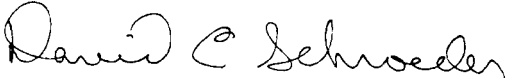


AN ABSTRACT OF THE THESIS OF

Ibrahim Z. Abdelsaheb for the Master of Science Degree in Physical Science presented on November 27, 1989.

Title: REMOVAL OF NITRATE FROM GROUND WATER BY REDUCTION METHOD.

Abstract approved: 

Committee Members: Dr. David Schoeder
Dr. Eric Trump
Dr. James Aber

Under controlled conditions, nitrates may be reduced to nitrite and then to nitrogen when a sample is run through a column containing a reducing agent. These reducing agents might include magnesium, cadmium, zinc, and Devarda's alloy. A suitable catalyst might be used to increase the rate of reduction. The amount of reducing agent, the contact period for reduction, and the temperature at which reduction takes place were tested.

The nitrates level in groundwater samples were measured using high-performance liquid chromatography (HPLC) with a reversed-phase column. A mobile phase

concentrate for mixing with samples to be analyzed was prepared from 0.3 F KH_2PO_4 + 0.075 F H_3PO_4 .

REMOVAL OF NITRATE FROM GROUND WATER BY THE REDUCTION METHOD

A Thesis
Presented to
the Physical Sciences Division
EMPORIA STATE UNIVERSITY

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

By
Ibrahim Z. Abdelsaheb
November 27, 1989

1'

Charles G. Gurdin

Approved by the Major Department

James S. Wolfe

Approved by the Graduate Council

470720

iv

DP JUN 7 '90

ACKNOWLEDGMENTS

The author wishes to express his thanks to the following people:

Dr. David Schroeder, Chairperson: For his guidance and expertise in the initiating, the labwork, and the composition of this thesis. His enthusiasm and attention to details not only in this project but also in the classes he teaches is an inspiration to the very best of one's abilities.

Dr. Eric Trump: For his guidance and assistance throughout my graduate career.

Dr. James Aber: For his guidance, assistance and suggestions which helped to strengthen this thesis.

Dr. Charles Greenlief: For his continuous guidance and Assistance throughout my graduate career.

TABLE OF CONTENTS

	Page
ABSTRACT	i
TITLE PAGE	iii
SIGNATURE PAGE	iv
ACKNOWLEDGMENTS	v
TABLE OF CONTENTS	vi
LIST OF FIGURES	vii
LIST OF TABLES	ix
Chapter 1. INTRODUCTION	1
Chapter 2. PREVIOUS WORK	7
Chapter 3. EXPERIMENTAL	9
Chapter 4. RESULTS AND DISCUSSION	20
Chapter 5. CONCLUSIONS	49
BIBLIOGRAPHY	50

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Nitrogen Cycle	2
2. Reduction column	17
3. Nitrate Chromatogram	21
4. Reduction of nitrate by Mg, and Mg-Cu at room temperature	23
5. Reduction of nitrate by Devarda's alloy, and Devarda's alloy treated with 0.01 M CuCl ₂ at room temperature	25
6. Reduction of nitrate by zinc metal at room temperature	27
7. Reduction of nitrate by zinc treated with 0.01 M CuCl ₂ at room temperature	30
8. Reduction of nitrate by zinc treated with 0.05 M CuCl ₂ at room temperature	34
9. Reduction of nitrate by zinc treated with 0.10 M CuCl ₂ at room temperature	35
10. Reduction of nitrate by zinc treated with 0.10 M CuCl ₂ at 20 C°	40
11. Reduction of nitrate by zinc treated with 0.10 M CuCl ₂ at 30 C°	41
12. Reduction of nitrate by zinc treated with 0.10 M CuCl ₂ at 40 C°	42

13. Reduction of nitrate by zinc treated with 0.10 M CuCl ₂ at 50 C°	44
14. Reduction of nitrate in well water by zinc treated by 0.10 M CuCl ₂ at 50 C°	46

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Nitrate reduction by magnesium at room temperature	22
2. Nitrate reduction by Mg-Cu mixture at room temperature	22
3. Nitrate reduction by Devarda's alloy at room temperature	24
4. Nitrate reduction by Devarda's alloy with 0.01 M CuCl ₂ at room temperature	26
5. Nitrate reduction by zinc metal at room temperature	29
6. Nitrate reduction by zinc with 0.01 M CuCl ₂ at room temperature	31
7. Nitrate reduction by zinc with 0.05 M CuCl ₂ at room temperature	32
8. Nitrate reduction by zinc with 0.10 M CuCl ₂ at room temperature	33
9. Nitrate reduction by zinc with 0.10 M CuCl ₂ at 20 C°	36
10. Nitrate reduction by zinc with 0.10 M CuCl ₂ at 30 C°	37
11. Nitrate reduction by zinc with 0.10 M CuCl ₂ at 40 C°	38

12. Nitrate reduction by zinc with 0.10 M CuCl ₂ at 50 C°	39
13. Nitrate reduction from well water by zinc with CuCl ₂ at 50 C°	45

Chapter 1. INTRODUCTION

Nitrate is a natural product of living systems and in ordinary circumstances, is converted slowly to atmospheric nitrogen or organic nitrogen (Fig. 1), by microorganisms and plants in the soil or in water. The World Health Organization (WHO) recommended that an acceptable level for nitrate-nitrogen in drinking water would be 11.9 mg/liter (Anthony 1978). Abnormal levels of nitrate-nitrogen may give rise to incidences of Methaemoglobinaemia in infants with fatality resulting in extreme cases. Nitrate also affects livestock at concentrations above 100 mg/l (National Institute of Environmental Health Sciences 1970).

Yet, because of the increasing amount of nitrate-rich effluent reaching rivers and other sources of drinking water, according to the WHO, nitrate content of drinking water has continued to rise in many parts of the world. Sewage plants and runoff from agricultural lands represent the two major sources of nitrate pollution of ground water (Anthony 1978). Although fertilizers have been implicated in such pollution, there is evidence that feedlots are a major source of nitrate pollution. The growth of livestock populations and concentration of livestock in feedlots have aggravated this problem.

The origin of most nitrate produced from feedlot wastes is amino nitrogen present in nitrogen-containing waste

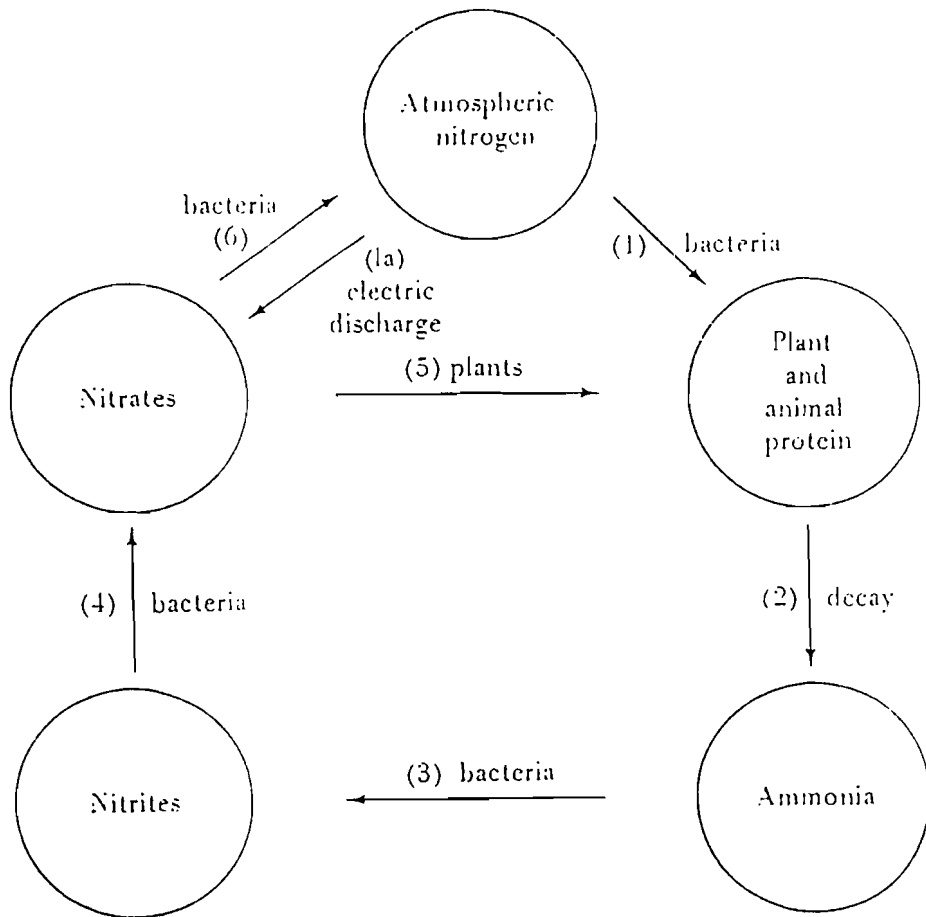
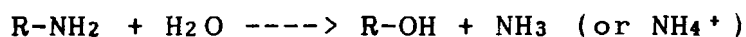
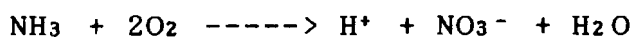


Fig. 1. Nitrogen cycle in nature: showing the dynamic processes through which nitrogen is interchanged among the atmosphere, organic matter, and inorganic compounds. Nitrate is formed by oxidation of ammonia, and can be reduced to nitrogen gas. Taken from Ralph (1982, Fig. 26-2).

products. As a first step in the degradation process, the amino nitrogen is hydrolyzed to ammonia, or ammonium ion:



This product is then oxidized through microorganism-catalyzed reactions to nitrate ion:



Under some conditions, an appreciable amount of the nitrogen originating from the degradation of feedlot wastes is present as ammonium ion. Ammonium ion is rather strongly bound to soil (soil is generally a good cation exchanger), and a small fraction is fixed as nonexchangeable ammonium ion in the crystal lattice of clay minerals. Because nitrate is not strongly bound to soil, it is readily carried through soil by water. Many factors, including soil type, moisture, and level of organic matter, affect the production of ammonia and nitrate ion originating from feedlot wastes (Stanley 1986).

