

AN ABSTRACT OF THE THESIS OF

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TITLE: **Removal of Organic Interferences in Analysis of Nitrate in Water by UV**

Spectroscopy

Abstract approved: 

The determination of nitrate-nitrogen in water is difficult. The relatively complex procedure, the presence of interfering substances, and the limited concentration range of the various techniques all contribute to the difficulty. UV spectroscopy methods can be used, but they only determine approximate concentrations due to the organic compounds which can produce absorbances at the same wavelength as nitrate does. Once organic compounds can be removed, the accuracy of nitrate-nitrogen analysis by UV spectroscopy would be greatly improved.

The main purpose of this research was to test methods for removal of organic compounds from water samples in order to improve the accuracy of the UV spectroscopy method for analysis of nitrate. Organic matter was not removed effectively by Prep-Sep C-18 Cartridges but was removed by XAD-4 resin. Pretreatment with XAD-4 produced results only slightly higher than the cadmium reduction method.

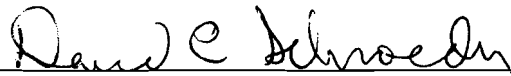
REMOVAL OF ORGANIC INTERFERENCES IN ANALYSIS OF NITRATE IN
WATER BY UV SPECTROSCOPY

A Thesis
Presented to
The Division of Physical Sciences
EMPORIA STATE UNIVERSITY

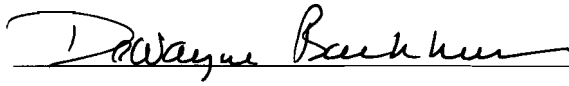
In Partial Fulfillment
Of the Requirements for the Degree
Master of Science in Physical Sciences

by
Miaoju Luo
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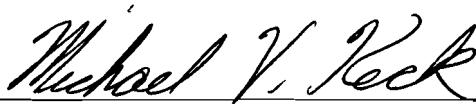
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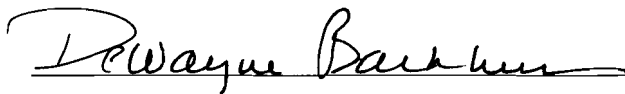
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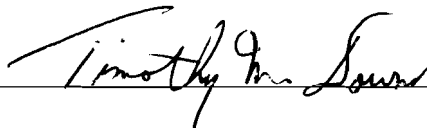
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Approved by the Major Division



Approved by the Dean of Graduate Studies and Research

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PREFACE

The element nitrogen is essential: all living systems need nitrogen to exist since it is used to build many essential components such as proteins, nucleic acids, vitamins, hormones, and enzymes. A concentration of nitrate exceeding 45 milligrams/Liter as nitrate or 10 milligrams/Liter as nitrogen is considered dangerous. The high concentration of nitrate in drinking water is a potential human health threat. Nitrate is converted in the gut to nitrite, which then combines with hemoglobin to form methemoglobin, thus decreasing the ability of the blood to carry oxygen.

The determination of nitrate-nitrogen in water is difficult. The relatively complex procedure, the presence of interfering substances, and the limited concentration ranges of the various techniques all contribute to the difficulty. UV spectroscopy methods can be used, but they only determine the approximate concentration due to the fact that organic compounds can produce absorbance at the same wavelength as nitrate does. Once organic compounds can be removed, the nitrate-nitrogen analysis by UV spectroscopy would be greatly facilitated.

The main purpose of this research was to test methods for removal of organic compounds from water samples in order to improve the accuracy of the UV spectroscopy method for analysis of nitrate. Organic matter was not removed effectively by Prep-Sep C-18 Cartridges but was removed by XAD-4 resin. Pretreatment with XAD-4 produced results only slightly higher than the cadmium reduction method.

TABLE OF CONTENTS

Section.....	Page
Chapter	
1. INTRODUCTION.....	1
Why nitrate is analyzed.....	1
Problems with current methods.....	2
Principle of UV method.....	2
Effect of Organic matter on UV method.....	3
Objectives of this study.....	3
2. LITERATURE REVIEW.....	4
3. PROCEDURE.....	7
I. Prep-Sep Cartridge Method.....	7
II. XAD-4 Resin Method.....	12
III. Modified Cadmium Reduction Method.....	17
4. RESULTS AND DISCUSSION.....	21
I. Prep-Sep Cartridge Method.....	21
II. XAD-4 Resin Method.....	24
III. Modified Cadmium Reduction Method.....	26
5. SUMMARY AND CONCLUSION.....	53
6. REFERENCES.....	56

LIST OF TABLES

Table	Page
1. Effect of Prep-Sep on Absorbances of Phosphate Buffered Mixture.....	33
2. Effect of Prep-Sep on Absorbances of Samples from Lake Wabaunsee.....	34
3. Effect of Prep-Sep on Absorbances of Samples in Lake Wabaunsee Under Acid Condition using Prep-Sep Cartridge Method.....	35
4. Nitrate-Nitrogen Concentration in Lake Wabaunsee Using XAD-4 Resin Method.....	36
5. Nitrate-Nitrogen Concentration in Lake Wabaunsee Using XAD-4 Resin Method... ..	37
6. Nitrate-Nitrogen Concentration in Lake Wabaunsee using Cadmium Reduction Method	41
7. Nitrate-Nitrogen Concentration in Lake Wooster using Cadmium Reduction Method	42
8. Nitrate-Nitrogen Concentration in Lake Wooster using Cadmium Reduction Method	43
9. Nitrate Concentration in Lake Wabaunsee under Acid Condition Using Prep-Sep Cartridge Method	46
10. Nitrate Concentration in Lake Wabaunsee under Acid Condition Using Prep-Sep Cartridge Method	47
11. Nitrate Concentration in Lake Wabaunsee without TBA Condition Using Prep-Sep Cartridge Method	48
12. Nitrate Concentration in Lake Wabaunsee with TBA Condition Using Prep-Sep Cartridge Method	49

LIST OF FIGURES

Figure	Page
1. Standard Curve for Nitrate-Nitrogen.....	29
2. Effect of Prep-Sep on Absorbances of Nitrate-Phenol Mixture.....	30
3. Effect of Acid on Nitrate-Nitrogen Conc. In Lake Wabaunsee using Prep-Sep Cartridge Method.....	31
4. Effect of TBA on Nitrate-Nitrogen Conc. In Lake Wabaunsee Using Prep-Sep Cartridge Method.....	31
5. Effect of XAD-4 on Absorbances of Nitrate-Nitrogen Standard.....	32
6. Nitrate-Nitrogen Concentration in Lake Wabaunsee using XAD-4 Resin Method.....	38
7. Nitrate-Nitrogen Concentration in Lake Wooster using XAD-4 Resin Method.....	38
8. Nitrate-Nitrogen Concentration in Lake Wabaunsee using XAD-4 Resin Method.....	39
9. “Time Window” for Nitrate-Nitrogen using Cadmium Reduction Method.....	39
10. Nitrate-Nitrogen Standard Curve using Cadmium Reduction Method.....	40
11. Effect of Prep-Sep on Nitrate Absorbance	40
12. Effect of Prep-Sep on Absorbances of Nitrate-Phenol Mixtures at 220 nm.....	44
13. Effect of Prep-Sep on Absorbances of Nitrate-Phenol Mixtures at 270 nm.....	44
14. Effect of Prep-Sep on Absorbances of Phosphate Buffer Mixtures at 220 nm....	45
15. Effect of Prep-Sep on Absorbances of Phosphate Buffer Mixtures at 270 nm....	45
16. Effect of pH on Removed of Organic Matter from Lake Wabaunsee Samples using Prep-Sep Method	50
17. Comparison of Nitrate Concentration in Lake Wabaunsee by using XAD-4 Resin and Cadmium Reduction Method	50
18. Comparison of Nitrate Concentration in Lake Wooster by using XAD-4 Resin and Cadmium Reduction Method (Sample Date:11/03/98).....	51
19. Comparison of Nitrate Concentration in Lake Wooster by using XAD-4 Resin and Cadmium Reduction Method (Sample Date: 12/16/98).....	51

CHAPTER 1. INTRODUCTION

Why nitrate is analyzed

The element nitrogen is essential: all living systems need nitrogen to exist since it is used to build many essential components such as proteins, nucleic acids, vitamins, hormones, and enzymes. Complex organisms such as animals can not use simple forms of nitrogen such as nitrate and ammonium and must get complex forms of nitrogen such as amino acids and nucleic acids. Plants provide the bulk of nitrogen for all living systems (most microbes - like bacteria - can make their own complex nitrogen compounds).

The accumulation of nitrate in the environment results mainly from non-point source runoff from the over-application of nitrogenous fertilizers and from poorly or untreated sewage. A concentration of nitrate exceeding 45 milligrams/Liter as nitrate or 10 milligrams/Liter as nitrogen is considered dangerous [1]. The high concentration of nitrate in drinking water is a potential human health threat [1, 3]. Nitrate is converted in the gut to nitrite, which then combines with hemoglobin to form methemoglobin, thus decreasing the ability of the blood to absorb oxygen. Infants are more susceptible to nitrate toxicity than older children or adults, which is also called "blue baby syndrome" [2]. A National Cancer Institute (NCI) [3] study suggests that the more nitrate persons consume in their water, the greater the probability of developing NHL (Non-Hodgkin's Lymphoma) [3]. Nitrate consumption is also being studied as a possible risk factor for stomach cancer, a disease that is less common in the United States than in Asia and some other parts of the world. The World Health Organization (WHO) is very active in pursuing reduced concentrations in drinking water [3].

Problems with current methods

There are a variety of methods available for the analysis of nitrate-nitrogen in water. These include American Public Health Association (APHA) Nitrate Method [4], the reduction of nitrate to nitrite [5], reversed-phase ion-interaction liquid chromatographic separation [6], second-derivative spectrophotometry [7], differential pulse polarography with simultaneous nitrogen purging [8], and formation of manganese and iron porphyrins [9]. Unfortunately, the relatively complex procedures, the presence of interfering substances, poor precision and the limited concentration ranges of the various techniques make the determination of nitrate-nitrogen difficult.

Principle of UV method

The ultraviolet (UV, 20-400 nm) and visible regions of the electromagnetic spectrum are energetic enough that the energy that is absorbed will affect the energy states of electrons occupying molecular orbitals within the molecule. If the energy of the radiation is equal to or greater than the energy of transition for an electron to be promoted to the next available molecular orbital, then energy will be absorbed by that electron which is promoted to the higher energy molecular orbital. This absorption of energy will occur when energy from the UV or visible regions is supplied. Infrared radiation is not energetic enough to cause electronic transitions within molecules.

In the UV method, the primary absorbance measurement is at 210 or 220 nm [10,11]. At this wavelength, nitrate and many organic compounds with pi bonds absorb. A second measurement is made at 270 nm, where the organic compounds absorb but

nitrate does not [17]. The absorbance at 270 nm is multiplied by an empirical factor and subtracted from the absorbance at 210 or 220 nm to determine the absorbance caused by nitrate only. Currently, the method is recommended for screening only [20] because the empirical correction factor varies from one compound to another.

