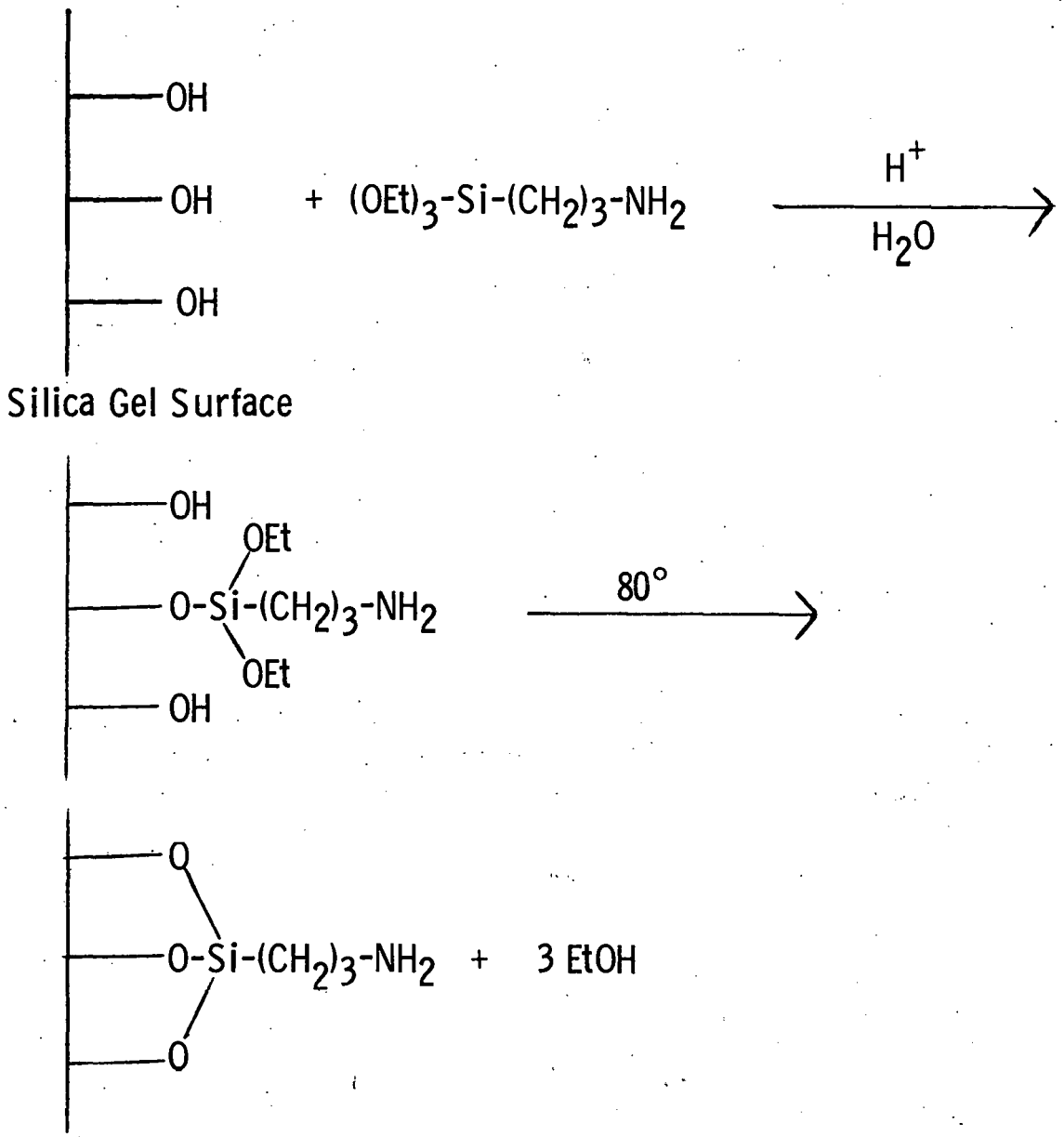

Figure 2. Surface bonding of the silane to silica gel.