Nitrates accumulate in the upper portion of the ground-water table in the absence of rapid ground-water movement. Nitrate concentration is reduced through dilution by ground-water table in the absence of rapid ground-water movement.

Research into ways of combating the problem of nitrate

contamination has been under way for many years in different parts of the world (Anthony 1978).

Methods of removing nitrates from water may be classified into several methods. First, the biological method, in which the reaction is bacterially catalyzed, requires a carbon source and a reducing agent such as methanol. With this method a conversion of 86% of the nitrate to nitrogen has been achieved (Stanley 1986). However, this method has two disadvantages: one is that it is time consuming process, the another is that it involves the use of toxic material (methanol).

The second method of removing nitrate from drinking water is the ion exchange method, which consists of passing the water successively over a solid cation exchanger and a solid anion exchanger, which replace cations and anions by hydrogen ion and hydroxide ion, respectively (Evan 1985). Although this method is capable of removing nitrate from water successfully, it is expensive, needs a disposal site, and microbial growth on the exchangers can diminish their efficiency.

The third method is the reverse osmosis method which consists of forcing water through a semipermeable membrane that allows the passage of water but not of other material (Evan 1985). The separation is not perfect. Depending upon how the membrane is prepared, the salt rejection is anywhere from 50% to 90%. Reverse-osmosis systems are readily

available. They are expensive to run, due to the high pressures required, 100-250 pound/inch². The pH must be maintained between 5.5 and 7.5 to protect the membrane.

Distillation is the fourth method of removing nitrate from drinking water (Evan 1985). This method consists of evaporation of water molecules followed by recondensation. The nitrates do not distill with the water and are left behind. Although the technology is readily available, the cost is still relatively high for ground-water treatment.

The fifth method is electrodialysis, which consists of applying a direct current across a body of water separated into vertical layers by membranes alternately permeable to cations and anions (Evan 1985). Cations migrate toward the cathode and anions toward the anode. Even though this method is practical and economical, it is not capable of removing more than 50% of the nitrate from water, and requires special care since the growth of microorganisms on the membrane can cause fouling.

The reduction method, which consists of passing water through a column containing a reducing agent that has been treated with a catalyst, and consequently nitrate is reduced to nitrogen gas (American Public Health Association 1985). With the use of the reduction method, we may avoid many of the weaknesses the other methods have. The method holds promise and can help achieving removal of nitrate to a great

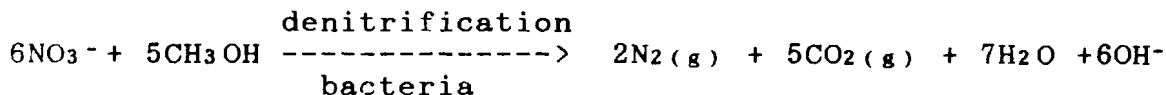
The objective of this project is to develop a method to

remove nitrate from drinking water. This method must not expensive, cannot involve the use of toxic materials, and does not need a disposal site for the wastes produced throughout the work.

Chapter 2. PREVIOUS WORK

Since 1945, it has been known that high-nitrate water, in excessive quantities, can lead to infantile cyanosis. The "blue baby" syndrome is caused by the conversion of oxygen-carrying hemoglobin in the blood to the nonoxygen carrying form known as methaemoglobin. More recently there has been increasing awareness that important correlations may exist between high-nitrate water and some forms of cancer (Anthony 1978).

Research into ways of combating this problem has been under way for many years at Britain's Water Research center (Anthony 1978). One approach is the modification of existing sewage treatment processes to include a special denitrification stage. In this process, denitrification depends on sludges that contain the living organisms capable of breaking nitrate down into nitrite, and then into nitrogen gas.



While processes of this kind can reduce dramatically the amount of nitrate reaching rivers from treatment plants, they cannot solve the special problems arising from nitrate rich ground water.

In the Sixteenth Edition of Standard Methods for the Examination of Water and Wastewater (American Public Health

Association 1985), a reduction method of nitrate using cadmium, has been proposed . In this method, determination of nitrate and nitrite, singly or together in potable, surface, and saline waters, as well as domestic and industrial wastewater, over a range of 0.5 to 10 mg N/L, can be achieved. Using the cadmium reduction method, nitrate is reduced almost quantitatively to nitrite in the presence of cadmium (Cd). This method uses commercially available Cd granules treated with copper sulfate (CuSO_4), to form a copper coating, but requires ethylenediaminetetraacetic acid (EDTA), making it unsuitable for drinking water.

Devarda's alloy reduction method was also mentioned in the Sixteenth Edition of Standard Methods for the Examinations of Water and Wastewater. With Devarda's alloy reduction method, nitrate and nitrite are reduced to ammonia under alkaline conditions in the presence of the reducing agent, Devarda's alloy (an alloy of 50% Cu, 45% Al, and 5% Zn). The reduction is carried out in a Kjeldahl distillation apparatus. Under hot alkaline conditions the ammonia formed distills and is trapped in a receiving flask containing boric acid.

However, the reduction method has not previously been conducted to remove nitrate from drinking water.

Chapter 3. EXPERIMENTAL

The removal of nitrate from water by the reduction method involves first choosing a suitable reducing agent. One should be concerned about the reduction potentials of these agents involved in the reaction and about their toxicity. The second consideration is to determine the optimum conditions of these reducing agents.

The first step in this work was to use the standard reduction tables to choose a reducing agent. Several metals were chosen to be used as reducing agent for the removal of nitrate from water. These metals were magnesium, copper, Devarda's alloy, and zinc.

Inspecting the effect of these reducing agents of removal of nitrate from water, was carried out first in a beaker rather than a column.

A standard nitrate solution was prepared prior to the analysis by diluting 50.0 ml of stock nitrate solution to 500 ml with distilled, deionized water, giving a final concentration of 10.0 mg of nitrate-nitrogen per liter. A mobile phase concentrate for mixing with nitrate samples to be analyzed by high-performance liquid chromatography (HPLC), was prepared from 0.1 F KH_2PO_4 + 0.025 F H_3PO_4 .

Prior to analyzing samples by HPLC, samples were filtered through 0.5 micrometer pore size filter to remove any suspended matter that might be present.

All HPLC analysis were performed on a Varian 2010 pump/2210 system. The variable-wavelength UV detector, model 2050, was set at 210 nm. The injector was Rheodyne 7125 with a 10 micro-liter loop. All HPLC analysis were performed at a flow rate of 1.0 ml/min at room temperature (Schroeder 1987).

(A): Removal of nitrate from water using magnesium metal at room temperature.

1: Apparatus and Reagents.

a: Saturated sodium hydroxide: Dissolve sodium hydroxide pellets in 100.0 ml distilled, deionized water, add NaOH to the solution until at saturation.

b: Magnesium granules: Wash and rinse 5.0 g of magnesium granules (20-mesh) with distilled water in a beaker. Wash three times.

2: Procedure.

Mix the saturated sodium hydroxide solution with magnesium granules in a beaker. With the aid of magnetic

stirrer and magnetic bar, stir mixture for 30 minutes. Rinse magnesium granules three times, with distilled water. Add 50.0 ml of 10 mg/L nitrate standard solution to magnesium granules. Stir the magnesium-nitrate mixture as mentioned above for one hour. Then with a 500 microliter micropipet, take samples at ten-minute intervals. Mix sample with 2.0 ml of mobile phase in a small plastic bottle, and analyze by HPLC.

(B): Removal of nitrate from water using a mixture of magnesium and copper at room temperature.

1: Apparatus and Reagents.

- a: Saturated sodium hydroxide: Prepared as described in section (a) of part (A) of this chapter.
- b: Magnesium and copper mixture: Wash and rinse three times, with distilled water, 5.0 g of magnesium and 5.0 g of copper in a beaker.

2: Procedure.

Mix the saturated sodium hydroxide in a beaker, with magnesium-copper mixture. Stir with aid of magnetic stirrer and magnetic bar for 30 minutes. Rinse mixture three times with distilled water. Add 50.0 ml of standard

nitrate solution to Mg-Cu mixture. Stir as above for one hour. Filter, then take samples with a 500 micro-liter micropipet every ten minutes, mix in a small plastic bottle with 2.0 ml of mobile phase.

(C): Removal of nitrate from water by Devarda's alloy at room temperature.

1: Apparatus and Reagents.

Devarda's alloy: Wash 5.0 g of Devarda's alloy (20-mesh) with distilled water in 100 mL beaker. Rinse three times

2: Procedure.

Mix 5.0 g of Devarda's alloy in 300 ml beaker with 50.0 ml of 10 mg/l nitrate standard solution. Use a magnetic stirrer, magnetic stirring bar to mix the alloy and nitrate solution for one hour. Filter, then take sample at ten-minute intervals. Mix sample in a small plastic bottle with 2.0 ml of mobile phase, and analyze by HPLC.

(D): Removal of nitrate from water by Devarda's alloy treated with 0.01 M copper chloride at room temperature.

1: Apparatus and Reagents.

a: Copper chloride reagents: Dissolve 0.1344 g CuCl_2 in 20.0 ml deionized, distilled water, transfer to 100 ml volumetric flask, dilute to 100 ml, giving a final concentration of 0.01 M.

b: Devarda's alloy: Prepared as described in section (C).

2: Procedure.

Mix the alloy with 100 ml of 0.01 CuCl_2 in 100 beaker, stir for twenty minutes with a magnetic stirrer and magnetic stirring bar. Rinse with distilled water copiously to remove all precipitated copper. Add 50.0 ml of 10.0 mg/L nitrate standard solution, mix for one hour. Filter, then take sample every ten minutes with a 500 micro-liter 1 micropipet. Mix with 2.0 ml of mobile phase in a small plastic bottle, and analyze by HPLC.

(E): Removal of nitrate from water by Zinc metal at room temperature.

1: Apparatus and Reagents.

Zinc granules: Wash 5.0 gm of zinc granules (20-mesh) with distilled water in a beaker. Rinse three times.

2: Procedure.