Effect of organic matter on UV method

The absorption at the nitrate wavelength due to dissolved organic matter is anywhere from two to four times as great as that at the wavelength used to determine dissolved organic matter (270 nm). The absorbance at 270 nm is used to determine the presence, or absence, of this dissolved organic matter that could also show absorbance at the wavelength selected for the nitrate-nitrogen determination. This method is not accurate when the dissolved organic matter concentrations are high and the nitrate-nitrogen concentration is low. The reason for the unreliability of the correction factor techniques comes from the different organic compounds present in different types of water.

Objectives of this study

The objective of this study was to improve the accuracy of the UV method for nitrate-nitrogen analysis by refining and testing methods between for the removal of dissolved organic matter in water samples. This removal process would eliminate most dissolved organic matter, making the analysis of nitrate-nitrogen by UV spectroscopy a simpler and more accurate method.

CHAPTER 2. LITERATURE REVIEW

The direct UV method is especially suited for samples that have low dissolved organic matter contents, such as uncontaminated natural waters and potable water supplies.

In addition to the correction factor techniques briefly mentioned, other nitrate-nitrogen methods have been proposed to deal with the interference due to dissolved organic matter using wavelengths at 210 nm and 230 nm. Armstrong's addition of an equal volume of concentrated sulfuric acid to a solution containing nitrate, when chloride is also present, causes a change in the nitrate absorption spectrum, the maximum being shifted to 230 nm [12]. The measurement at 230 nm is easier because the absorbance of other substances is less than at 210 nm, and may even be diminished in the presence of the sulfuric acid. The high acid concentration increases the reactivity of nitrate so that it may be destroyed by a suitable reducing agent, a hydrazine sulfate solution, allowing an accurate measurement of the non-nitrate absorbance of the sample. The difference in the two readings is proportional to the nitrate concentration. The sample should not contain more than 2.5 parts per million nitrate-nitrogen but should contain more than 2 grams of chloride per liter. Samples of higher nitrate concentration may be diluted, and, if the chloride concentration is too low, hydrochloric acid may be added.

A rapid and accurate method for determining nitrate has been proposed by Bastian [13] for determining nitrate in alkaline earth carbonate mixtures. The method utilizes ultraviolet absorption of nitrate ion in dilute perchloric acid. The method consists of

dissolving the sample in dilute perchloric acid and reading the absorbance at 210 nm. Interferences due to metal ions are removed by passing a weak perchloric acid solution of the material through a cation exchange resin.

The proposed method for potable waters by Navons [14] is also based on the absorption of nitrate at 220 nm. The absorbance of a water sample containing nitrate ion is measured at 220 nm against a duplicate portion of the sample, a blank, in which the nitrate ion has been reduced to ammonia by the action of a zinc-copper couple in an acidified medium. The use of the blank corrects for all interfering substances except nitrite. It is assumed that nitrite ion concentrations in potable waters are low, and is therefore not a significant factor. Waters having a nitrate ion concentration above 8.8 mg/L must be diluted in order to use this proposed method.

The variability of the dissolved organic matter correction techniques and the possible lowering of precision by diluting a sample to bring the absorbance within the linear range of UV spectrophotometric analysis emphasizes the need for a non-arbitrary method with improved accuracy. Such a method has been proposed by Rennie [12], which removes not only the dissolved organic matter prior to analysis, but also some of the cationic interferences that affect the determination of nitrate.

Because of the difficulties encountered in dealing with dissolved organic matter and the potential effectiveness of activated charcoal, Rennie and his associates investigated the organic matter content, nitrate content as received, and the extent of nitrate retention on approximately 20 types of activated charcoals. Unfortunately, most of the charcoals tested contain nitrate and organic matter that is easily leached out. Also, the

charcoals retained 19 to 84 percent of the nitrate under acidic conditions. Nevertheless, methods using activated charcoal have been investigated further.

For much of the organic absorbance in water is due to humic substances. Thursman [19] recommends the use of XAD-4 resin for removal of these substances, but this has not been tested in conjunction with nitrate analysis.

Sample preparation cartridges are available for adsorption of organic compounds from solution. The Prep-Sep cartridge with C-18 packing (saturated hydrocarbon branches with 18 carbon atoms) is especially recommended [15] but have not been used in the analysis of nitrate.

The following section describes experiments to determine the effectiveness of the Prep-Sep C-18 cartridge and XAD-4 resin in removing the organic interferences in the UV analysis of nitrate.

CHAPTER 3. PROCEDURE

I. Prep-Sep Cartridge Method

A. Apparatus

Absorbance was measured at 220 nm and 270 nm with a GCA-McPherson double-beam spectrophotometer using a 1-cm path-length fused-silica cell.

Fisher Prep-Sep disposable columns are prepackaged with 40Å pore sizes, sorbent C₁₈ with 12 milliliter in reservoir capacity and 300 milligram in packing quantity [16].

B. Reagents

1. Distilled, deionized water, stored in a glass container (to eliminate the additional absorbance caused by plastic), was used for all solutions and dilutions.
2. A stock nitrate solution was prepared by weighing 0.72313 gram of potassium nitrate, dried in an oven at 105° C for 24 hours, dissolved in water and diluted to 1000 ml. This was then preserved with 2 milliliter of chloroform per liter giving a final concentration of 100.24 milligram of nitrate-nitrogen per liter.
3. A standard nitrate solution was prepared by diluting 100 mL (weigh: 99.324 gram) of stock nitrate solution to 1000 mL with water, giving a final concentration of 9.986 milligram of nitrate-nitrogen per liter.

4. A stock phenol solution was prepared by weighing 0.01176 gram of phenol, dissolved in water and diluted to 1000 mL, producing a final concentration of 11.76 milligram of phenol per liter.
5. A standard phenol was prepared by diluting 8.55 milliliter (weigh: 8.523 gram) of stock phenol solution to 1000 mL with water, giving a final concentration of 0.100 milligram of phenol per liter (which is equal to 100 parts per million).
6. Phosphate buffer was prepared by dissolving one commercial buffer capsule in 100 mL of distilled, deionized water. Its pH was 7.00 at 25°C.
7. A standard potassium chloride (KCl) solution was prepared by weighing 18.624 gram of potassium chloride (KCl), dissolved it in water and diluted to 250 mL, giving a final concentration of one mole per liter (1M) of potassium chloride (KCl) solution.

C. Procedure

1. Standard curve

a) Standard Sample Preparation

Varying amounts of standard nitrogen solution were weighed into 50 mL volumetric flasks. The samples were diluted to volume with distilled, deionized water.

b) Instrument Adjustment

The instrument was turned on and allowed to warm up for 10 minutes. Cell cleanliness was tested by measuring absorbance

against air; cells were rinsed with chromic acid if this absorbance was greater than 0.1.

c) Record Absorbance

Each sample absorbance was measured at 220 nm and 270 nm. Two sets of absorbances (with filtration and without filtration) were recorded (Figure 1).

2. Measurement of phenol adsorption

Six samples were prepared; one of which was a blank (distilled, deionized water), one was a standard nitrate-nitrogen but without phenol, and the remaining four samples contained different concentrations of nitrate-nitrogen and phenol. Two sets of absorbances (with filtration and without filtration) were recorded (Figure 2).

3. Measurement of phenol adsorption in buffer

Three samples were prepared, one of which was a blank (just distilled, deionized water), and the other two with the same concentration of nitrate-nitrogen but one with phenol and another one without phenol. Two sets of absorbances (with filtration and without filtration) were recorded (Table 1).

4. Measurement of the concentration of nitrate-nitrogen in Lake

Wabaunsee samples with buffer added

Six samples were prepared, one blank (distilled, deionized water and buffer), one was a standard nitrate-nitrogen and the rest with

samples from different locations in lake Wabaunsee (North, East, West, Southeast) and buffer. All samples were filtered and refrigerated until analyzed. Two sets of absorbances (with filtration and without filtration) were recorded (Table 2).

5. Measurement of the concentration of nitrate-nitrogen in Lake Wabaunsee samples with acid added

Six samples were prepared, one was a blank (distilled, deionized water and two drops of 1M hydrochloric acid), one was a standard nitrate-nitrogen and the rest were samples from different locations in lake Wabaunsee (North, East, West, Southeast) with two drops of 1M hydrochloric acid. All samples were filtered and refrigerated until analyzed. Two sets of absorbances (with filtration and without filtration) were recorded (Table 3).

6. Measurement of the concentration of nitrate-nitrogen in Lake Wabaunsee samples with acid added. (Samples collected at different timing)

Seven samples were prepared. One sample was a blank (distilled, deionized water and two drops of 1M hydrochloric acid), one was a standard nitrate-nitrogen and the rest were samples from different locations in lake Wabaunsee (North, East, West, Southeast, Southwest) with two drops of 1M hydrochloric acid. All samples were filtered and refrigerated until analyzed. Two sets of

absorbances (with filtration and without filtration) were recorded (Figure 3).

7. Measurement of the concentration of nitrate-nitrogen in Lake Wabunsee samples with TBA added

Seven samples were prepared. One sample was a blank (distilled, deionized water and 100 microliter of ion-pair reagent, tetrabutylammonium phosphate (TBA). The concentration of TBA is 0.005 M after mixing), one was a standard nitrate-nitrogen and the rest were samples from different locations in lake Wabaunsee (North, East, West, Southeast, Southwest) with 100 micrometer of reagent TBA. All samples were filtered and refrigerated until analyzed. Two sets of absorbances (with filtration and without filtration) were recorded (Figure 4).

II. XAD-4 Resin Method (Isolation of Aquatic Humic Substances by Adsorption Chromatography)

A. Apparatus

All samples were passed through XAD-4 resin chromatography column treatment before being measured. Absorbance was measured at 220 nm and 270 nm with GCA- McPherson double-beam spectrophotometer using a 1-cm path-length cell.

The chromatography column was 50 mL in volume with a 2mm bore Teflon[®] stopcock. Amberlite XAD-4 resin are used in cleanup and sampling procedures. XAD-4 resin was 20/60 in Mesh and 100 gram quantity [16]. The chromatography column contained 20 ml of resin.

B. Reagents

1. Distilled, deionized water, stored in a glass container (to eliminate the additional absorbance caused by the absorbant of plastic) was used for all standard solution and dilutions.
2. A stock nitrate solution was prepared by weighing 0.72313 gram of potassium nitrate, dried in an oven at 105° C for 24 hours, dissolved in water and diluted to 1000 mL. This was then preserved with 2 milliliter of chloroform per liter giving a final concentration of 100.24 milligram of nitrate-nitrogen per liter.
3. A standard nitrate solution was prepared by diluting 100 mL (weigh: 99.324 gram) of stock nitrate solution to 1000 mL with water, giving a final concentration of 9.986 milligram of

- nitrate-nitrogen per liter.
4. A stock sodium hydroxide (NaOH) solution was prepared by weighing 40.292 gram of sodium hydroxide (NaOH), dissolved in water and diluted to 1000 mL, producing a final concentration of 1.007 mole per liter.
 5. A standard sodium hydroxide (NaOH) solution was prepared by diluting 10 mL (weigh: 9.9971 gram) of stock solution to 100 mL with distilled, deionized water, giving a final concentration of 0.1 mole per liter.
 6. A standard hydrochloric acid (HCl) solution was prepared by diluting 10 mL of 1 N hydrochloric acid (HCl) to 1000 mL with distilled, deionized water. Its pH value was measured by digital pH/MV Meter. Distilled, deionized water was added until its pH reached 2.0.