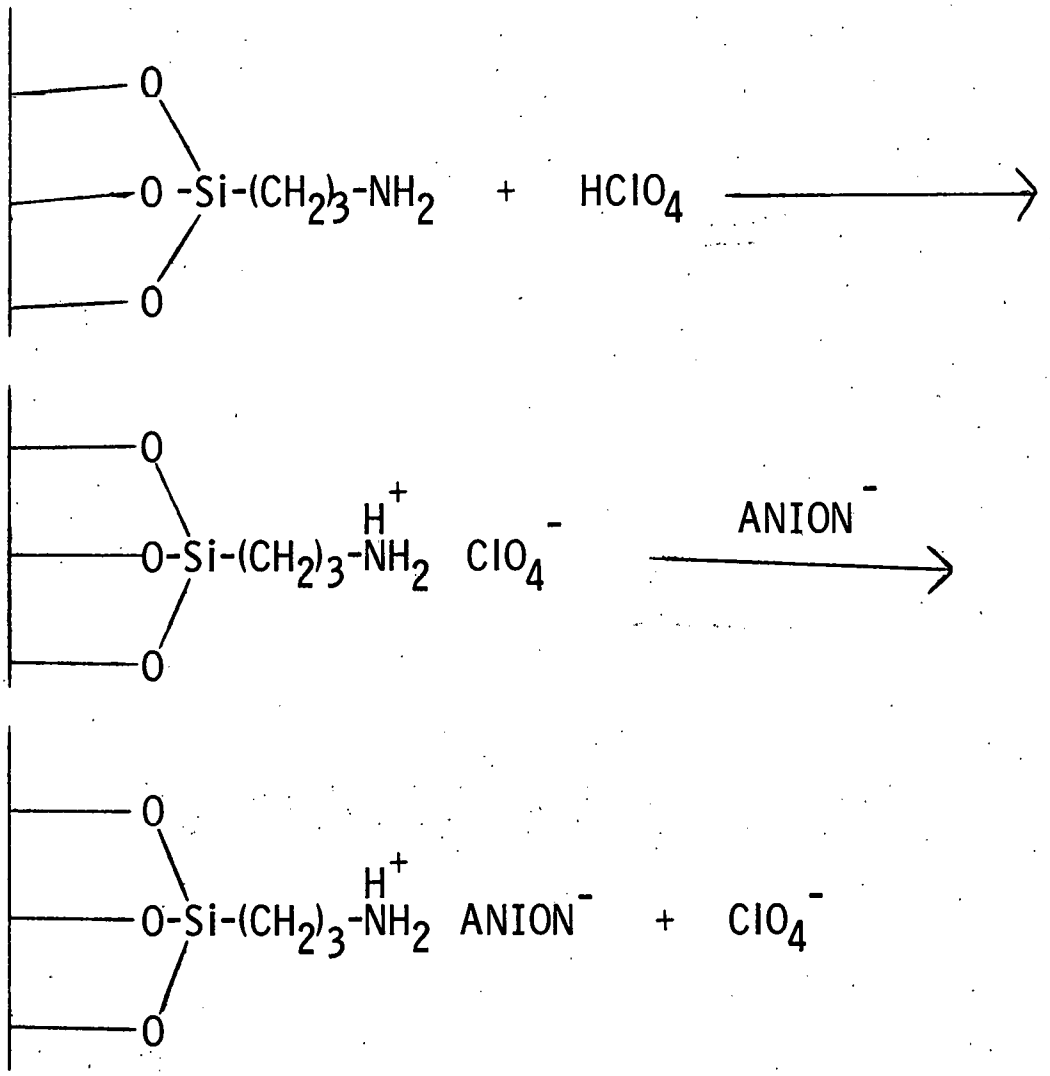

Figure 3. Conversion of the silylated silica gel to an anion exchange resin and the exchange of an anion.