Mix in a beaker 50 g of zinc granules with 50.0 ml of 10 gm/l nitrate standard solution, stir for one hour with a magnetic stirrer and magnetic stirring bar. Filter, then take sample every ten minutes with a 500 micro-liter micropipet. Mix with 2.0 mL of mobile phase in a small plastic bottle, and analyze by HPLC.

(F): Removal of nitrate from water by zinc metal treated with 0.01 M copper chloride at room temperature.

1: Apparatus and Reagents.

a: Copper chloride 0.01 M reagent: Prepared as described in section (D).

b: Zinc granules: prepared as described in section (E) of the experimental chapter.

2: Procedure.

Steps followed in section (D) procedure were repeated in this section with the exception of using zinc granules instead of Devarda's alloy.

(G): Removal of nitrate from water by zinc treated with 0.05 M copper chloride at room temperature.

1: Apparatus and Reagents.

a: Copper chloride reagent: Dissolve 0.672 g CuCl_2 in 20.0 ml of deionized, distilled water, transfer to 100 ml volumetric flask, dilute to 100 ml, giving a final concentration of 0.05 M CuCl_2 .

b: Zinc granules: Prepared as described in section (E).

2: Procedure.

The steps followed in section (D) procedure were repeated in this section, with the exception of using 0.05 M CuCl_2 instead of 0.01 M CuCl_2 and using zinc granules instead of Devarda's alloy.

(H): Removal of nitrate from water by zinc treated with 0.1 M copper chloride at room temperature.

1: Apparatus and Reagents.

a: Copper chloride reagent: Dissolve 1.340 g CuCl_2 in 20.0 ml of deionized, distilled water, transfer to a 100 ml volumetric flask, dilute to 100 ml, giving a final concentration of 0.1 M CuCl_2 .

b: Zinc granules: Prepared as described in section (E).

2: Procedure.

All steps followed in section (D) procedure were repeated in this section, with the exception of using zinc granules instead of Devarda's alloy, and using 0.1 M CuCl_2 instead of 0.01 M CuCl_2 .

(I): Removal of nitrate from water by zinc treated with 0.1 M copper chloride at 20, 30, 40, and 50 C°.

1: Apparatus and Reagents.

-
- a: Reduction column: Construct the column from a 53.5 cm long glass tube of 1.1 cm inner diameter, insert in a condenser (Fig. 2). Insert a glass wool plug into bottom of column and fill with zinc granules which have been treated with 0.1 M CuCl_2 .
- b: Constant temperature bath: A Haake type FE constant temperature bath has been used.
- c: Nitrate standard solution: Dissolve 0.577 g potassium nitrate in 20 ml of deionized, distilled water, dilute to 4.0 liter, giving a final concentration of 20.0 mg N/L nitrate.
- d: Copper chloride reagent: Prepared as described in section (a) part (H) of the experimental chapter.
- e: Zinc granules: wash 64.0 gm of zinc granules (20-mesh)

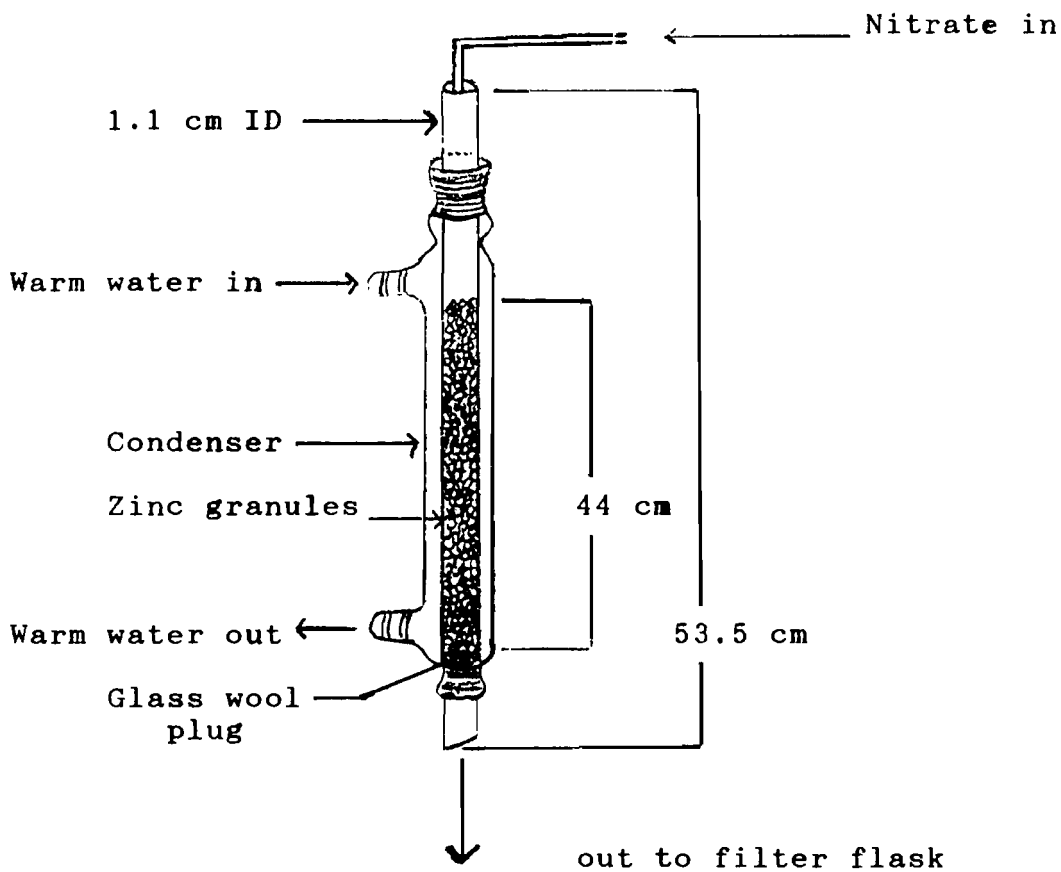


Fig. 2. Reduction column. Nitrate is reduced to nitrogen in the presence of zinc. Heated water circulates around the column and maintains a uniform temperature. Modified from American Public Health Association (1985, fig. 418:1).

with distilled water, rinse three times.

2: Procedure.

Mix zinc granules with 100 ml of 0.1 M CuCl_2 in a beaker, stir for twenty five-minutes with magnetic stirrer and magnetic stirrer bar. Rinse with distilled water copiously to remove all precipitated copper. Transfer zinc granules to reduction column. Connect bottom of column to a 125 ml filter flask. Through a bent 100 cm long glass tube, solution flow from a four liter glass container to the column. Nitrate flow can be controlled by two ways. The first one is by partially clamping a rubber hose that connects the glass container to the bent glass tube. The second way is by partially clamping a rubber hose connects the aspirator to filter flask. Wash column with nitrate solution flowing from the container; discard the first 100 ml. Collect samples at ten-minute intervals, and analyze by HPLC.

(J): Removal of nitrate from well water using zinc treated with 0.1 M CuCl_2 at 50 C°.

1: Apparatus and Reagents.

- a: Reduction column: Constructed as described in section (I).
- b: Constant temperature bath: A haake type FE constant temperature bath was used.
- c: Well water containing nitrate : During February of 1989, a well water sample was collected from a farm in Lyon county in Kansas. The exact source of ground water was not certain. Conditions of well, depth, aquifer are unknown. The HPLC analysis for this sample revealed that it contains 7.1 mg N/L nitrate. county in Kansas. The HPLC analysis for this sample revealed that it contains 7.1 mg N/L nitrate.
- d: 0.1 M CuCl_2 reagent: Prepared as described in section (a) part (H) of the experimental chapter.
- e: Zinc granules: Prepared as described in section (I).

2: Procedure.

All steps followed in procedure in section (I) of the experimental chapter were repeated, at this time with the well water.

Chapter 4. RESULTS AND DISCUSSION

A typical chromatogram of standard nitrate solution is shown in Fig. 3, the analog signal for a standard containing 4.0 mg/l as N. The nitrate retention time was 2.7 minutes.

Tables 1 and 2 show the percent nitrate reduced by magnesium and a mixture of magnesium-copper at 30 C°, respectively. As shown in Fig. 4, the percent nitrate reduced by the Mg-Cu mixture is almost three times more than that by the magnesium only. This result gives a clear indication of the suitability of Mg-Cu mixture for nitrate reduction.

In an attempt to explore a better reducing agent, Devarda's alloy has been used with a nitrate standard containing 10 mg/l as N at 30 C° (Table 3). Comparing Figures 4 and 5 shows that there was not a great difference in the amount of nitrate that has been reduced by the Mg-Cu mixture and by Devarda's alloy.

The next step was the use of Devarda's alloy treated with 0.01 M copper chloride solution at 30 C° (Table 4). As shown in Fig. 5, the use of a treated Devarda's alloy was much more successful in reducing the nitrate, in comparison with the previously described methods.

The metal zinc was also used in an attempt to remove nitrate from water (Table 5). The percent nitrate reduced

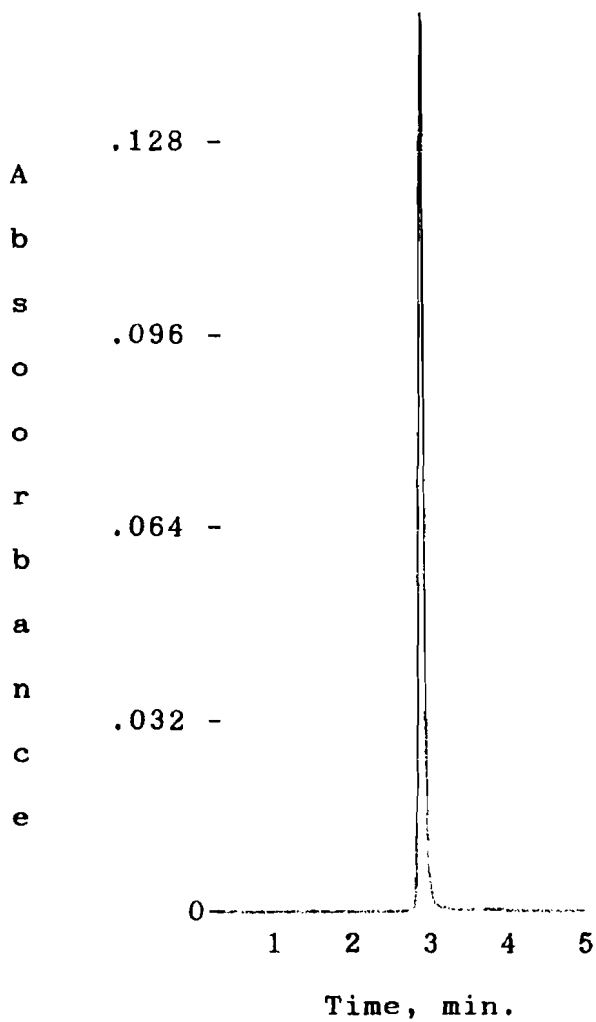


Fig. 3. Chromatogram for 4.0 mg/l nitrate-N in distilled, deionized water.