C. Procedure

1. Measurement of XAD-4 resin

a) Standard Sample Preparation

Varying amounts of standard nitrogen solution were weighed into 50 mL volumetric flasks. The samples were diluted to volume with distilled, deionized water.

b) Instrument Operation

The operation of UV-Spectroscopy was the same as Prep-Sep Cartridge method. Every time when using XAD-4 column,

XAD-4 column should be rinsed through by 2 void volume of distilled water, washed by 3 void volume of 0.1 N of sodium-hydroxide, and neutralized by 3 void volume of hydrochloric acid (PH=2).

c) Record Absorbance:

Each sample absorbance was measured at 220 nm and 270 nm. Two sets of absorbances (with XAD-4 resin and without XAD-4 resin) were recorded (Figure 5).

2. Measurement of the concentration of nitrate-nitrogen in

Lake Wabaunsee

Four samples were prepared; one sample was a blank (distilled, deionized water), one was a standard nitrate-nitrogen, one was a sample without XAD-4 resin treatment and the rest were the samples after XAD-4 resin treatment.

All samples were under filtration and pre-refrigerated treatment. Two sets of absorbances (with XAD-4 resin treatment and without XAD-4 resin treatment) were recorded (Table 4).

3. Measurement of the concentration of nitrate-nitrogen in Lake Wabaunsee according to the elution order

Seven samples were prepared, one was a blank (distilled, deionized water), one was a standard nitrate-nitrogen, one was a sample without XAD-4 resin treatment and the rest

were samples base on the coming through order after XAD-4 resin treatment.

All samples were filtered and refrigerated until analyzed.

Two sets of absorbances (with XAD-4 resin treatment and without XAD-4 resin treatment) were recorded (Table 5).

4. Measurement of the concentration of nitrate-nitrogen in Lake Wabaunsee according to the elution order

Ten samples were prepared; one sample was a blank (distilled, deionized water), one was a standard nitrate-nitrogen, one was a sample without XAD-4 resin treatment and the rest were samples bases on the coming through order after XAD-4 resin treatment. Sample was from Lake Wabaunsee (composite), filtered and refrigerated until analyzed. Two sets of absorbances (with XAD-4 resin treatment and without XAD-4 resin treatment) were recorded (Figure 6).

5. Measurement of the concentration of nitrate-nitrogen in Lake Wooster according to the elution order

Eleven samples were prepared; one was a blank (distilled, deionized water), one was a standard nitrate-nitrogen, one was a sample without XAD-4 resin treatment and the rest were samples base on the coming through order after XAD-4 resin treatment. Sample was from Lake Woodster (composite), filtered

and refrigerated until analyzed. Two sets of absorbances (with XAD-4 resin treatment and without XAD-4 resin treatment) were recorded (Figure 7).

6. Measurement of the concentration of nitrate-nitrogen in Lake Wooster according to the elution order. The sample was also from Lake Wooster (composite) but collected at different dates.

Eleven samples were prepared; one was a blank (distilled, deionized water), one was a standard nitrate-nitrogen, one was a sample without XAD-4 resin treatment and the rest were samples based on the coming through order after XAD-4 resin treatment. Sample was from Lake Wooster (composite), under filtration and pre-refrigerated treatment. Two sets of absorbances (with XAD-4 resin treatment and without XAD-4 resin treatment) were recorded (Figure 8).

III. Modified Cadmium Reduction Method [18]

A. Apparatus

Absorbance was measured at 543 nm with a HACH DR/3000 Spectrophotometer using a 1-inch path-length glass cell. The concentration of nitrite reaction product was determined.

B. Reagents

1. A standard nitrate solution was prepared by diluting 100 mL (Weight: 99.324 gram) of stock nitrate solution to 1000 mL with water, giving a final concentration of 9.986 milligram of nitrate- nitrogen per liter.

Distilled, deionized water, stored in a glass container (to eliminate the additional absorbance caused by plastic), was used for all solutions and dilutions.

2. A standard nitrite solution was prepared by 500 microliter (weight: 0.497g) 250 mg/L as nitrogen of potassium-nitrite standard solution and diluted to 1000 ml, giving a final concentration of 0.125 milligram of nitrate-nitrogen per liter.
3. A 1-naphthyl-ethylenediamine-dihydrochloride (NED) solution was prepared by weighing 0.500 gram NED, diluted into 500 mL water, and stored in a brown bottle. (NED should prepared monthly)
4. Several packs of Nitra-Ver^R -6 dosage.

C. Procedure

1. "Time Window" for nitrite-nitrogen

a) Standard Sample Preparation

There were two samples needed to prepare, one was filled with distilled, deionized water and another was filled with standard nitrite standard solution in 50 mL volumetric flask. Added 2.0 milliliter NED to each flask. Samples were analyzed after 10 minutes but within two hours.

b) Instrument Adjustment

The instrument was turned on and allowed to warm up for 5 minutes. Cell cleanliness was tested by measuring absorbance against blank. Cells were rinsed with chromic acid if the absorbance display was not within plus or minus 0.01.

c) Record Absorbance

Sample absorbance was recorded every 5 minutes until the value of absorbance dropped dramatically. Zero was reset by using "R" cell between every interval. A set of absorbance were recorded (Figure 9).

2. Nitrite (NO₂⁻) Standard Calibration Curve

Six sample were prepared and in 50 milliliter volumetric flasks, one was a blank (distilled, deionized water) and the rest were standard nitrate-nitrogen but with a different concentrations. Two mL NED was added to each of

those samples. Recorded their absorbances every 5 minutes.

A set of absorbances were recorded (Figure 10).

3. Measurement of the concentration of nitrite-nitrogen from Lake Wabaunsee

Three samples were prepared and in 50 mL volumetric flasks, one was a blank (distilled, deionized water), one was a standard nitrite, and the rest were the product of cadmium reduction (nitrate changed to nitrite completely because of overdose of cadmium). Two mL NED was added to each of samples. Recorded their absorbances every 5 minutes. A set of absorbances were recorded (Table 6).

4. Measurement of the concentration of nitrite-nitrogen from Lake Wooster

Three samples were prepared and in 50 milliliter volumetric flasks, one was a blank (distilled, deionized water), one was a standard nitrite, and the rest were the product of cadmium reduction (nitrate changed to nitrite completely because of overdose of cadmium). Two mL NED was added to each of samples. Recorded their absorbances every 5 minutes. A set of absorbances were recorded (Table 7).

5. Measurement of the concentration of nitrite-nitrogen from Lake Wooster

Three samples were prepared and in 50 milliliter volumetric flasks, one was a blank (distilled, deionized water), one was a standard nitrite, and the rest were the product of cadmium reduction (nitrate changed to nitrite completely because of overdose of cadmium). Two mL NED was added to each of samples. Recorded their absorbances every 5 minutes. A set of absorbances were recorded (Table 8).

CHAPTER 4. RESULTS AND DISCUSSION

I. Prep-Sep Cartridge Method

The standard curve for nitrate-nitrogen (Figure 11) shows that Beer's law is obeyed when the concentration of nitrate-nitrogen is between zero to 10 milligrams per liter (mg as N/L). Figure 1a shows that the absorbance of nitrate-nitrogen didn't change after the treatment of Prep-Sep Cartridge Method. In another words, the Prep-Sep Cartridge had no effect on nitrate concentration.

Figure 2 shows that absorbance contributed by phenol obeyed Beer's Law. Figure 12 and Figure 13 show that Prep-Sep Cartridge treatment couldn't remove phenol effectiveness as well.

Figure 14 and Figure 15 show that phenol could be removed by Prep-Sep Cartridge when phosphate buffer was added. In another words, phenol can be eliminated by Prep-Sep Cartridge when solvent's pH value is 7. This may caused by the change of ionic strength. But this result was not easy to obtain due to the difficulty of preparation of cartridge. It was essential to rinse Cartridge by distilled, deionized water (add phosphate buffer) several times before Cartridge was used to filtrate the sample.

Table 2 shows the determination concentration of nitrate-nitrogen from different location in Lake Wabaunsee on February 1, 1998 by using Prep-Sep Cartridge Method under phosphate buffer condition. From the absorbance results at 270 nm (with filtration and without filtration), it indicated that cartridge treatment couldn't trap all the organic compounds in the Lake Wabaunsee sample. So, the Prep-Sep was effective in removing phenol when phosphate buffer was added, but was not effecting in removing the rest of organic compounds.

According to Beer's Law, the percentage of organic compounds not removed (P_1) was determined by

$$P_1 = A_{270f} / A_{270nf} * 100 \quad (4-1)$$

Where A_{270f} was the sample absorbance at 270 with Prep-Sep Cartridge treatment, and A_{270nf} was the sample absorbance at 270 nm without Prep-Sep Cartridge treatment. The absorbance (ΔA) contributed by trapped organic compounds at 220 nm was determined by

$$\Delta A = A_{220nf} - A_{220f} \quad (4-2)$$

where A_{220nf} was the sample absorbance at 220 without Prep-Sep Cartridge treatment, and A_{220f} was the sample absorbance at 220 nm with Prep-Sep Cartridge treatment. The absorbance (A) contributed to nitrate-nitrogen by organic compounds at 220 nm was determined by

$$A = \Delta A * 100 / (100 - P_1) \quad (4-3)$$

The concentration of nitrate-nitrogen (C_{sample}) in lake sample was determined by

$$C_{\text{sample}} = C_{\text{standard}} * (A_{\text{sample}} - A) / A_{\text{standard}} \quad (4-4)$$

Where A_{sample} was the lake sample absorbance at 220 nm without Prep-Sep cartridge treatment, A_{standard} was the standard absorbance at 220 nm., and C_{standard} was the standard concentration of nitrate-nitrogen.

Table 3 shows the concentration of nitrate-nitrogen locations of Lake Wabaunsee on February 1, 1998 by using Prep-Sep cartridge method under acid condition. The nitrate-nitrogen concentration from Lake Wabaunsee was calculated according to equation (4-1), (4-2), (4-3) and (4-4). By comparing the proportion of organic compounds was trapped by Cartridge from Table 5 and

Table 2, it indicated that cartridge was more effective under acidified condition than under phosphate buffer condition. It also showed Prep-Sep cartridge method could eliminate all organic compounds at neither condition. But the agreement of nitrate-nitrogen concentration determination was quite good according to Figure 16.

Table 9 shows the first trial of concentration of nitrate-nitrogen locations of Lake Wabaunsee on April 5, 1998 by using Prep-Sep cartridge method under acid condition. Table 10 shows the second trial of concentration of nitrate-nitrogen locations of Lake Wabaunsee on the same date by using the same method. The nitrate-nitrogen concentration from Lake Wabaunsee was calculated according to equation (4-1), (4-2), (4-3) and (4-4). The difference between Series1 and Series2 in Figure 3 showed that the performance of Prep-Sep Cartridge Method was quite consistent.

Table 11 shows the concentration of nitrate-nitrogen locations of Lake Wabaunsee on June 28, 1998 by using Prep-Sep cartridge method without TBA reagent. Table 12 shows the concentration of nitrate-nitrogen locations of Lake Wabaunsee on the same date by using the same method but with TBA reagent. Reagent TBA acted as an ion pair and was able to combine with organic compounds, which had opposite charge to TBA. The nitrate-nitrogen concentration from Lake Wabaunsee was calculated according to equation (4-1), (4-2), (4-3) and (4-4). We hoped more organic compounds be removed due to the bigger size if non-neutral organic compound existed in water sample. Unfortunately, this was not the case in water sample from Lake Wabaunsee based

on the data (% Org. not removed) from Table 11 and Table 12. Figure 4 shows the performance of Prep-Sep cartridge method was not consistent under TBA condition from the dramatically changed in the nitrate-nitrogen concentration result.

