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Investigations on Nitrate Procedures Applicable to Hanford Monitoring Well Samples

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INVESTIGATIONS ON NITRATE PROCEDURES APPLICABLE TO HANFORD MONITORING WELL SAMPLES

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ABSTRACT

A literature review and experimental studies were used to develop an alternate method for determining the nitrate concentrations in Hanford well waters. The present phenoldisulfonic acid method appears to be sensitive to a negative interference by chloride ions in the well waters. Two methods were chosen for experimental study, the nitrate specific ion electrode and the cadmium reduction procedure.

Utilizing a buffer reagent, well water nitrate concentrations between 1-1000 ppm NO_3-N can be precisely and accurately determined by the nitrate specific ion electrode method. Precision of ±5-10 percent throughout the working range and spiked recoveries of 90-100 percent were observed.

The cadmium reduction-colorimetric technique utilizing a chloride-EDTA buffer solution can be used to analyze low level nitrate well samples. The working curve is 0.02-0.80 ppm NO_3-N. With dilution before or after column elution, nitrate concentrations up to 500 ppm NO_3-N were successfully determined.

Precision of 5-13 percent and spike recoveries of 93-116 percent were found on Hanford well samples.

ACKNOWLEDGEMENTS

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INTRODUCTION

Surveillance of groundwater beneath the site is a principal part of Hanford's comprehensive environmental monitoring program. This program is designed to evaluate all significant potential pathways by which the public might receive exposure from radioactive and nonradioactive pollutants from site operations.

During plutonium recovery and general waste discharges, nitrates have been released to the ground on the Hanford Site. Aside from monitoring the nitrate to assure compliance with Environmental Protection Agency Interim Primary Drinking Water Standards, nitrate plumes have been utilized to trace the movements of contaminated groundwater on the Hanford Reservation. Because nitrate ions are present in most of the Hanford wastes and are only slightly affected by soil sorption mechanisms, nitrate is a good choice to obtain the necessary hydrologic data to predict groundwater movement. At present, about 310 wells on the Hanford Project are monitored.

Presently A.S.T.M.[2] recommends the brucine colorimetric method to analyze nitrates in waters. Standard Methods[2,3] is in the process of evaluating new procedures to succeed the phenoldisulfonic acid colorimetric procedure. The EPA[4] presently recommends both the brucine and cadmium reduction methods to determine the nitrate concentration in water. Because the phenoldisulfonic acid method utilized for the Hanford Monitoring Well Program is being dropped, alternate procedures were evaluated in this study. Furthermore, audit samples consisting of spiked groundwaters (0.5 to 5 ppm NO_3^-) showed only 52-64 percent recovery when measured by the phenoldisulfonic acid method. Analysis of these same samples with prepackaged reagents (Hach Chemical Company) showed 95-106 percent recovery. It thus appears that some consistuent (probably chloride) in the Hanford groundwaters is interfering with the phenoldisulfonic acid method.

The interference problem and instances of sporadic, unexplained changes in nitrate concentrations over time for some wells precipitated this study to investigate alternate analytical procedures for nitrate analyses.

The nitrate concentrations are reported as ppm NO_3-N. To convert to ppm NO_3, multiply by the factor 4.43.

LITERATURE REVIEW OF ANALYTICAL PROCEDURES FOR NITRATE ANALYSIS

Phenoldisulfonic Acid Colorimetric Procedures

Briefly, the method presently used for Hanford groundwaters is to take an aliquot of well water, add one drop saturated sodium bicarbonate, and evaporate to dryness very carefully.

Next, two ml of phenoldisulfonic acid reagent is added to the dried sample. After ten minutes, ten ml of distilled water are added followed by concentrated ammonium hydroxide dropwise until a stable yellow color develops. If the solution is not clear, suspended particulates are filtered before the sample is transferred to a 100 ml volumetric flask and brought to volume.

Standard nitrate samples in distilled water are treated accordingly and absorbance at 410 mμ vs distilled water are made. The working range by this procedure is 0.1-2.3 ppm NO_3-N for a 100 ml sample aliquot.