Ultraviolet Absorbance

Ultraviolet detection was chosen because it is highly sensitive and somewhat selective, and because of the availability of an ultraviolet spectrophotometer in most laboratories. The nitrate ion has two absorption peaks in the ultraviolet: one at 203 nm (molar absorptivity = 1×10^4 moles^{-1} cm^{-1}) and the other at 300 nm (molar absorptivity = 7.5 moles^{-1} cm^{-1}) (20). Because interferences are much larger at 203 nm and since the loss in sensitivity is not significant, 220 nm (molar absorptivity = 3.82×10^3 moles^{-1} cm^{-1}) was the wavelength chosen to carry out the determination. A spectrum of nitrate is shown in Figure 4. Figure 5 shows that the system obeys Beer's Law at 220 nm. Preparation of the calibration curve is necessary only once, as the calibration curve did not change with time. Calibration curves will have to be made for each instrument.

As the light transmitted at 220 nm is of high energy, error may arise from improper cleaning of the cells. Care should be taken to ensure complete rinsing of cleaning solution and to remove streaks or particles from the outside of the cuvette.

Effect of Experimental Variables

pH Dependence

The pH is very important in this procedure, as the separation of nitrate from interferences is pH dependent. The anions are separated on the basis of acidic strength. As the pH is lowered, the weaker anions are protonated. The protonated anions have no charge and therefore go through the column with little or no interaction with the resin. For this reason, the pH of the sample is adjusted to 3-3.5 before being passed