II. XAD-4 Resin Method (Isolation of Aquatic Humic Substances by Adsorption Chromatography)

The standard curve for nitrate-nitrogen (Figure 1) shows that Beer's law is obeyed when the concentration of nitrate-nitrogen is between zero to 10 milligrams per liter (mg as N /L). Figure 5 shows that the absorbance of nitrate-nitrogen didn't change after the treatment by XAD-4 Resin Method. In another words, the XAD-4 resin has no effect on nitrate.

Table 4 shows the concentration of nitrate-nitrogen form composite of Lake Wabaunsee on May 3, 1998 by using XAD-4 Resin Method. By comparing the absorbance of nitrate-nitrogen at 220 nm and at 270 nm. . The nitrate-nitrogen concentration from Lake Wabaunsee was calculated according to equation (4-1), (4-2), (4-3) and (4-4). It indicated that about eighty-three percent (83%) of organic compounds was removed after XAD-4 Resin treatment. But it was too early to determine the concentration of nitrate-nitrogen based on just one elution.

Table 5 shows the concentration of nitrate-nitrogen from composite of Lake Wabaunsee on May 3, 1998 by using XAD-4 Resin Method according to the order of elution. The nitrate-nitrogen concentration from Lake Wabaunsee was

calculated according to equation (4-1), (4-2), (4-3) and (4-4). By comparing the concentration of nitrate-nitrogen based on the elution order, it indicated the concentration of nitrate-nitrogen was vary in different elution which was reasonable because the first elusion might contain some of water which was used to rinse the column. That would dilute the first elution significantly. So, the concentration of nitrate-nitrogen in the first elution should be much lower than the rest elusion. It would be a good idea to discard the first 25-milliliter elusion.

Figure 6 shows the concentration of nitrate-nitrogen from composite of Lake Wabaunsee on October 3, 1998 by using XAD-4 Resin Method according to the order of elusion (discarded the first 25-milliliter elusion). The nitrate-nitrogen concentration from Lake Wabaunsee was calculated according to equation (4-1), (4-2), (4-3) and (4-4). By comparing the concentration of nitrate-nitrogen based on the elusion order, it indicated the concentration of nitrate-nitrogen was around 0.094 milligram per liter for about four consecutive times (which was about 150 milliliter elusion after discarded the first 25 milliliter). The concentration of nitrate-nitrogen was 0.081 milligram per liter by the Cadmium Reduction method (Table 6).

Figure 7 shows the concentration of nitrate-nitrogen from composite of Lake Wooster on November 3, 1998 by using XAD-4 Resin Method according to the order of elution (discarded the first 25-milliliter elution). The nitrate-nitrogen concentration from Lake Wooster was calculated according to equation (4-1), (4-2), (4-3) and (4-4). By comparing the concentration of nitrate-nitrogen based on the elusion order, it indicated the concentration of nitrate-nitrogen was around

0.449~0.459 milligram per liter for about six consecutive times (which was about 150 milliliter elution after discarded the first 25 milliliter). The concentration of nitrate-nitrogen was 0.401 milligram per liter by the Cadmium Reduction method (Table 7).

Figure 8 shows the concentration of nitrate-nitrogen from composite of Lake Wooster on December 16, 1998 by using XAD-4 Resin Method according to the order of elution (discarded the first 25-milliliter elution). The nitrate-nitrogen concentration from Lake Wooster was calculated according to equation (4-1), (4-2), (4-3) and (4-4). By comparing the concentration of nitrate-nitrogen based on the elution order, it indicated the concentration of nitrate-nitrogen was around 0.643 ~ 0.654 milligram per liter for about four consecutive times (which was about 100 milliliter elution after discarded the first 25 milliliter). The concentration of nitrate-nitrogen was 0.573 milligram per liter by Cadmium Reduction method (Table 8).

III. Modified Cadmium Reduction Method

Figure 9 indicates that the “Time Window” for nitrite-nitrogen was between 15 ~ 40 minutes. The absorbance of nitrite-nitrogen at before or after the “Time Window” was not consistent.

The standard curve for nitrate-nitrogen (Figure 10) shows that Beer’s law was obeyed when the concentration of nitrite-nitrogen is between zero to 0.17 milligrams per liter (mg as N /L). The absorbance of last data (Figure 10) was out

of range significantly (the concentration of nitrite-nitrogen was 0.251 milligram per liter).

Table 6 shows the concentration of nitrite-nitrogen from composite of Lake Wabaunsee on October 3, 1998 by using Cadmium Reduction Method. The concentration of nitrate-nitrogen was considered the same as nitrite-nitrogen because the over-dosage of cadmium was able to convert nitrate to nitrite completely. The concentration of nitrate-nitrogen (C_{sample1}) in lake sample was determined by

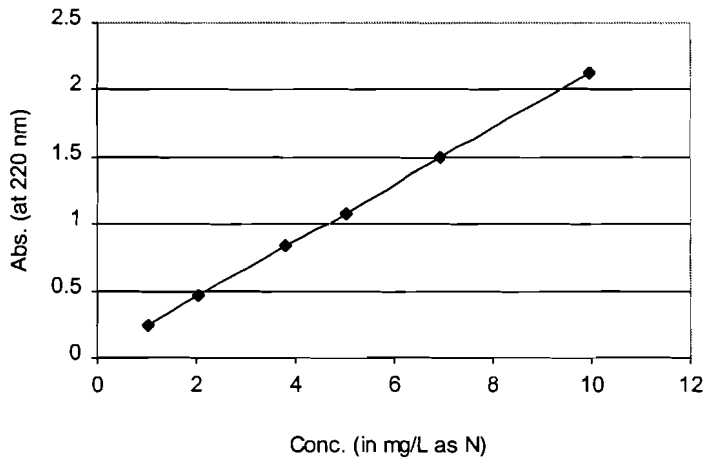
$$C_{\text{sample1}} = C_{\text{standard1}} * A_{\text{sample1}} / A_{\text{standard1}} \quad (4-5)$$

Where A_{sample1} was the lake sample absorbance at 543 nm after Cadmium Reduction treatment, $A_{\text{standard1}}$ was the standard absorbance at 543 nm., and $C_{\text{standard1}}$ was the standard concentration of nitrite-nitrogen. By comparing the concentration of nitrate-nitrogen from Figure 6 (0.094 mg/L as N) and the concentration of nitrite-nitrogen from Table 6 (0.081 mg/L as N), the difference was about 0.014 milligram per liter which was about 17% in relative difference (Figure 17).

Table 7 shows the concentration of nitrate-nitrogen from composite of Lake Wooster on November 3, 1998 by using the Cadmium Reduction Method. The concentration of nitrate-nitrogen in Lake Wooster was calculated by using Equation (4-5). By comparing the concentration of nitrate-nitrogen from Figure 7 (0.449 mg/L as N) and the concentration of nitrite-nitrogen from Table 7 (0.401 mg/L as N), the difference was about 0.048 milligram per liter and was about 12% in relative difference (Figure 18).

Table 8 shows the concentration of nitrate-nitrogen from composite of Lake Wooster on December 16, 1998 by using Cadmium Reduction Method. The concentration of nitrate-nitrogen in Lake Wooster was calculated by using Equation (4-5). By comparing the concentration of nitrate-nitrogen from Figure 8 (0.649 mg/L as N) and the concentration of nitrite-nitrogen from Table 10-5 (0.573 mg/L as N), the difference was about 0.076 milligram per liter and was about 13% in relative difference (Figure 19).

Figure1. Standard Curve for Nitrate-Nitrogen



X Value in Conc.:	1.032	2.022	3.801	5.003	6.933	9.972
Y Value in Abs.:	0.242	0.468	0.841	1.085	1.497	2.124

Summary Output:

Regression Statistics

Multiple R: 0.999941

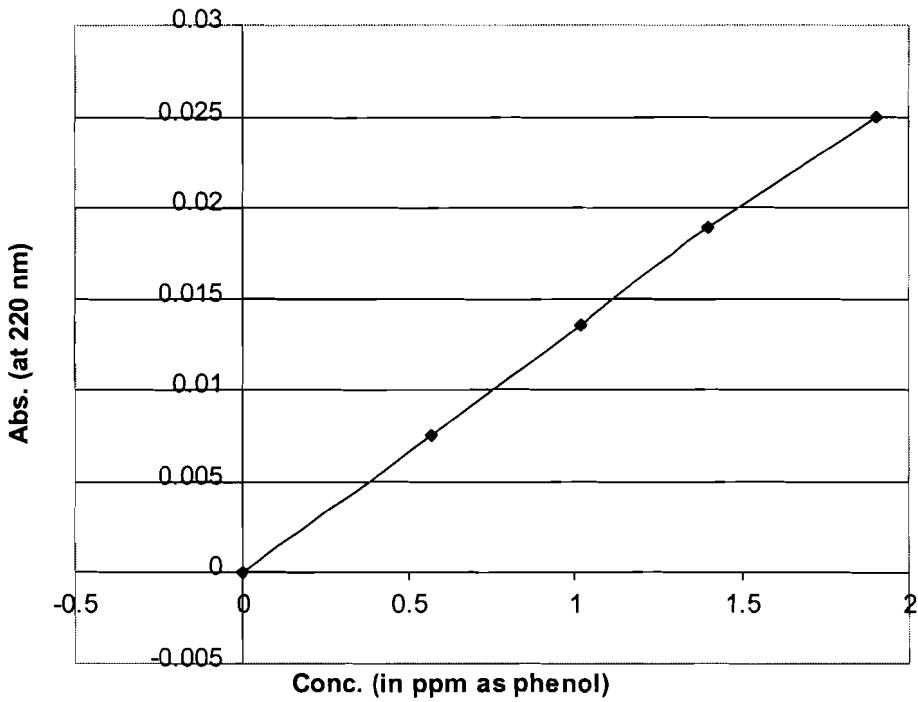
R Square : 0.999883

Adjusted F: -1.5

Standard E: 0.008367

Observation: 1

Figure 2: Effect of Prep-Sep on Absorbance of Nitrate-Phenol Mixture



X Value:	0	0.566	1.013	1.398	1.902
Y Value:	0	0.008	0.014	0.019	0.025

Summary Output:

Regression Statistics

Multiple R: 0.99937
R Square: 0.998739
Adjusted F: -1.66667
Standard E: 0.000397
Observation: 1

Figure 3: Effect of Acid on Nitrate-Nitrogen Concentration in Lake Wabaunsee Using Prep-Sep Cartridge Method

Series1: Sample Date (April 5, 1998), Series2: Sample Date (May 3, 1998)