This procedure is very sensitive to negative interferences caused by chlorides[2] and is being considered for deletion as a Standard Method.[3]

Brucine Colorimetric Method

The brucine method is based upon the reaction of nitrate ion with brucine sulfate in a 13N H_2SO_4 solution at a temperature of 100°C. The resulting yellow color is measured at 410 mμ. The effects of dissolved salts are eliminated by addition of sodium chloride to all blanks, standards and samples. Chlorine interferences are eliminated by addition of orthotolidine. Fe^{+2}, Fe^{+3}, and Mn^{+4} give slight positive interferences when present at concentrations greater than one ppm. All strong oxidizing and reducing agents interfere. The largest drawbacks to the brucine method are the necessity of absolute temperature control during the color development period and the non-Beer's law standard curve obtained.[4] Holty and Potworsk[5] presented data on groundwaters where the standard curve doubled back on itself such that 2.5, 102 and 168 ppm nitrate standards had the same absorbance. Aside from these drawbacks the brucine method shows comparable precision and sensitivity as the phenoldisulfonic acid method. The typical working range is 0.1-2.0 ppm NO_3-N.

Other Colorimetric Methods

Szekely[6] and Winters[7] report a spectrophotometric procedure for nitrates which works for samples with nitrate concentrations above 7 ppm NO_3-N. The color reagent used is p-diaminodiphenylsulfone (4,4' diaminodiphenylsulfone). The reagent reacts with nitrate to form a yellow dye which is stable in acid with peak absorbance at 410 mμ. Halide interferences are removed by precipitation with Ag_2SO_4 and filtering. Fe^{+2} causes a negative interference and can be removed by addition of ammonium persulfate. Winters has successfully used the reagent to determine nitrate in synthetic nuclear wastes with many potential interferents. The working range for NO_3^- by Szekely's procedure is 7-70 ppm NO_3-N but he reports the addition of diphenylamine to the p-diaminodiphenylsulfone increases the sensitivity such that 0.06-.4 ppm NO_3-N becomes the

working curve. The method is slightly temperature dependent, but more sensitive than and not affected by nitrite as are the standard colorimetric procedures described.

NO_3^- Specific Ion Electrode

Nitrate measurement by specific ion electrode is mechanically a very simple procedure that is similar to a pH measurement. If the electrode method could be shown to be sensitive, accurate and free of interferences, it unquestionably would be the preferred procedure. The specific ion-electrode measures activity rather than concentration and is influenced by other anions such as nitrate, bicarbonate, organic acid anions, chloride and carbonates. Within the last eight years numerous researchers have investigated the applicability of the specific ion electrode to nitrate measurement in groundwaters and soil extracts. Through the use of buffer solutions much of the ionic strength and other anion dependence can be controlled.

Bremner, et al.,[8] measured soil extracts by several techniques including the electrode and found good agreement for nitrate concentrations above 2 ppm NO_3-N for nonsaline soils.

Mahendrappa[9] studied the electrode extensively and found the electrode acceptable on soil extracts at concentrations of 2 ppm NO_3-N or above. Sulfamic acid treatment removed nitrite interferences. The electrode response was observed to vary gradually such that the millivolt reading for a standard was displaced 20-30 mv over a 3 to 4 week period but the slope of the electrode maintained the same value. Thus, one or two standards should be analyzed on a frequency of at least 30 minutes to compensate for the drift.

Oien and Selmer-Olsen[10] also concluded that the lower limit of electrode use was 2 ppm NO_3-N for soil extracts. Milham, et al.,[11] used a buffer solution to reduce ionic strength, nitrite and other anion effects on the electrode and found a working range of 2 ppm to 1000 ppm NO_3-N in soil extracts and groundwaters. Electrode response was quite rapid (<10 seconds) at concentrations above 20 ppm NO_3-N and 60 seconds at the 2 ppm NO_3-N level. Precision was ± three percent and recovery of spiked nitrate was >98 percent.