Table 1

Reduction of nitrate in water by magnesium at room temperature.

Flow rate : 1 ml/min
Wavelength : 210 nm
Range : 0.32

Sample	Retention Time (min)	Peak Height (cm)	Contact time (min)	% Red
Std.*	2.51	18.4	----	----
1	2.51	15.5	10.0	15.7
2	2.51	15.2	20.0	17.3

Std.*: Nitrate standard solution containing 10 mg/l as N.

Table 2

Reduction of nitrate from water by magnesium and copper at room temperature.

Flow rate : 1 ml/min
Wavelength: 210 nm
Range : 0.32

Sample	Retention Time (min)	Peak Height (cm)	Contact time (min)	% Red.
Std.*	2.51	18.4	----	----
1	2.52	11.6	10.0	40.4
2	2.52	11.5	20.0	40.9
3	2.52	8.90	30.0	54.2

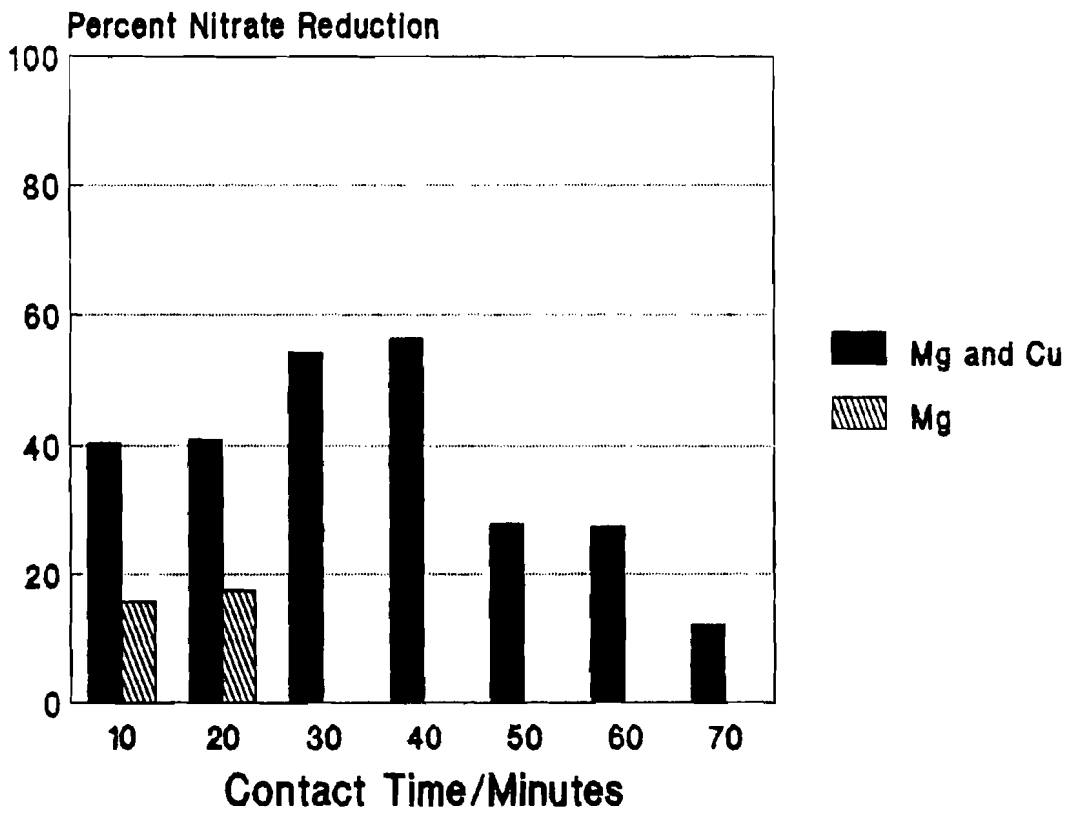


Fig. 4. Reduction of nitrate by Mg and Mg-Cu at room temperature (see tables 1 and 2).

Table 2 (continued)

Sample	Retention Time (min)	Peak Height (cm)	Contact time (min)	% Red.
4	2.52	8.50	40.0	56.3
5	2.52	14.0	50.0	28.0
6	2.52	14.1	60.0	27.5
7	2.52	15.9	70.0	12.1

Table 3

Reduction of nitrate in water by Devarda's alloy at room temperature.

Flow rate : 1 ml/min

Wavelength : 210 nm

Range : 0.32

Sample	Retention Time (min)	Peak Height (cm)	Contact time (min)	% Red
Std.*	2.60	21.2	----	----
1	2.60	24.6	10.0	----
2	2.60	22.8	20.0	----
3	2.60	19.8	30.0	7.00
4	2.60	15.2	40.0	28.4
5	2.60	17.0	50.0	20.0
6	2.60	15.9	60.0	25.1
7	2.60	14.6	70.0	31.2
8	2.60	15.0	80.0	29.3
9	2.60	12.5	90.0	41.1

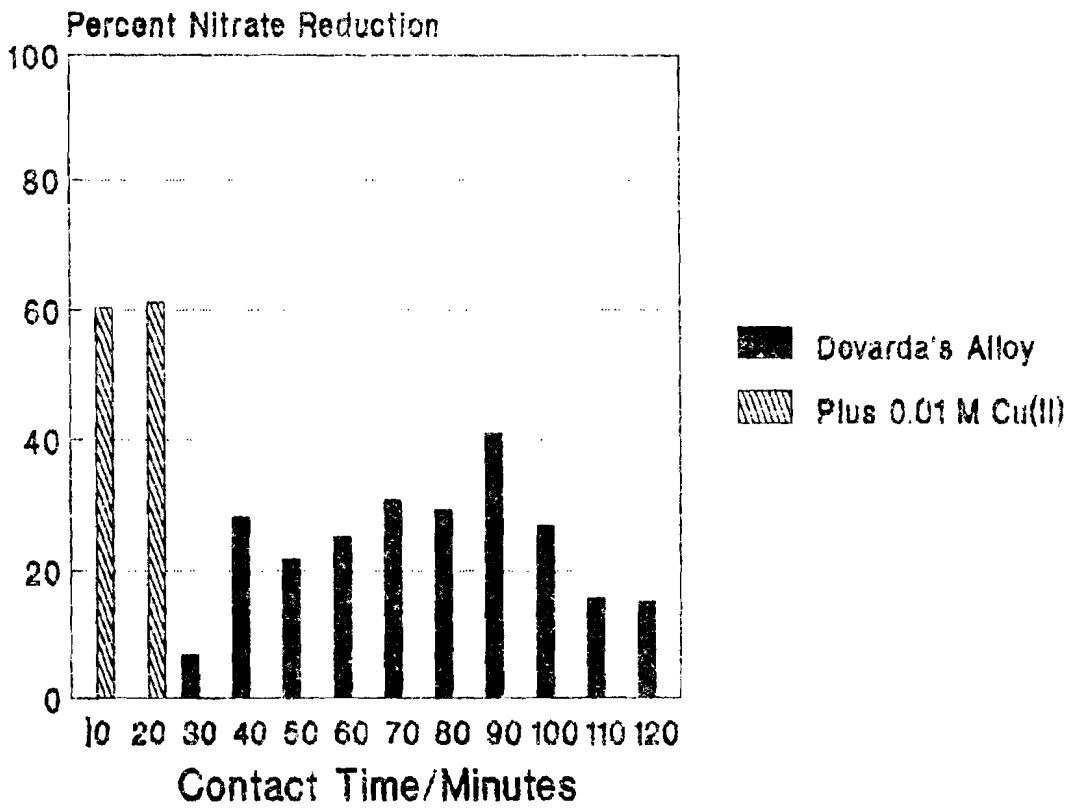


Fig. 5. Reduction of nitrate by Devarda's alloy and with 0.01 M Cu(II) at room temperature (see tables 3 and 4).

Table 3 (continued)

Sample	Retention Time (min)	Peak Height (cm)	Contact time (min)	% Red.
10	2.60	15.5	100.0	27.0
11	2.60	17.9	110.0	15.6
12	2.60	18.0	120.0	15.2

Std.*: Nitrate standard solution containing 10 mg/L as N.

Table 4

Reduction of nitrate in water by Devarda's alloy treated
with 0.01 M CuCl₂ at room temperature.

Flow rate : 1 ml/min
Wavelength: 210 nm
Range : 0.32

Sample	Retention Time (min)	Peak Height (cm)	Contact time (min)	% Red.
Std.*	2.52	22.7	----	----
1	2.52	9.02	10.0	60.3
2	2.52	8.82	20.0	61.2

Std.*: Nitrate standard solution containing 10 mg/l as N.

Table 5

Reduction of nitrate in water by zinc at room temperature.

Flow rate : 1 ml/min

Wavelength: 210 nm

Range : 0.16

Sample	Retention Time (min)	Peak Height (cm)	Contact time (min)	% Red.
Std.*	2.71	15.3	----	----
1	2.71	19.5	10.0	----
2	2.71	13.7	20.0	10.1
3	2.71	13.9	30.0	9.22
4	2.71	14.2	40.0	7.25
5	2.71	14.0	50.0	9.22
6	2.71	13.3	60.0	13.1

Std.*: Nitrate standard solution containing 10 mg/L as N.

by zinc granules at 30 C° is shown in Fig. 6, and it is obvious from the figure that the zinc was less effective in reducing the nitrate than the previously described methods.