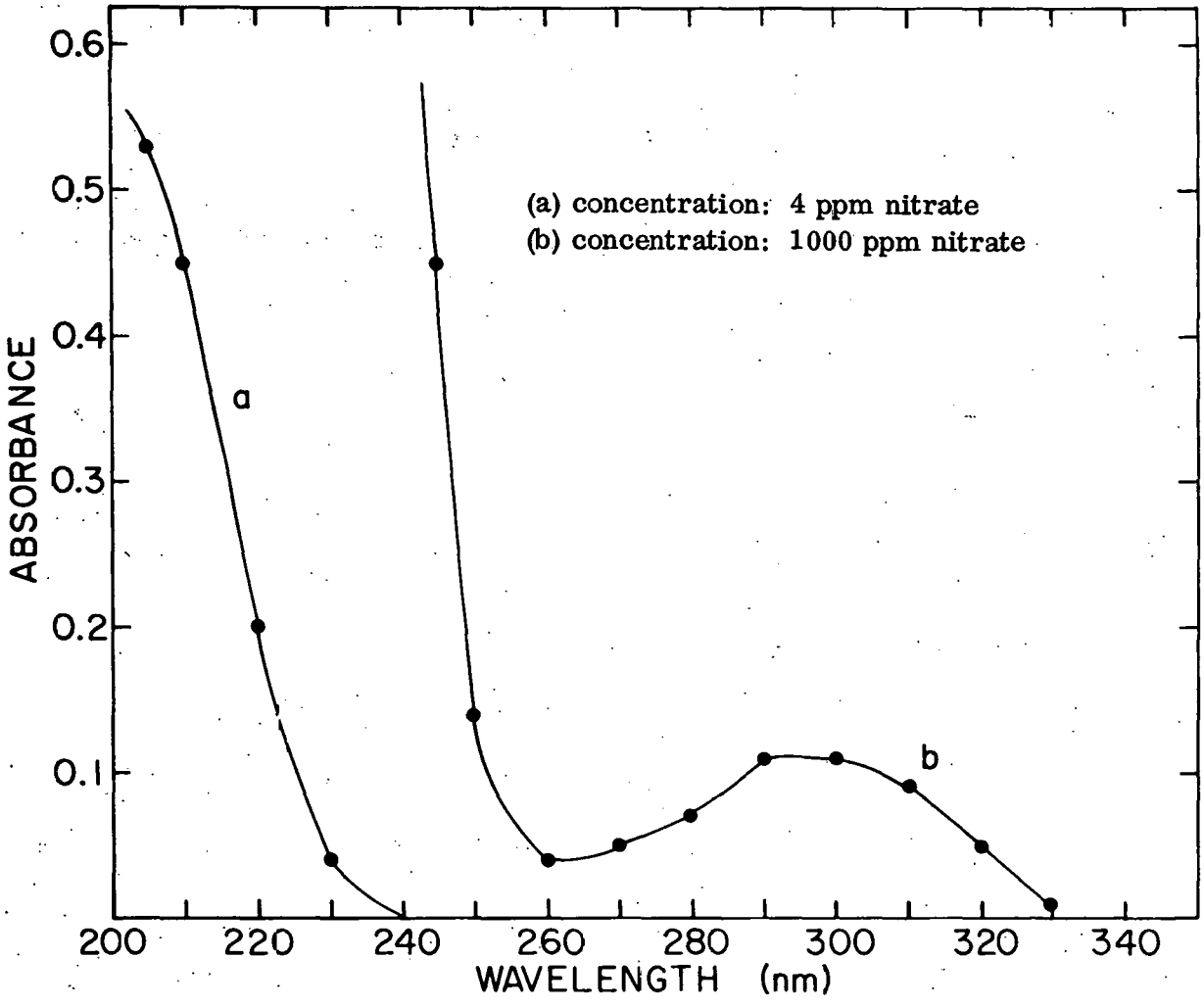

Figure 4. The spectrum of nitrate.