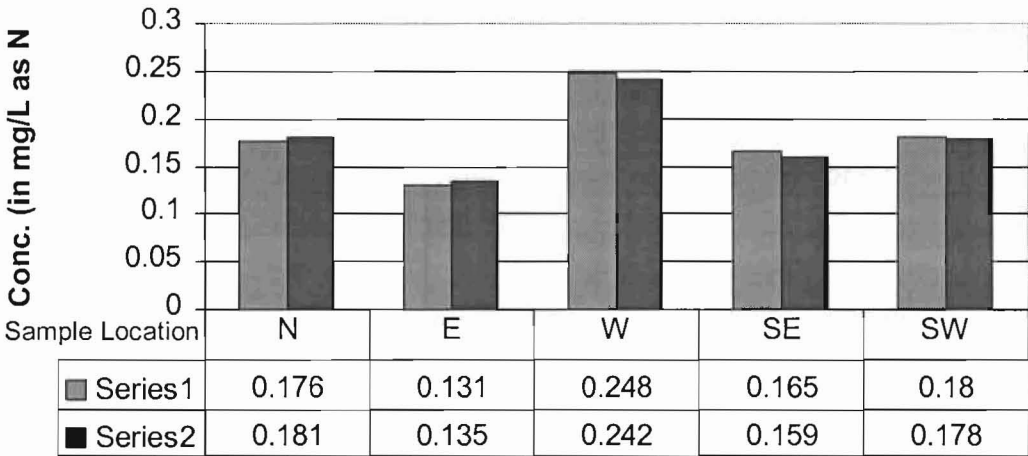


Figure 4: Effect of TBA on Nitrate-Nitrogen Concentration in Lake Wabaunsee Using Prep-Sep Cartridge Method

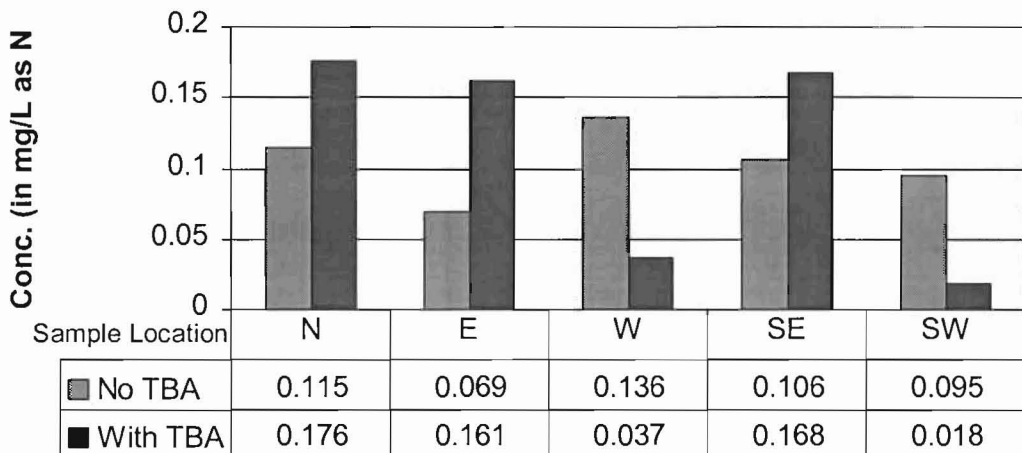
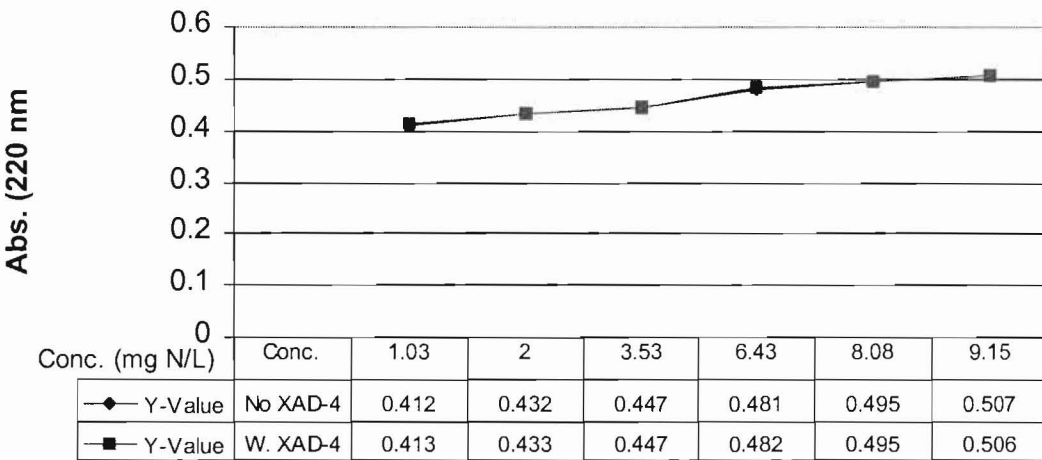


Figure 5: Effect of XAD-4 on Absorbances of Nitrate-Nitrogen Standard



**Table 1. Effect of Prep-Sep on Absorbances
of Phosphate Buffered (pH=7) Mixture**

1. Sample Preparation:

2. Absorbance:

<u>Sample #</u>	<u>Weight</u> Of stock(g)	<u>Conc.</u> (mg N/L)	<u>Phenol</u> (ppm)	<u>220 nm</u>		<u>270nm</u>	
				<u>No Tr.</u>	<u>Tr.</u>	<u>No Tr.</u>	<u>Tr.</u>
Blank	0	0	0	0.000	0.000	0.000	0.000
1	17.684	3.542	1.501	0.866	0.862	0.004	0.000
2	17.684	3.542	0	0.865	0.861	0.000	0.000

No Tr.: as no treatment

Tr.: as with treatment

**Table 2. Effect of Prep-Sep on Absorbances of
Samples from Lake Wabaunsee**

1. Sample Preparation:

2. Absorbance:

Sample #	Weight	Conc.	220 nm				270nm	
			Of stock(g)	(mg N/L)	No Tr.	Tr.	No Tr.	Tr.
Blank	0	0	0.000	0.000	0.000	0.000	0.000	
Std.	14.067	2.818	0.674	0.674	0.000	0.000	0.000	
N	0	0	0.079	0.069	0.009	0.007	0.007	
E	0	0	0.086	0.071	0.012	0.008	0.008	
W	0	0	0.061	0.057	0.007	0.005	0.005	
SE	0	0	0.075	0.061	0.010	0.007	0.007	

No Tr.: as no treatment

Tr.: as with treatment

**Table 3. Effect of Prep-Sep on Absorbances of
Samples in Lake Wabaunsee under Acid Condition
Using Prep-Sep Cartridge Method**

1. Sample Preparation:

2. Absorbance:

Sample #	Weight	Conc.	220 nm		270nm	
			<u>No Tr.</u>	<u>Tr.</u>	<u>No Tr.</u>	<u>Tr.</u>
	Of stock(g)	(mg N/L)				
Blank	0	0	0.000	0.000	0.000	0.000
Std.	8.840	1.771	0.427	0.427	0.000	0.000
N	0	0	0.087	0.072	0.037	0.025
E	0	0	0.089	0.069	0.043	0.028
W	0	0	0.069	0.066	0.038	0.027
SE	0	0	0.085	0.072	0.037	0.026

No Tr.: as no treatment

Tr.: as with treatment

**Table 4: Nitrate-Nitrogen Concentration in Lake Wabaunsee
Using XAD-4 Resin Method**

1. Sample Preparation:

2. Absorbance:

<u>Sample #</u>	<u>Weight</u> Of stock(g)	<u>Conc.</u> (mg N/L)	<u>220 nm</u>		<u>270nm</u>	
			<u>No Tr.</u>	<u>Tr.</u>	<u>No Tr.</u>	<u>Tr.</u>
Blank	0	0	0.000	0.000	0.000	0.000
Std.	7.858	1.574	0.375	0.375	0.000	0.000
Sample	0	0	0.077	0.034	0.039	0.007

3. Result:

<u>Sample#</u>	<u>% Org. (not Removed)</u>	<u>Conc. In Lake (mg N/L)</u>
Lake Sample	93	0.104

No Tr.: as no XAD-4 resin treatment

Tr.: as with XAD-4 resin treatment

**Table 5: Nitrate-Nitrogen Concentration in Lake Wabaunsee
Using XAD-4 Resin Method**

<u>1. Sample Preparation:</u>			<u>2. Absorbance:</u>	
<u>Sample #</u>	<u>Weight</u>	<u>Conc.</u>	<u>220 nm</u>	<u>270nm</u>
	<u>Of stock(g) (mg N/L)</u>			
Blank	0	0	0.000	0.000
Std.	6.552	1.312	0.321	0.000
A	0	0	0.092	0.053
E1	0	0	0.005	0.001
E2	0	0	0.005	0.009
E3	0	0	0.008	0.013

3. Result:

<u>Sample#</u>	<u>% Org. (Removed)</u>	<u>% Org. (Not Removed)</u>	<u>Conc. (mg L/N)</u>
A	0	100	0.179
E1	98	2	0.011
E2	84	16	0.172
E3	76	24	0.353

A: Sample from lake without XAD-4 resin treatment

E: Sample from lake with XAD-4 resin treatment. (Based on Elution Order)

Figure 6: Nitrate-Nitrogen Concentration in Lake Wabaunsee Using XAD-4 Resin Method

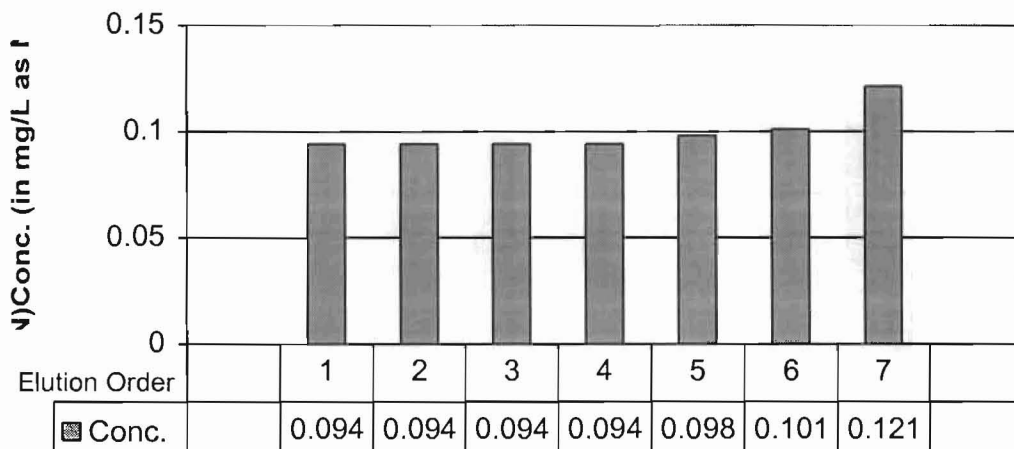


Figure 7: Nitrate-Nitrogen Concentration in Lake Wooster Using XAD-4 Resin Method