The effect of copper chloride solution on reactivating the zinc granules, and the effect of CuCl₂ concentration were investigated. Increasing the concentration of CuCl₂ was one way to arrive at better nitrate removal from water. Tables 6, 7, and 8 show data of using zinc treated with CuCl₂ of 0.01, 0.05, 0.10 M respectively, at 30 C°. By comparing Fig. 7, 8, and 9, it was clear that increasing the CuCl₂ concentration increases the effectiveness of the zinc in reducing the nitrate. It was also clear that the treatment of zinc with CuCl₂ makes it a better reducing agent in removing nitrate from water than the zinc when used without treatment, or the magnesium, or the Mg-Cu mixture, or the Devarda's alloy. So the method that will be used in the coming parts of this research will be the zinc that is treated with 0.1 M CuCl₂.

The temperature factor was also investigated, in an attempt to reach the right temperature at which nitrate might be removed totally from drinking water. The range of temperature that was used with the zinc treated with 0.1 M CuCl₂ was 20, 30, 40, and 50 C° (Tables 9, 10, 11, and 12). These results were plotted as shown in Figures 10, 11, 12, and these figures show that the best results were achieved

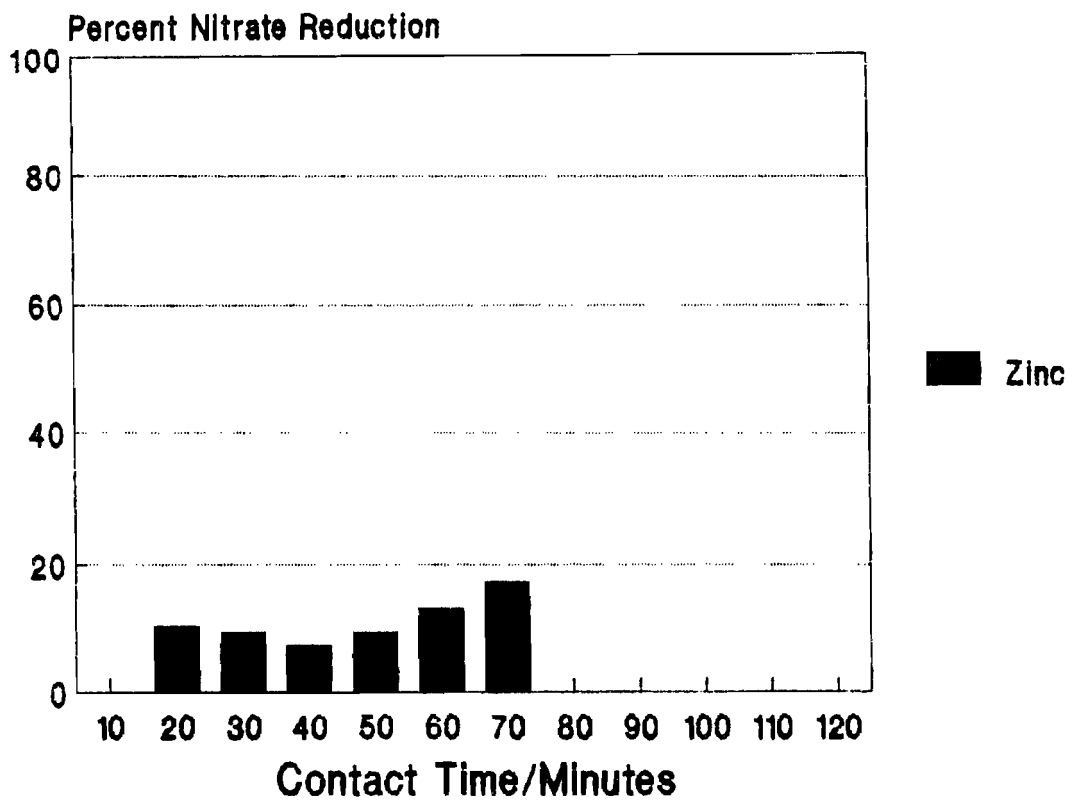


Fig. 6. Reduction of nitrate by zinc at room temperature
(see table 5).

Table 6

Reduction of nitrate in water by zinc treated with 0.01 M
CuCl₂ at room temperature.

Flow rate : 1 ml/min
Wavelength: 210 nm
Range : 0.32

Sample	Retention Time (min)	Peak Height (cm)	Contact time (min)	% Red.
Std.*	2.70	23.0	----	----
1	2.70	23.2	10.0	----
2	2.70	15.6	20.0	32.0
3	2.70	17.0	30.0	26.2
4	2.70	14.8	40.0	35.6
5	2.70	13.2	50.0	42.6
6	2.70	12.1	60.0	47.4
7	2.70	10.8	70.0	53.1
8	2.70	9.25	80.0	59.8
11	2.70	0.42	120.0	98.2

Std.*: Nitrate standard solution containing 10 mg/l as N.

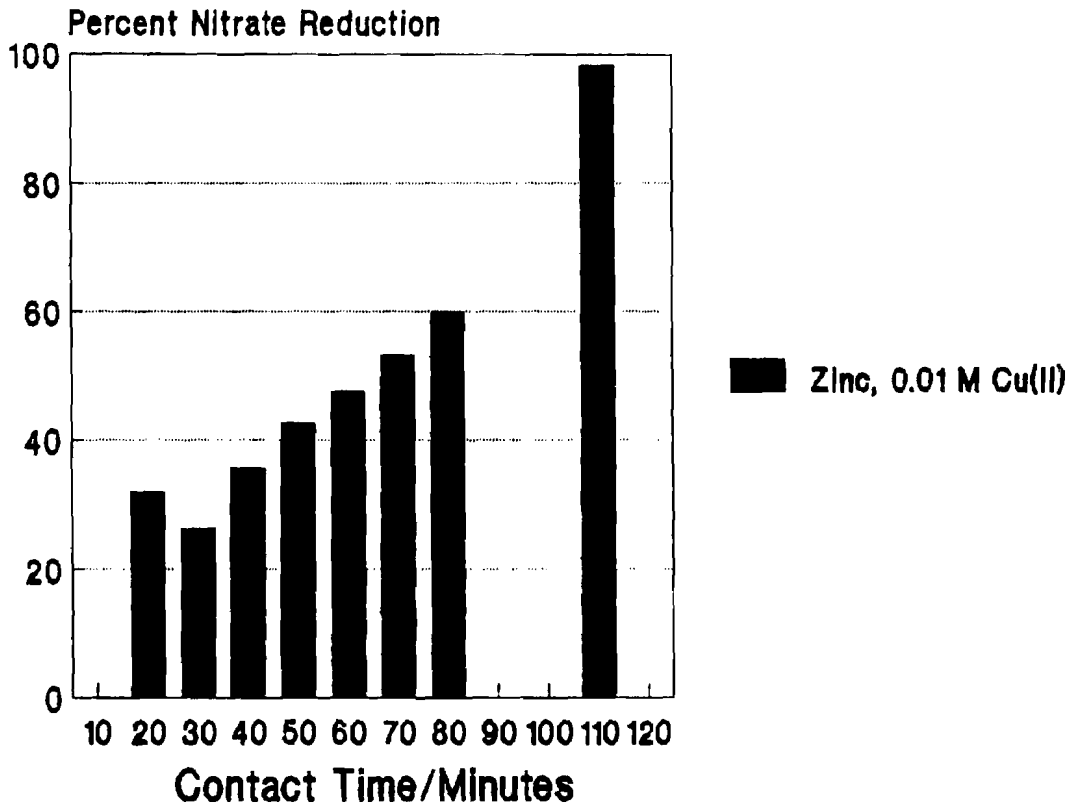


Fig. 7. Reduction of nitrate by zinc with 0.01 M Cu(II) at room temperature (see table 6).

Table 7

Reduction of nitrate in water by zinc treated with 0.05 M
CuCl₂ at room temperature.

Flow rate : 1 ml/min
Wavelength : 210 nm
Range : 0.32

Sample	Retention Time (min)	Peak Height (cm)	Contact time (min)	% Red.
Std.*	2.70	20.7	----	----
1	2.70	15.5	10.0	25.2
2	2.70	11.8	20.0	43.1
3	2.70	8.60	30.0	58.5
4	2.70	8.00	40.0	61.4
5	2.70	6.25	50.0	69.8
6	2.70	6.10	60.0	70.6
7	2.70	4.35	70.0	79.0
8	2.70	8.32	80.0	59.8

Std.*: Nitrate standard solution containing 10 mg/l as N.

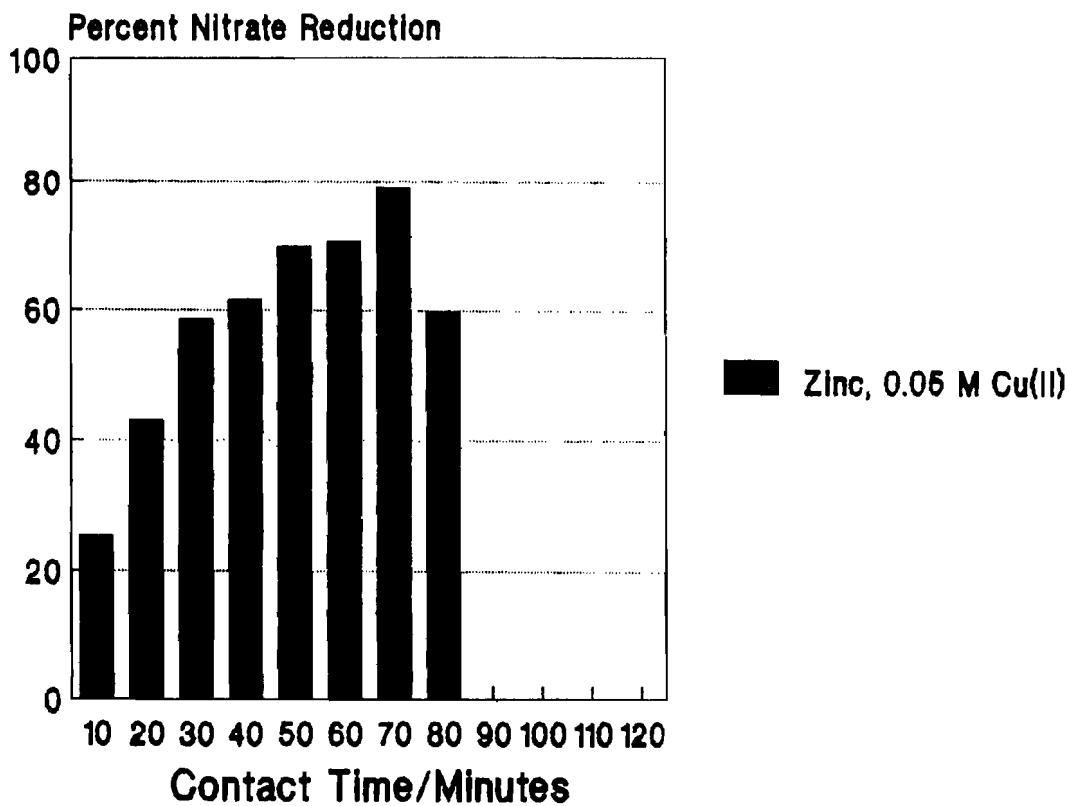


Fig. 8. Reduction of nitrate by zinc with 0.05 M Cu(II) at room temperature (see table 7).