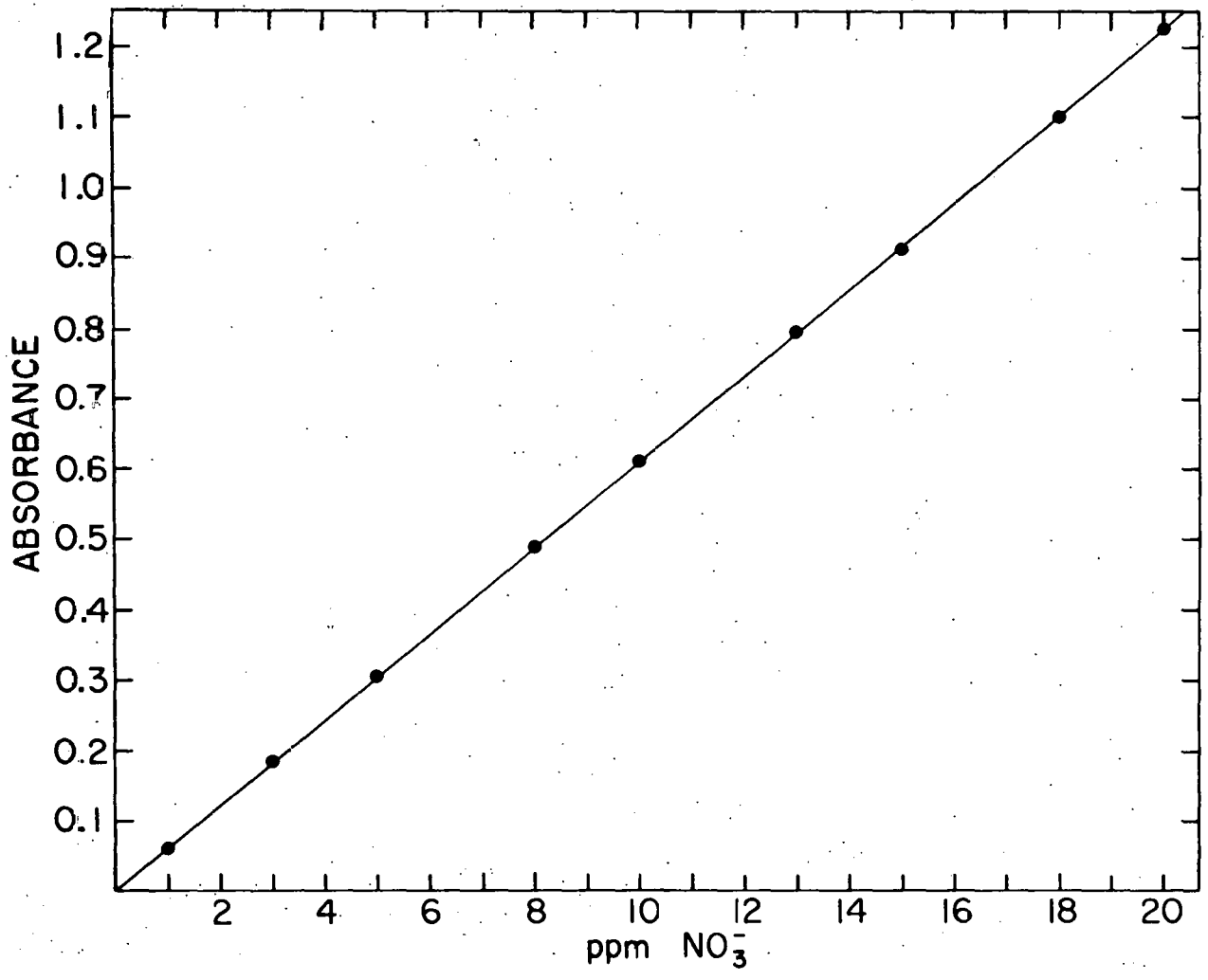

Figure 5. Nitrate calibration curve.

through the column. At this pH carbonate is primarily in the protonated form and goes through the column quickly. As the pH of the eluent is lowered to 2, anions such as nitrite and acetate are eluted from the column. As the pH of the eluent is further lowered to 0.3, nitrate and other strong anions are eluted from the column.

Keeping the pH low is also important in order to separate some cations from nitrate. The silica gel matrix will retain several metal cations at higher pH values. This is due to the interaction between the metal and the hydroxyl groups on the silica gel. As the pH is lowered, the interaction between metals and silica gel decreases (21).

The pH of the solution has no effect on the absorbance of nitrate, but does decrease the absorbance of carbonate and nitrite.

Flow Rate

Precise control of the flow rate in this procedure is not critical. No change in results was observed at flow rates from 1-5 ml/min. Increasing the flow rate to 10 ml/min gave low results, probably because of insufficient interaction time between the nitrate and the resin. All results in this paper were obtained using a flow rate of 5 ml/min, as this seemed to be the optimum flow rate.

Other Variables

Resin capacity, column diameter, resin size, amount of resin used, and other variables affect the volume and concentration of eluent necessary to elute certain anions. Since these variables are not exactly reproducible, a few preliminary tests should be made after the resin has been placed in the column and before samples are analyzed. To do this, a standard solution containing 5 ppm nitrate and 5 ppm nitrite is prepared. The column is activated by passing 25 ml of 1 M perchloric acid through the column,

followed by 15 ml of distilled water. The pH of the standard nitrate and nitrite solution is adjusted to 3-3.5. Five milliliters of the standard solution is passed through the column and washed with 5 ml of pH 3-3.5 perchloric acid. Thirty milliliters of 0.02 M perchloric acid is added to the column. Two hundredths molar perchloric acid is passed through the column and the effluent is collected in 5 ml volumetric flasks. The absorbance of the effluent is measured at 220 nm. The nitrate should be eluted in the first 10-15 ml. The nitrate should start coming off the column slowly after 15-25 ml (see Figure 6). If the nitrite and nitrate are coming off too slowly, increase the concentration of the 0.02 M perchloric acid until the nitrate and nitrite are coming off at the correct times. If the nitrate is coming off too quickly, decrease the concentration of the 0.02 M perchloric acid until the nitrate comes off at the correct time. When the proper concentration has been determined, this concentration should be used for all determinations with that particular resin and column. This procedure will also give the optimum point at which the eluent should be changed from 0.02 to 1 M perchloric acid. For example, if the nitrate starts to come off the resin in the 16-20 ml volume increment, this is the point that the eluent should be changed to 1 M perchloric acid (see Figure 7). This eluent change causes the nitrate to be eluted in 10-15 ml instead of 30 ml required without the eluent change. After this is done, a few standard solutions of nitrite and nitrate should be ran through the entire procedure to ensure correct results are being obtained.