Sample Date: November 3, 1998

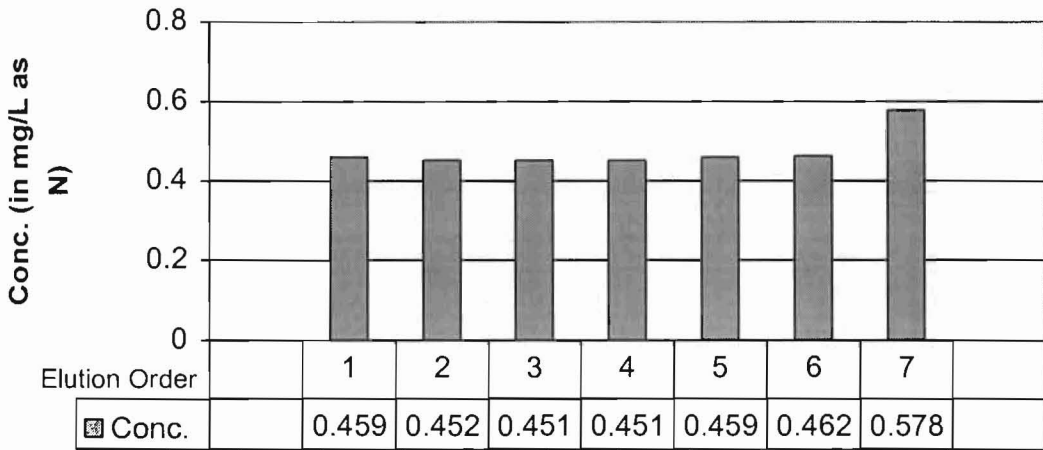


Figure 8: Nitrate-Nitrogen Concentration in Lake Wabaunsee Using XAD-4 Resin Method

Sample Date: December 6, 1998

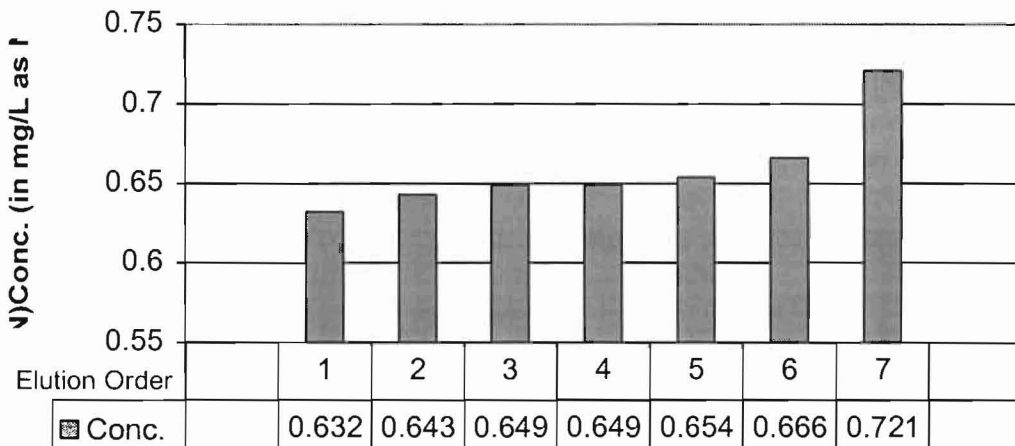


Figure 9: "Time Window" for Nitrite-Nitrogen Using Cadmium Reduction Method

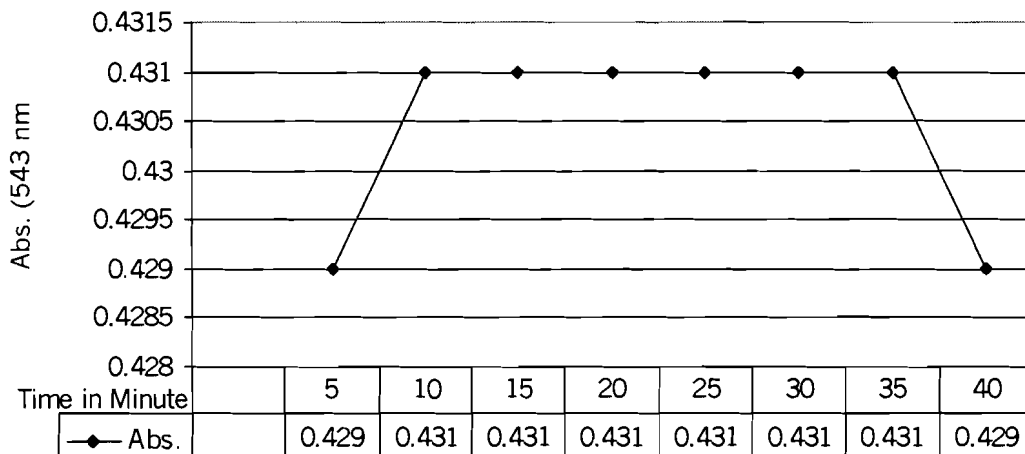
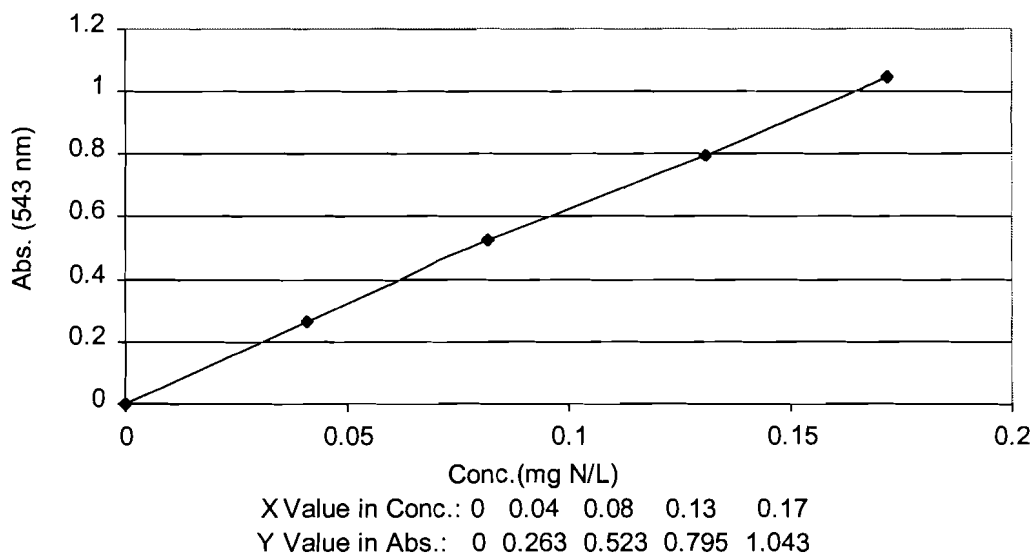


Figure 10: Nitrate-Nitrogen Standard Curve Using Cadmium Reduction Method

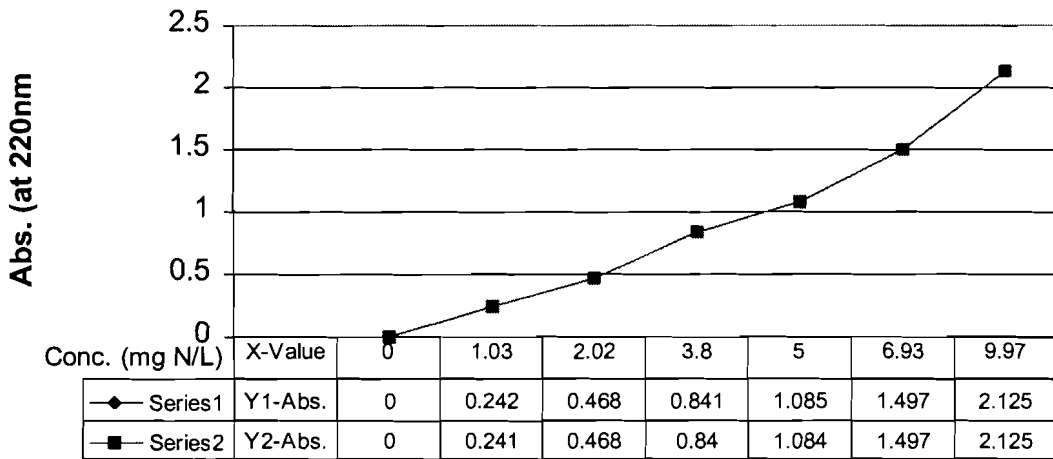


Summary Output:

Rgression Statistics

Multiple R: 0.99938 R Square: 0.99876
 Adjusted F: -1.66667 Standard E: 0.016831
 Observation: 1

Figure 11: Effect of Prep-Sep on Nitrate Absorbance
Series1: no treatment, Series2: with treatment



**Table 6. Nitrite-Nitrogen Concentration in Lake Wabaunsee
Using Cadmium Reduction Method**

1. Sample Preparation:

<u>Sample #</u>	<u>Weight</u>	<u>Conc.</u>
	<u>Of stock(g)</u>	<u>(mg N/L)</u>
Blank	0	0
Standard	0.125	0.013
Sample	0	0

2. Absorbance: (at 543 nm)

<u>Time(in Min.)</u>	<u>15</u>	<u>20</u>	<u>25</u>	<u>30</u>	<u>35</u>	<u>40</u>
Blank	0.000	0.000	0.000	0.000	0.000	0.000
Standard	0.116	0.117	0.117	0.118	0.118	0.117
Sample	0.186	0.187	0.187	0.187	0.187	0.186

Table 7. Nitrite-Nitrogen Concentration in Lake Wooster

Using Cadmium Reduction Method

1. Sample Preparation:

<u>Sample #</u>	<u>Weight</u>	<u>Conc.</u>
	<u>Of stock(g)</u>	<u>(mg N/L)</u>
Blank	0	0
Standard	1.151	0.115
Sample	0	0

2. Absorbance: (at 543 nm)

<u>Time(in Min.)</u>	<u>15</u>	<u>20</u>	<u>25</u>	<u>30</u>	<u>35</u>	<u>40</u>
Blank	0.000	0.000	0.000	0.000	0.000	0.000
Standard	1.385	1.386	1.386	1.387	1.387	1.385
Sample	1.204	1.205	1.205	1.206	1.206	1.204

**Table 8. Nitrite-Nitrogen Concentration in Lake Wooster
Using Cadmium Reduction Method**

1. Sample Preparation:

<u>Sample #</u>	<u>Weight</u>	<u>Conc.</u>
	<u>Of stock(g)</u>	<u>(mg N/L)</u>
Blank	0	0
Standard	1.250	0.125
Sample	0	0

2. Absorbance: (at 543 nm)

<u>Time(in Min.)</u>	<u>15</u>	<u>20</u>	<u>25</u>	<u>30</u>	<u>35</u>	<u>40</u>
Blank	0.000	0.000	0.000	0.000	0.000	0.000
Standard	1.525	1.526	1.526	1.527	1.527	1.525
Sample	1.744	1.745	1.745	1.745	1.745	1.744