Table 8

Reduction of nitrate in water by zinc treated with 0.10 M
CuCl₂ at room temperature.

Flow rate : 1 ml/min
Wavelength : 210 nm
Range : 0.32

Sample	Retention Time (min)	Peak Height (cm)	Contact time (min)	% Red.
Std.*	3.40	22.8	----	----
1	3.40	22.8	10.0	----
2	3.40	8.80	20.0	61.4
3	3.40	7.60	30.0	66.7
4	3.40	6.60	40.0	71.2
5	3.40	3.10	50.0	86.4
6	3.40	3.70	60.0	84.0
7	3.40	2.30	70.0	89.9
8	3.40	1.60	80.0	92.9
9	3.40	9.30	90.0	59.2
10	3.40	12.2	100.0	46.5

Std.*: Nitrate standard solution containing 10 mg/l as N.

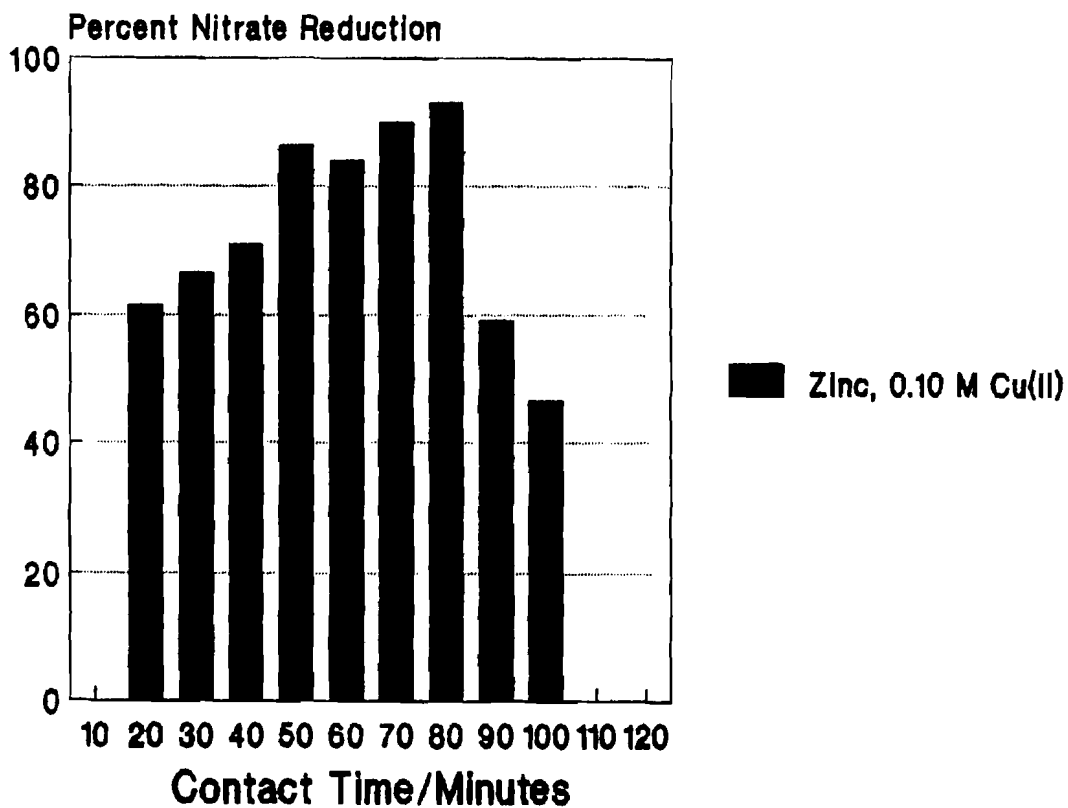


Fig. 9. Reduction of nitrate by zinc with 0.10 M Cu(II) at room temperature (see table 8).

Table 9

Reduction of nitrate in water by zinc treated with 0.10 M
CuCl₂ at 20 C°.

Flow rate : 1 ml/min
Wavelength : 210 nm
Range : 0.32

Sample	Retention Time (min)	Peak Height (cm)	Time (min)	% Red.
Std.**	2.60	13.9	----	----
1	2.60	5.63	10.0	59.6
2	2.60	1.50	20.0	89.7
3	2.60	0.91	30.0	93.5
4	2.60	2.64	40.0	81.1
5	2.60	5.15	50.0	63.1
6	2.60	4.05	60.0	71.0
7	2.60	3.30	70.0	76.3
8	2.60	2.80	80.0	80.0
9	2.60	3.10	90.0	78.0
10	2.60	3.10	100.0	78.0
11	2.60	2.98	110.0	78.6
12	2.60	2.65	120.0	81.0

Std.**: Nitrate standard solution containing 20 mg/l as N.

Table 10

Reduction of nitrate in water by zinc treated with 0.10 M
CuCl₂ at 30 C°.

Flow rate : 1 ml/min
Wavelength : 210 nm
Range : 0.32

Sample	Retention Time (min)	Peak Height (cm)	Time (min)	% Red.
Std.**	2.71	16.3	----	----
1	2.71	14.4	10.0	----
2	2.71	7.30	20.0	62.10
3	2.71	7.10	30.0	65.00
4	2.71	5.60	40.0	72.30
5	2.71	5.51	50.0	87.21
6	2.71	5.52	60.0	82.50
7	2.71	5.00	70.0	89.85
8	2.71	4.40	80.0	92.11
9	2.71	7.25	90.0	61.21
10	2.71	8.25	100.0	46.55

Std.**: Nitrate standard solution containing 20 mg/l as N.

Table 11

Reduction of nitrate in water by zinc treated with 0.10
CuCl₂ at 40 C°.

Flow rate : 1 ml/min
Wavelength : 210 nm
Range : 0.32

Sample	Retention Time (min)	Peak Height (cm)	Time (min)	% Red.
Std.**	2.80	16.1	----	----
1	2.80	5.50	10.0	65.9
2	2.80	1.94	20.0	88.0
3	2.80	3.82	30.0	76.3
4	2.80	4.87	40.0	69.7
5	2.80	1.20	50.0	92.5
6	2.80	1.12	60.0	93.0
7	2.80	1.00	70.0	93.8
8	2.80	1.29	80.0	92.0
9	2.80	1.21	90.0	92.5
10	2.80	1.60	100.0	90.1
11	2.80	0.81	110.0	95.0
12	2.80	1.31	120.0	92.0

Std.**: Nitrate standard solution containing 20 mg/L as N.

Table 12

Reduction of nitrate in water by zinc treated with 0.10 M
CuCl₂ at 50 C°.

Flow rate : 1 ml/min
Wavelength : 210 nm
Range : 0.32

Sample	Retention Time (min)	Peak Height (cm)	Time (min)	% Red.
Std.**	2.70	15.8	----	----
1	2.70	8.25	10.0	47.7
2	2.70	0.10	20.0	99.4
3	2.70	0.70	30.0	95.6
4	2.70	0.80	40.0	95.0
5	2.70	0.69	50.0	95.6
6	2.70	0.61	60.0	96.1
7	2.70	0.80	70.0	95.1
8	2.70	0.11	80.0	99.3
9	2.70	0.11	90.0	99.3
10	2.70	0.11	100.0	99.3
11	2.70	0.11	110.0	99.3
12	2.70	0.11	120.0	99.3

Std.**: Nitrate standard solution containing 20 mg/l as N.

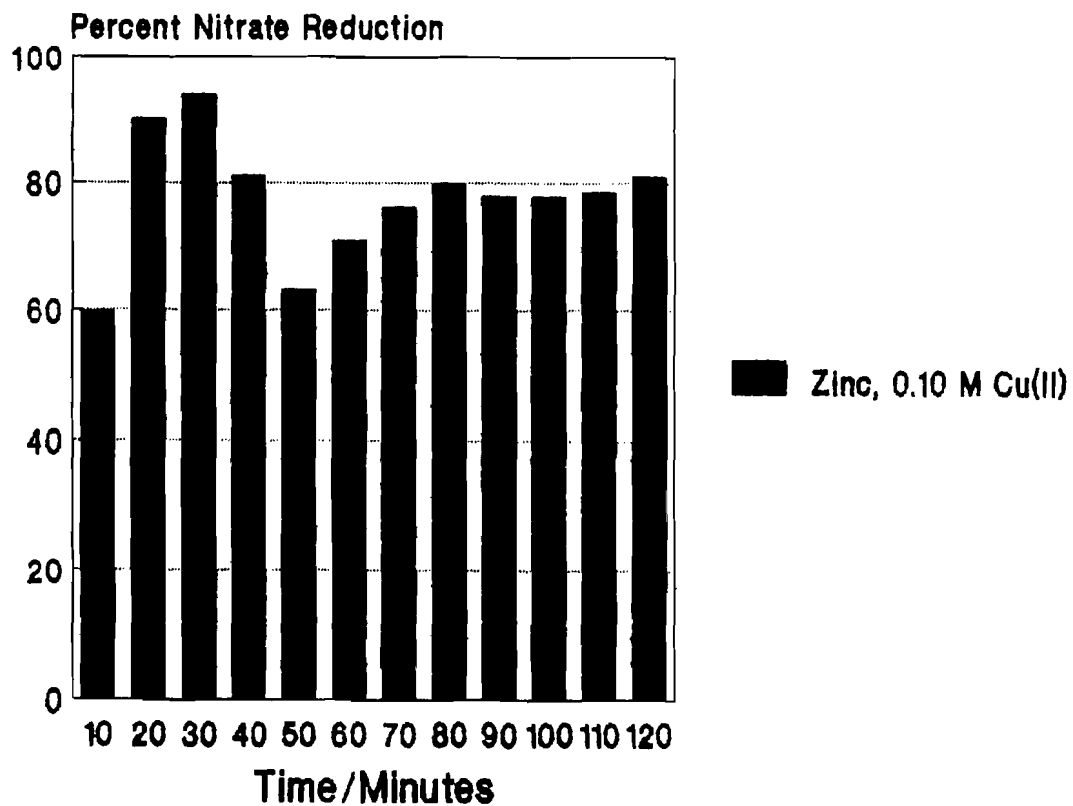


Fig. 10. Reduction of nitrate by zinc with 0.10 M Cu(II) at 20 C° (see table 9).