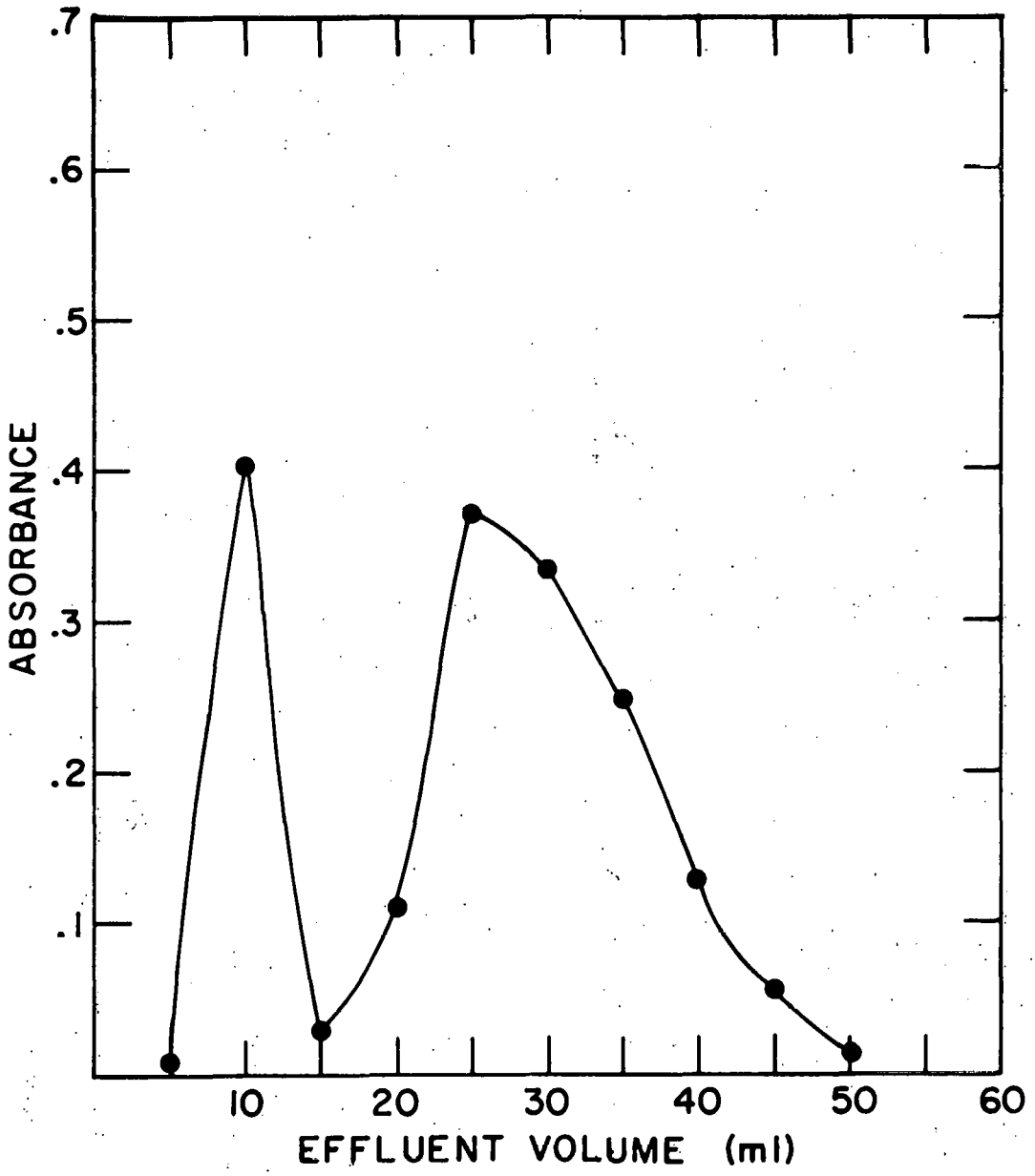

Figure 6. Elution of nitrite and nitrate.
Eluent: 0.02 M perchloric acid.