Figure 12: Effect of Prep-Sep on Absorbances of Nitrate-Pheno Mixtures at 220 nm

Series1: no treatment, Series2: with treatment

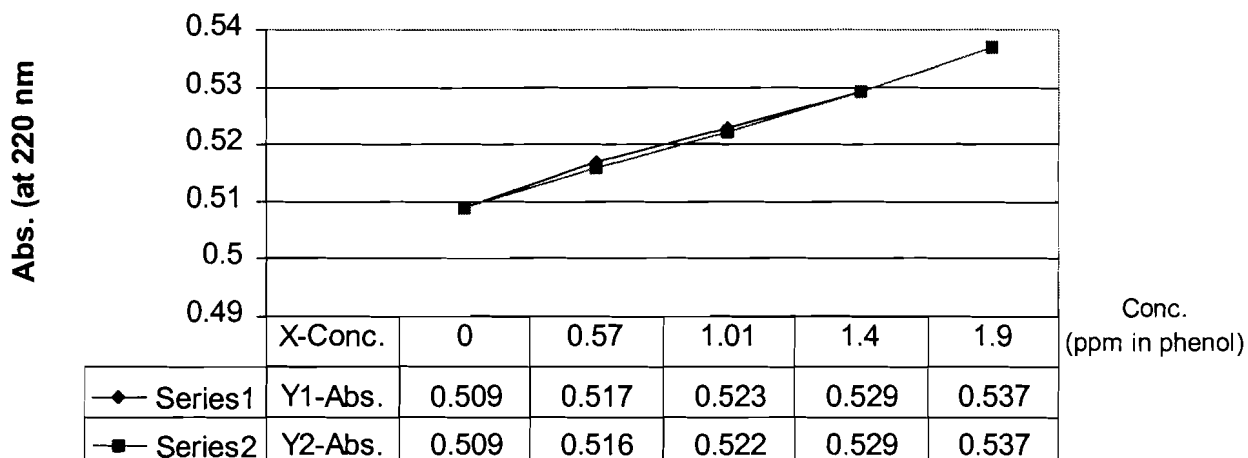


Figure 13: Effect of Prep-Sep on Absorbances of Nitrate-Pheno Mixtures at 270 nm

Series1: no treatment, Series2: with treatment

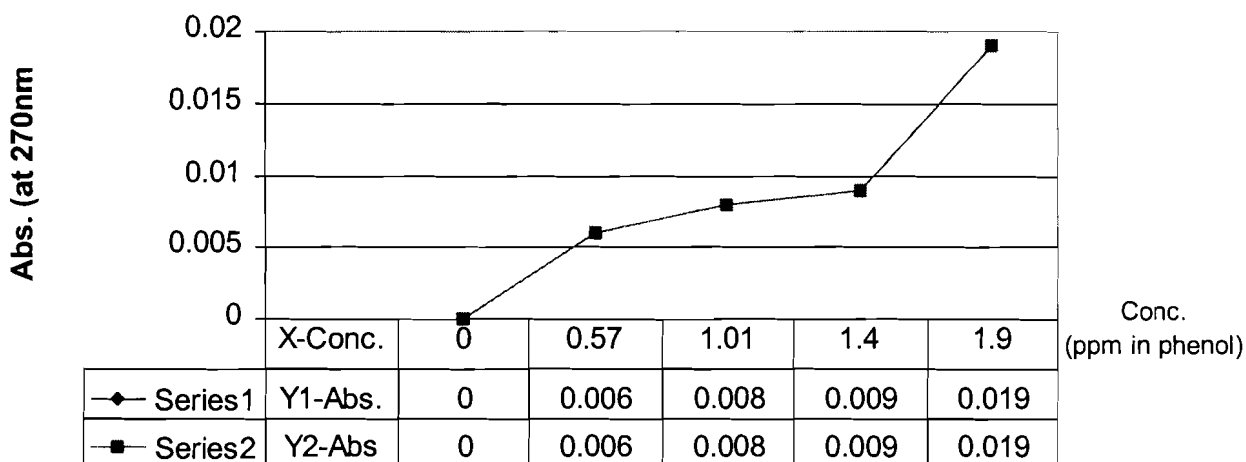


Figure 15: Effect of Prep-Sep on Absorbances of Phosphate Buffer Mixture at 270 nm

Series1: no treatment, Series2: with treatment

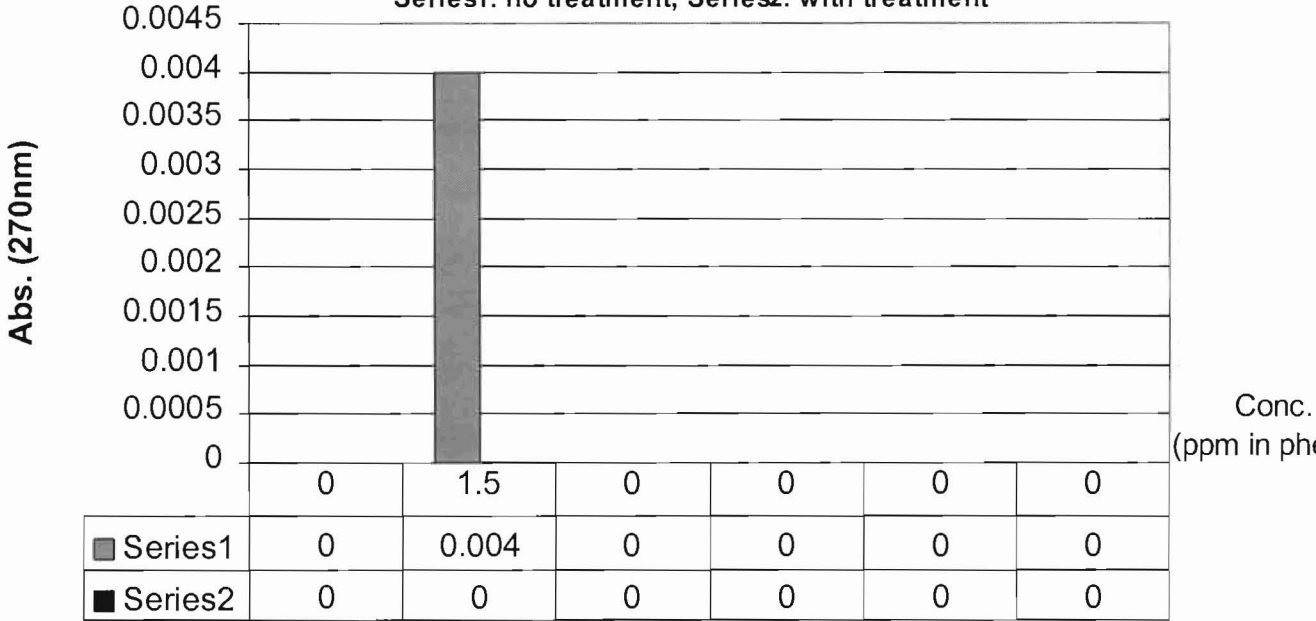
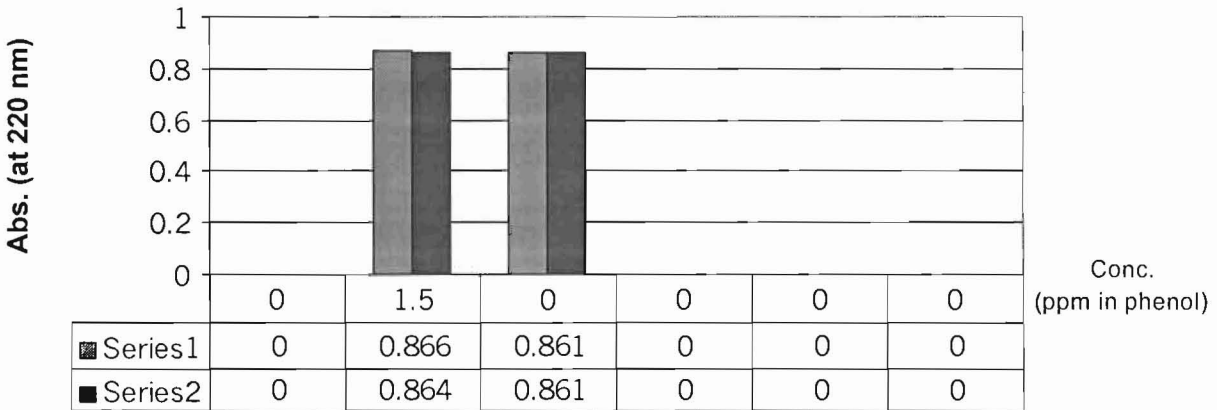


Figure 14: Effect of Prep-Sep on Absorbances of Phosphate Buffer Mixtures

Series1: no treatment, Series2: with treatment



**Table 9: Nitrate Concentration in Lake Wabaunsee under Acid Condition Using Prep-Sep
Cartridge Method (Sample Date: April 5, 1998)**

1. Sample Preparation:

2. Absorbance:

Sample #	Weight Of stock(g)	Conc. (mg N/L)	220 nm		270nm	
			No Tr.	Tr.	No Tr.	Tr.
Blank	0	0	0.000	0.000	0.000	0.000
Std.	6.295	1.261	0.300	0.300	0.000	0.000
N	0	0	0.082	0.079	0.039	0.027
E	0	0	0.084	0.068	0.036	0.025
W	0	0	0.079	0.072	0.039	0.028
SE	0	0	0.079	0.065	0.037	0.024
SW	0	0	0.084	0.072	0.041	0.028

3. Result:

Sample#	% Org. (not Removed)	Abs. (by nitrate)	Conc. In Lake(mg N/L)
N	69	0.042	0.176
E	69	0.031	0.131
W	73	0.059	0.246
SE	64	0.039	0.167
SW	69	0.043	0.180

No Tr.: as no treatment

Tr.: as with treatment

**Table 10: Nitrate Concentration in Lake Wabaunsee under Acid Condition Using Prep-Sep
Cartridge Method (Sample date: April 28, 1998)**

1. Sample Preparation:

2. Absorbance:

<u>Sample #</u>	<u>Weight</u>	<u>Conc.</u>	<u>220 nm</u>		<u>270nm</u>	
			<u>No Tr.</u>	<u>Tr.</u>	<u>No Tr.</u>	<u>Tr.</u>
	<u>Of stock(g)</u>	<u>(mg N/L)</u>				
Blank	0	0	0.000	0.000	0.000	0.000
Std.	7.360	1.474	0.355	0.354	0.000	0.000
N	0	0	0.080	0.069	0.026	0.018
E	0	0	0.082	0.068	0.025	0.017
W	0	0	0.077	0.072	0.025	0.019
SE	0	0	0.081	0.066	0.025	0.017
SW	0	0	0.083	0.069	0.027	0.018

4. Result:

<u>Sample#</u>	<u>% Org. (not Removed)</u>	<u>Abs. (by nitrate)</u>	<u>Conc. In Lake(mg N/L)</u>
N	69	0.043	0.181
E	67	0.033	0.135
W	76	0.058	0.242
SE	66	0.038	0.161
SW	66	0.043	0.178

No Tr.: as no treatment

Tr.: as with treatment

**Table 11: Nitrate Concentration in Lake Wabaunsee without TBA added Using Prep-Sep
Cartridge Method (Sample date: June 28, 1998)**

1. Sample Preparation:

2. Absorbance:

<u>Sample #</u>	<u>Weight</u>	<u>Conc.</u>	<u>220 nm</u>		<u>270nm</u>	
			<u>No Tr.</u>	<u>Tr.</u>	<u>No Tr.</u>	<u>Tr.</u>
	<u>Of stock(g)</u>	<u>(mg N/L)</u>				
Blank	0	0	0.000	0.000	0.000	0.000
Std.	6.305	1.263	0.309	0.310	0.000	0.000
N	0	0	0.084	0.081	0.042	0.039
E	0	0	0.109	0.103	0.043	0.040
W	0	0	0.088	0.084	0.041	0.038
SE	0	0	0.081	0.076	0.040	0.037
SW	0	0	0.084	0.079	0.041	0.038

5. Result:

<u>Sample#</u>	<u>% Org. (not Removed)</u>	<u>Abs. (by nitrate)</u>	<u>Conc. In Lake(mg N/L)</u>
N	93	0.028	0.115
E	93	0.017	0.069
W	93	0.034	0.136
SE	93	0.026	0.106
SW	93	0.023	0.095