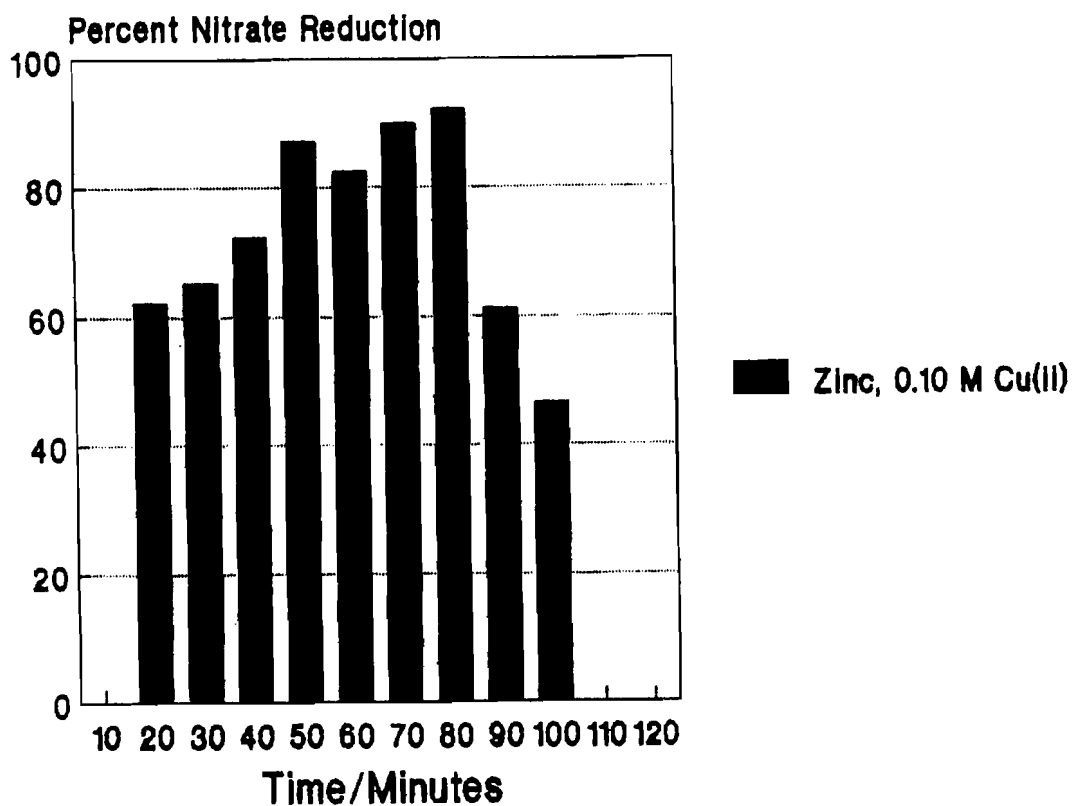


Fig. 11. Reduction of nitrate by zinc with 0.10 M Cu(II) at 30 C° (see table 10).

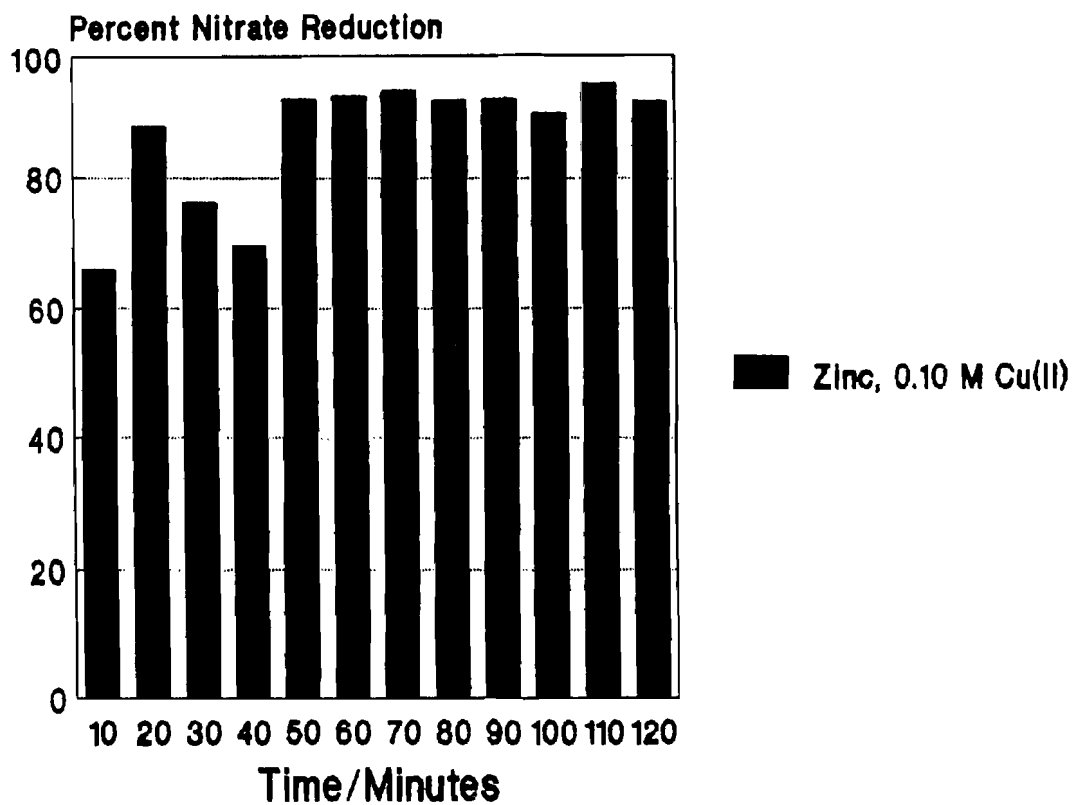


Fig. 12. Reduction of nitrate by zinc with 0.10 M Cu (II) at 40 C° (see table 11).

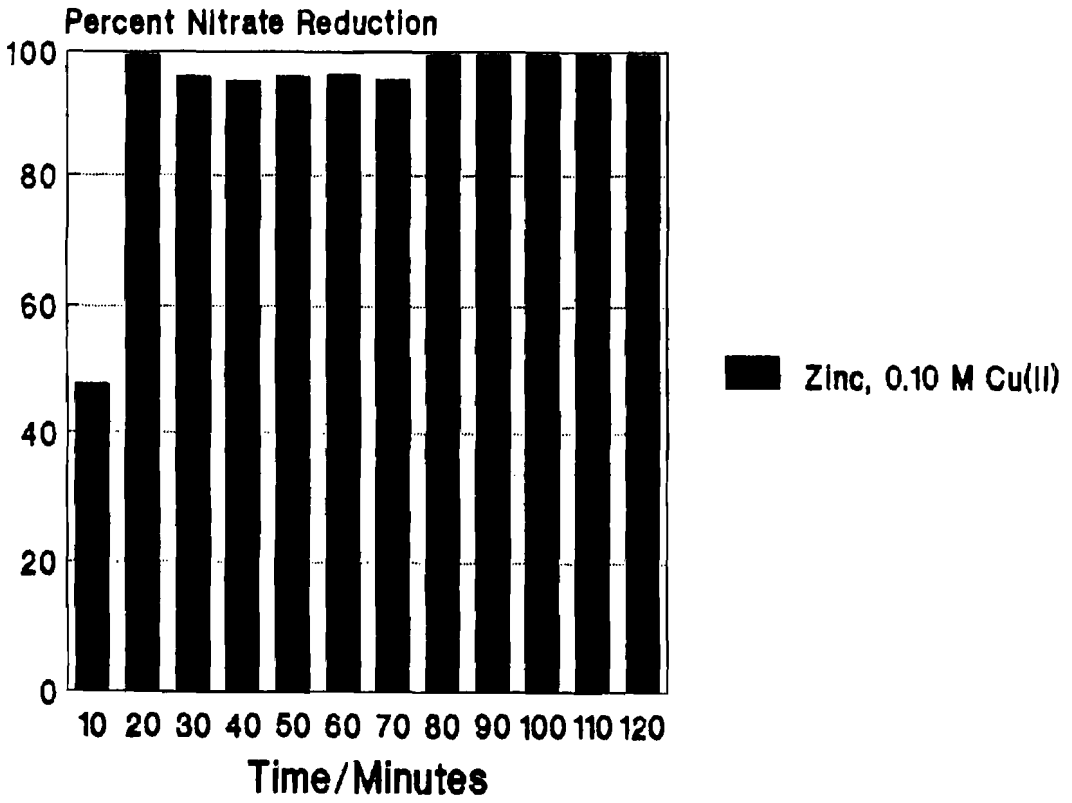
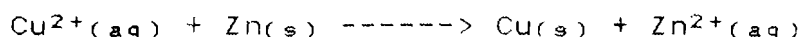


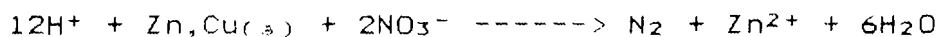
Fig. 13. Reduction of nitrate by zinc with 0.10 M Cu(II) at 50 C° (see table 12).

at a temperature of 50 C°, at which nearly 100 percent removal of nitrate from water was achieved after 70 minutes (Fig. 13).