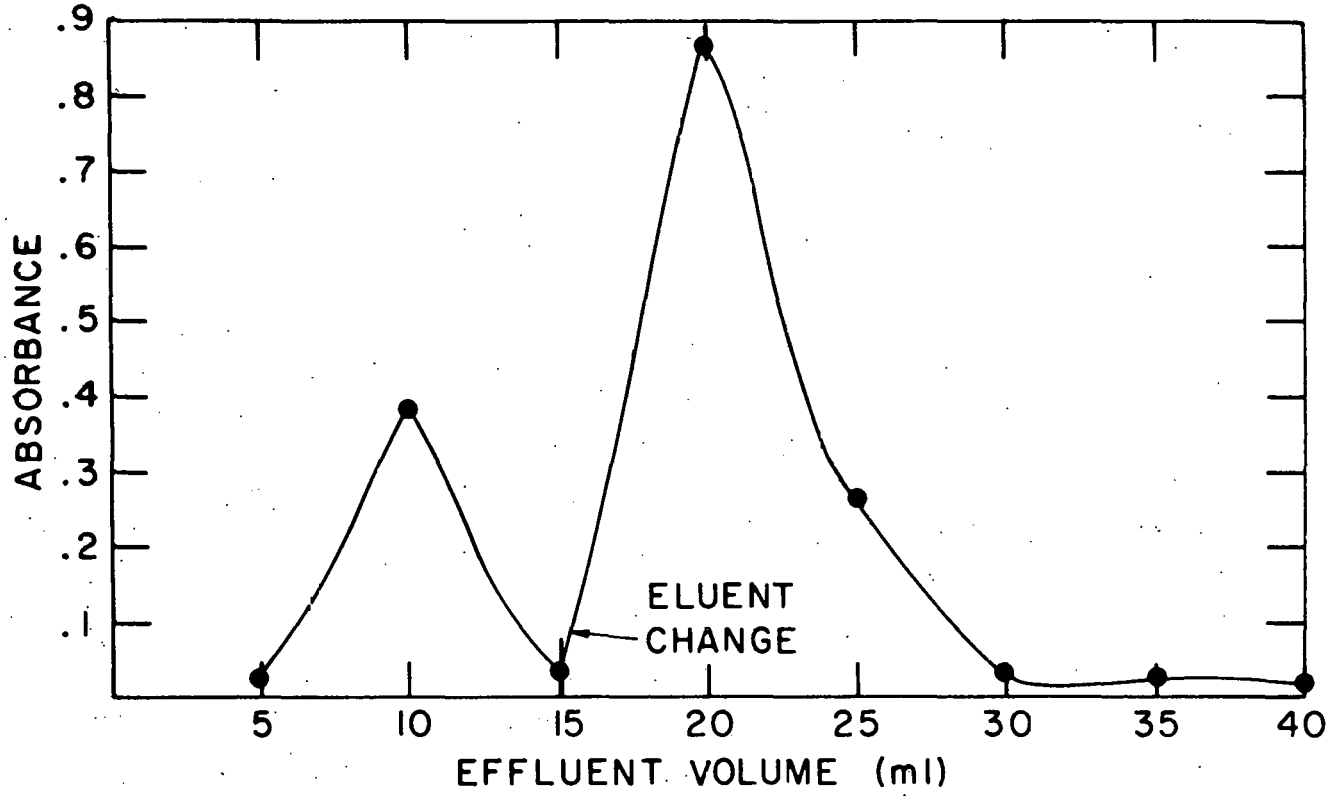

Figure 7. Elution of nitrite and nitrate. The eluent is changed from 0.02 M perchloric acid to 1 M perchloric acid at the point indicated.

Interference Study

Since several anions and cations and many organic compounds absorb in the ultraviolet at 220 nm, an interference study was made to determine if the nitrate is separated from interferences. The results of this study are shown in Table I. The sample size was 5 ml for all but the 100 ppm and the 1 ppm nitrate samples, which were 1 ml and 10 ml respectively. One determination was carried out for each sample. Presumably better results could be obtained if the determinations were carried out in triplicate.

Most anions commonly found in potable water are shown not to interfere at concentrations normally found in potable water. Iron (III) at 10 ppm did not interfere but at 100 ppm did. Tartrate, oxalate, and citrate at concentrations of 10 ppm interfere slightly. These are divalent anions which are harder to elute. Ten parts per million bromide causes a slight interference but is rarely found in potable water in concentrations above 1 ppm. Nitrite can be tolerated up to 10 ppm. Chromium (VI) does not interfere at a concentration of 5 ppm. Chromium (VI) is different from other interferences as the chromium (VI) remains on the column, probably in the dichromate form. If the water being analyzed contains appreciable amounts of chromium (VI), a yellow band will form at the top of the resin. The chromium (VI) can be removed by washing with strong ammonium hydroxide. As a further check, a synthetic sample containing 2.0 ppm nitrate, 1.0 ppm nitrite, 500 ppm carbonate, 100 ppm sulfate, and 100 ppm acetate was analyzed with a result of 2.1 nitrate found.