No Tr.: as no treatment

Tr.: as with treatment

Table 12: Nitrate Concentration in Lake Wabaunsee with TBA added Using Prep-Sep Cartridge
Method (Sample date: June 28, 1998)

1. Sample Preparation:

2. Absorbance:

<u>Sample #</u>	<u>Weight</u>	<u>Conc.</u>	<u>220 nm</u>		<u>270nm</u>	
			<u>No Tr.</u>	<u>Tr.</u>	<u>No Tr.</u>	<u>Tr.</u>
	<u>Of stock(g)</u>	<u>(mg N/L)</u>				
Blank	0	0	0.000	0.000	0.000	0.000
Std.	6.305	1.263	0.309	0.304	0.000	0.000
N	0	0	0.084	0.080	0.041	0.037
E	0	0	0.109	0.104	0.042	0.039
W	0	0	0.088	0.084	0.041	0.038
SE	0	0	0.081	0.077	0.040	0.036
SW	0	0	0.085	0.083	0.040	0.035

3. Result:

<u>Sample#</u>	<u>% Org. (not Removed)</u>	<u>Abs. (by nitrate)</u>	<u>Conc. In Lake(mg N/L)</u>
N	89	0.043	0.176
E	93	0.039	0.161
W	95	0.009	0.037
SE	90	0.040	0.168
SW	90	0.044	0.180

No Tr.: as no treatment

Tr.: as with treatment

Figure 16: Effect of pH on Removal of Organic Matter from Lake Wabausee Samples Using Prep-Sep Metho
Series1: Phosphate Buffer, Series2: Acid

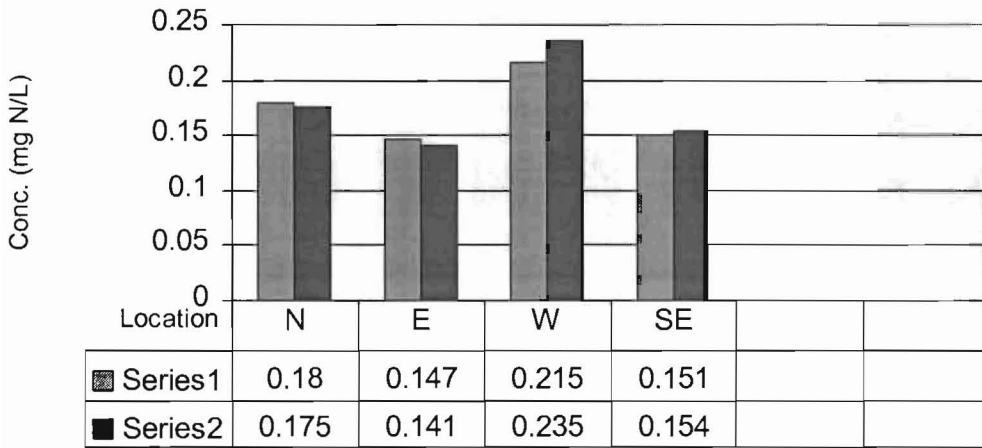


Figure 17: Comparison of Nitrate-Nitrogen Concentration in Lake Wabausee between XAD-4 Resin and Cadmium Reduction Method
Series1: XAD Resin, Series2: Cadmium Reduction, E0: no treatment

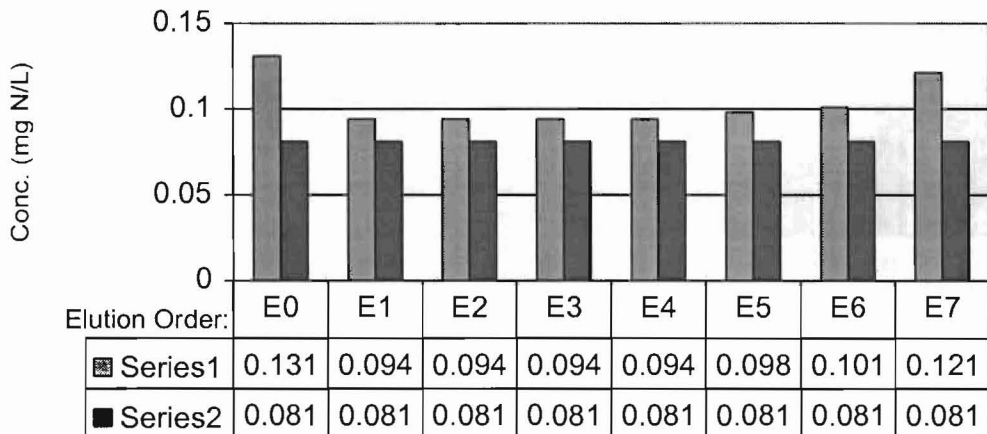


Figure 18: Comparison of Nitrate-Nitrogen Concentration in Lake Wooster between XAD-4 Resin and Cadmium Reduction Method
Series1: XAD Resin, Series2: Cadmium Reduction, E0: no treatment
Sample Date: November 3, 1998

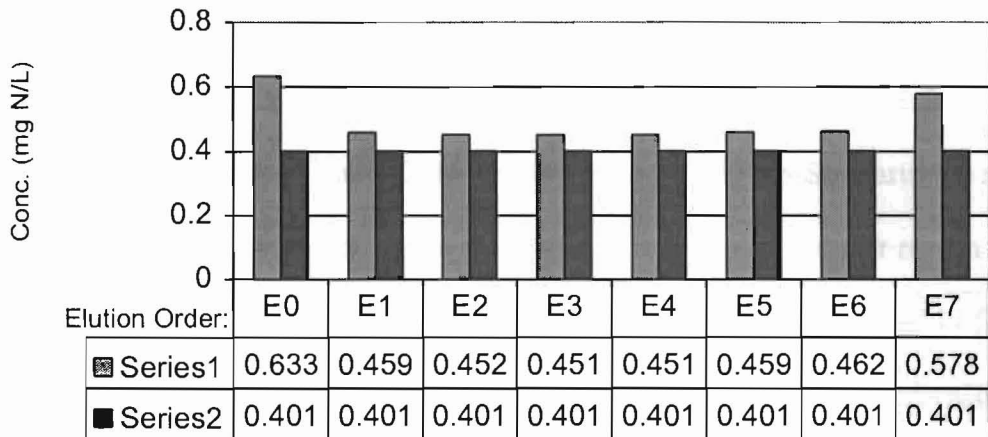
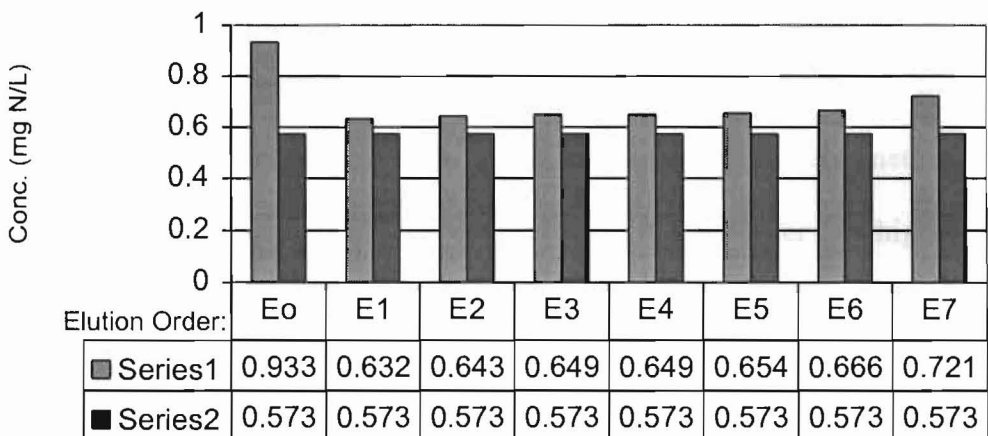


Figure 19: Comparison of Nitrate-Nitrogen Concentration in Lake Wooster between XAD-4 Resin and Cadmium Reduction Method
Series1: XAD Resin, Series2: Cadmium Reduction, Eo: No Treatment
Sample Date: December 16, 1998



CHAPTER 5. SUMMARY AND CONCLUSIONS

The nitrate-nitrogen concentration of samples taken from Lake Wooster and Lake Wabaunsee were determined by the ultraviolet spectrophotometric method. This section deals with the problems encountered due to interferences from dissolved organic matter, and also with the problems in the methods themselves.

When dealing with the removal of dissolved organic matter, two pre-treatments were used: Prep-Sep cartridge and XAD-4 resin method. The Prep-Sep cartridge method is not recommended. One reason is that it is difficult to prepare. Another reason is that the performance of the cartridge is not constant. It will make it more difficult to figure out when you want to do some trouble-shooting. On the other hand, the performance of XAD-4 resin is constant and it is easy to prepare.

In Figure 17, the resulting nitrate-nitrogen concentrations for each elution from Lake Wabaunsee by using XAD-4 resin method are listed. The table also lists the day the samples were taken, and the method used for analysis. The modified cadmium reduction is taken as the reference method (Table 6).

The first comparison is between the XAD-4 resin and the Cadmium Reduction results. From the table, it can be seen that every nitrate-nitrogen concentration by using XAD-4 resin method is higher than the one by using Cadmium Reduction method. The XAD-4 resin method, using the 220 nm wavelength alone, it is 63 per cent higher. When combined with 270 nm wavelength, on the average, the results are 17 per cent higher. There was an exception at Elution#7. The average UV nitrate-nitrogen concentration is

61 per cent higher. This is believed to be due mainly to the saturated XAD-4 resin column.

In Figure 18, the resulting nitrate-nitrogen concentrations for each elution from Lake Wooster by using XAD-4 resin method are listed. The table also lists the day the samples were taken, and the method used for analysis. The modified cadmium reduction is taken as the reference method (Table 7).

The first comparison is between the XAD-4 resin results and the Cadmium Reduction results. From the table, it can be seen that every nitrate-nitrogen concentration by using XAD-4 resin method is higher than the one by using Cadmium Reduction method. The UV method, using the 220 nm wavelength alone, it is 56 per cent higher. When combined with 270 nm wavelength, on the average, the result is just 12 per cent higher.

These higher XAD-4 resin nitrate-nitrogen concentrations prove that there is dissolved organic matter present, and that it causes an increase in the nitrate-nitrogen concentrations. The XAD-4 resin treatment, using the 220 nm wavelength alone, is not an effective, accurate method for nitrate-nitrogen determination.

The use of the organic correction is definitely more effective in determining nitrate-nitrogen concentration. The XAD-4 resin concentration listed in the table is providing better agreement with the Cadmium Reduction concentration. Even though the XAD-4 resin treatment has a definite advantage, there is still room for improvement, especially when high levels of dissolved organic matter are present.

When determining nitrate by ultraviolet spectroscopy, the presence of dissolved organic matter in a water sample causes an increase in the nitrate-nitrogen concentration.

Through the use of XAD-4 resin treatment, the dissolved organic matter interference may be empirically corrected. Unfortunately, this technique is unreliable when the dissolved organic matter content is high.

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Miaoju Luo

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7/29/1999

Date

Removal of Organic Interferences in
Analysis of Nitrate in Water by UV
Spectroscopy

Title of Thesis/Research Project

Dorey Cooper

Signature of Graduate Office Staff

August 17, 1999

Date Received