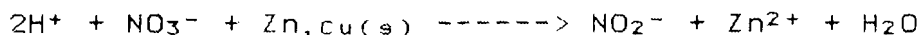
The net reaction occurring between the CuCl₂ and Zn was the spontaneous reduction of Cu²⁺ and the oxidation of Zn(s):



On the other hand, the reduction of nitrate by zinc will produce either nitrogen gas:



or produces nitrite instead of nitrogen gas:



Applying the best conditions that have been investigated on nitrate-containing well water of 7.1 mg/L as N (Table 13) was the last step in this research. Fig. 14 shows that a removal of nearly 100 percent of nitrate from the well water was achieved.

In general several factors play an important role in improving the ability of the reduction method to remove nitrate from drinking water. First, as the amount of zinc

Table 13

Reduction of nitrate in well water by zinc treated with 0.10
M CuCl₂ at 50 C°.

Flow rate : 1 ml/min
Wavelength : 210 nm
Range : 0.08

Sample	Retention Time (min)	Peak Height (cm)	Time (min)	% Red.
Std.W	2.80	16.3	----	----
1	2.80	0.41	10.0	97.5
2	2.80	0.21	20.0	98.7
3	2.80	0.19	30.0	98.8
4	2.80	0.25	40.0	98.5
5	2.80	0.29	50.0	98.2
6	2.80	0.39	60.0	97.6
7	2.80	0.39	70.0	97.6
8	2.80	0.35	80.0	97.9
9	2.80	0.35	90.0	97.9
10	2.80	0.36	100.0	97.8
11	2.80	0.38	110.0	97.7
12	2.80	0.39	120.0	97.6

Std.W: Well water containing 7.1 mg/l nitrate as N.

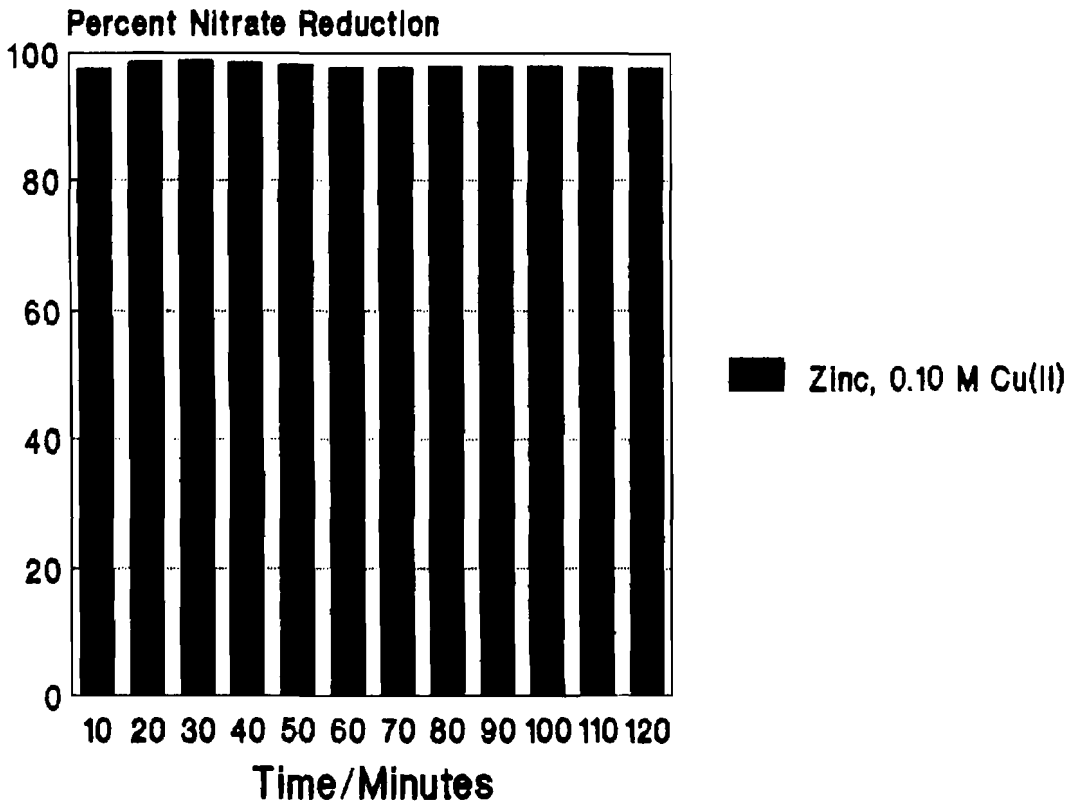
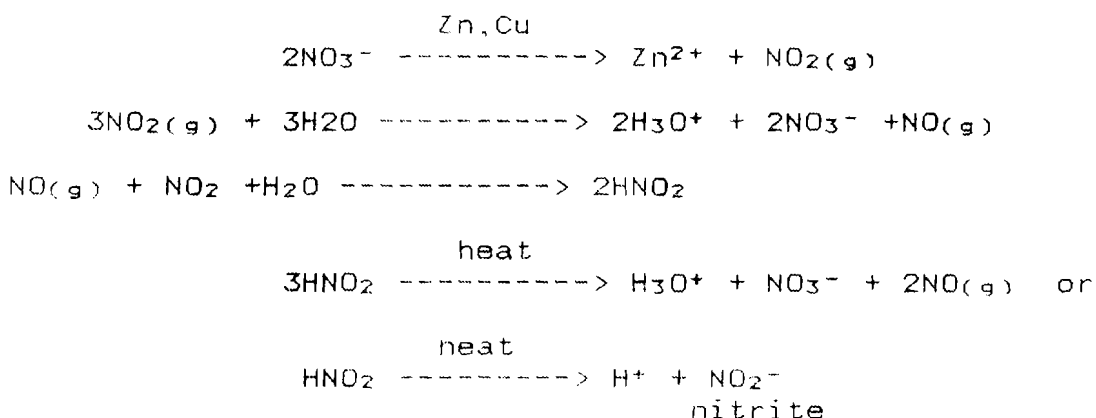


Fig. 14. Reduction of nitrate in well water by zinc with 0.10 M Cu(II) at 50 C° (see table 13).

granules and their surface area increases, the amount of nitrate that is reduced increases also. Second, addition of the Copper chloride to the column frequently, will reactivate the zinc, and improve its reduction capability of nitrate. Third, the time the nitrate spends inside the reduction column is very important, and the longer the time, the more nitrate will be reduced. This might be adjusted by two ways: one, by adjusting the vacuum at the aspirator, and the other is by partially clamping the outlet tube of the column. The flow rate used in the last part of this project was about 1 ml/min.

The fluctuations shown in the various figures in this research might be resulted from the formation of some intermediates which eventually produce more nitrate in solution, as shown in the following reactions:



Another reason behind these fluctuations might be resulted from the changing of nitrate flow from the column.

Further study is needed to minimize or overcome any problem that has been encountered during this project. Several aspects might be studied in this regard. First: working with another reducing agent that is capable of removing nitrate from water in a shorter time than the one achieved in this project. Second: inspecting a catalyst that is efficient to increase the rate of reduction. Third: Considering the work at a temperature higher than 50 C°. Fourth: Exploring the factors affecting formation of nitrite from nitrate reduction. Formation of small concentrations of nitrite have been observed after reduction of nitrate, especially at 20 C° and after a period of one hour of running nitrate in column. Fifth: measuring the amount of dissolved zinc in water on a time range, and at different water pH. Sixth: studying the presence of carbonate in well water which will react with the zinc in column and eventually plug the column.

Finally: examining the reproducibility of the results produced by this project.

Chapter 5. CONCLUSIONS

The removal of nitrate by the reduction method has been investigated for nitrate standard solutions and well water.

The use of any of the following reduction methods: magnesium metal, Devarda's alloy, mixture of Mg-Cu, or zinc metal treated with CuCl_2 ($< 0.1 \text{ M}$) at a temperature lower than 40 C° , is not recommended. These methods have two major problems:

- A: Incomplete reduction of nitrate and formation of nitrite which is more harmful than nitrate itself.
- B: removal of nitrate by any of these methods is a time consuming procedure.

On the other hand removal of nitrate from water by zinc granules treated with CuCl_2 ($> \text{ or } = 0.1 \text{ M}$) at a temperature higher than 40 C° , overcame these two major problems that the other methods have.

The percent nitrate reduction from well water at 50 C° , after one hour by this method was 97.6%.

Based on the simplicity, speed, safety, and lower cost of this method, I recommend its adoption as a routine procedure for removal of nitrate from ground water.

BIBLIOGRAPHY

- American Public Health Association. 1985. Standard Methods For the Examinations of Water and Wastewater, 16th ed. Washington, D. C. American Public Health Association, P. 391-400.
- Anthony, T. 1978. Fluidized Bed Technology Takes Nitrate From Water. London, Journal of Water and Sewage work (January), 76 (1978).
- Evan, K. N. 1985. Groundwater Treatment Technology. New York, Van Nostrand Reinhold Company, P. 111-130.
- Harvard Graphics, a graph drawing microcomputer program by Software Publishing Corporation.
- National Institute of Environmental Health Sciences. 1970. Nitrates, Nitrites, and Methemoglobinemia. research Triangle Park, North Carolina, National institute of Environmental Health Sciences, Environmental Review No.2.
- Ralph, H. P. 1982. 3rd ed. General Chemistry, Principles and Modern Applications. New York, Macmillan Publishing Company, Inc, p. 633.
- Schroeder, D. C. 1987. The Analysis of Nitrate in Environmental Samples by Reversed-Phase HPLC. Journal of Chromatographic Science 25, 405 (1987).
- Stanley, E. M. 1986. Environmental Chemistry, 4th ed. California, Brooks/Cole Publishing Company, P. 210-274.