Table I

Interference Study

Nitrate Added	Interference Added	Nitrate Found
5.0 ppm	none	5.0 ppm
5.0	none	4.9
5.0	none	5.0
100.0	none	100.0
1.0	none	1.0
5.0	10 ppm bromide	5.3
5.0	100 ppm iron (III)	7.2
5.0	10 ppm iron (III)	5.0
5.0	1000 ppm carbonate	5.0
5.0	1000 ppm acetate	4.9
5.0	1000 ppm sulfate	5.2
5.0	1000 ppm phosphate	5.0
5.0	1000 ppm chloride	5.0
5.0	100 ppm nitrite	14.2
5.0	10 ppm nitrite	5.1
5.0	5 ppm chromium (VI)	5.0
5.0	10 ppm tartrate	5.3
5.0	10 ppm oxalate	5.5
5.0	100 ppm citrate	5.7

Analysis of Real Samples

To show the applicability of the method, several real samples were analyzed. The results are shown in Table II. In the first two cases the water was collected from the tap after allowing the water to run for several minutes and analyzed the same day. Known amounts of nitrate were added to these samples and they were analyzed again to see if the added nitrate could be determined. Satisfactory results were obtained.

In the latter two cases the method is compared to the brucine method. The brucine method was carried out exactly as described in Standard Methods of Chemical Analysis (17). Since chlorine interferes in the brucine determination, the tap water was allowed to stand for two days to allow the chlorine to escape. The water gave a negative test with ortho-tolidine after two days, indicating that no chlorine remained. Satisfactory agreement is obtained between the two methods for the tap water analysis. In the analysis of the water from a small creek near Kelley, Iowa, the sample size was 1 ml for the anion exchange method. For the brucine method, the sample had to be diluted twenty times to get within the optimum concentration range. An error of 0.5 ppm nitrate in the determination by the brucine method would result in an error of 10 ppm because of the dilution, and the brucine method is accurate to only 0.5 ppm nitrate.

Table II

Analysis of Real Samples

Iowa State University Tap Water

Date Taken	Date Analyzed	Nitrate Added	Nitrate Found
8-13-75	8-13-75	none	4.4 ppm
8-13-75	8-13-75	2.0 ppm	6.3 ppm
9-4-75	9-4-75	none	4.0 ppm
9-4-75	9-4-75	2.0 ppm	6.0 ppm

Iowa State University Tap Water: Taken 9-4-75

Analyzed 9-6-75

Nitrate Found by Brucine Method	Nitrate Found by Anion Exchange Method
3.3 ppm	3.4 ppm

Small Creek Near Kelley, Iowa: Taken 8-14-75

Analyzed 8-15-75

Nitrate Found by Brucine Method	Nitrate Found by Anion Exchange Method
56 ppm	65 ppm

SUMMARY

Nitrate is separated from interfering species with a weak-base anion-exchange resin and is determined by measuring the absorbance due to nitrate at 220 nm. The weak-base anion-exchange resin is easily synthesized, is quite stable, and behaves nicely in a column. The method requires little sample preparation and is rapid, requiring approximately 10 min per sample.

The detection limit is 0.1 ppm nitrate with a range of 0.1 to 100 ppm nitrate. The relative error and the relative standard deviation is typically less than 2% and 1% respectively. This is due to the high sensitivity of the ultraviolet measurement of 0.061 absorbance unit per part-per-million nitrate.

Interferences from iron (III), iodide, bromide, nitrite, and some organics were observed. Concentrations of these substances high enough to cause interference are not usually found in potable water.

This method should be easily adapted to automatic detection by using a flow-through cell in the ultraviolet spectrophotometer with a recorder connected to the spectrophotometer. Since flow-through cells have a very small volume, a much smaller sample could be used; and with automatic recording, the concentration of nitrate could be determined from the peak area. Automatic detection would simplify the method considerably.

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