Puryear[12] has compared determinations of nitrate on Hanford well samples by specific ion electrode and the phenoldisulfonic acid methods. In the range 5-20 ppm NO_3-N, the agreement was good. More comparisons are needed at concentrations lower than 5 ppm NO_3-N.

Copper-Cadmium Reduction Procedures

This method reduces nitrate to nitrite and the total nitrite (originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored compound. The resultant color is measured spectrophotometrically at 540 nm between 10-120 minutes of color development. There are few known interferences and the procedure is very sensitive. Nitrate is reduced to nitrite by passing the sample through a column containing cadmium filings or powder. An ammonium chloride-EDTA carrier solution is used to minimize metallic and chloride effects.

Galcs and Booth[13] report a working range of 0.01 to 1.0 ppm NO_3-N. Precision on industrial wastes, sewage, river, ocean and tap water was 1-10 percent. Recovery of nitrate spikes in these waters was 94-102 percent.

A further procedure incorporating the copper-cadmium reduction method with direct analysis of the nitrite by the new NO_x specific ion electrode[14] was suggested by one of the authors (COH). No published works on this method were found so the procedure was explored further during this study.

The experimental procedures which appear promising for nitrate determinations include the nitrate specific ion electrode, the copper-cadmium reduction and subsequent analysis by colorimetric or NO_x specific ion electrode and the diphenylamine and p-diaminodiphenylsulfone colorimetric technique.

To date the nitrate electrode, and both cadmium reduction procedures have been explored. Work on the last colorimetric technique has been postponed until arrival of one of the color reagents.

EXPERIMENTAL METHODS

Stock Solutions:

Nitrate (1000 ppm N) = 7.218g of oven dried KNO_3 (reagent grade) was dissolved in de-ionized distilled water. 2 ml chloroform was added and the solution brought to 1000 ml volume.

Nitrite (1000 ppm N) = 4.9285g of oven dry $NaNO_2$ (reagent grade) was dissolved in de-ionized distilled water. 2 ml chloroform was added and the solution brought to 1000 ml volume.

Equipment:

Orion Nitrate Ion Electrode Model 92-07

Orion Nitrous Oxide Electrode Model 95-46

Orion Reference Electrode Model 90-01

Brinkman Model E436 Recording Potentiograph

Magnetic Stirrer

Bausch and Lomb Spectronic 20 Spectrophometer

Beckman DK2A Spectrophometer

Other Solutions:

Buffer Solution for Electrode $(NO_3)^{11}$

$Al_2(SO_4)_3$	0.01 M
Ag_2SO_4	0.01 M
H_3BO_3	0.02 M
Sulfamic Acid	0.02 M

pH to 3.0 with sulfuric acid (.1 M).

Acid Buffer Solution for NO_x Electrode

190g	Na_2SO_4
53 ml	H_2SO_4 (Conc.)

to 1000 mls with water
pH of 1:10 dilution should be 1.2.

Buffer Solution for Cd Reduction - Colorimetric Procedure

NH_4Cl	0.15 M
EDTA	1 g/l disodium ethylene diamine tatracetate

pH to 8.5 with NH_4OH (Conc.).

Color Reagent for Cd Reduction - Colorimetric Procedure

10g	Sulfanilamide
1g	N(1-napthyl)-ethylene-diamine dihydrochloride
100mls	Phosphoric acid (Conc.)

to final volume 1000 ml.

Copper-Cadmium Column

The cadmium powder is cleaned with dilute (6N) HCl and copperized with 2 percent copper sulfate solution.

The dimensions of the cadmium column are 1.7 cm diameter by 5 cm length.

RESULTS AND DISCUSSIONS

Nitrate Electrode

The response of the nitrate electrode coupled to a single junction reference electrode filled with 4 M KCl saturated with AgCl was determined for nitrate standards in de-ionized

distilled water. Readings were taken as soon as the electrode reached equilibrium or after ten minutes on low nitrate solutions. All samples were stirred slowly. The electrode response was Nernstian over the range 10-1000 ppm NO_3-N and reproducible over the range 1-1000 ppm NO_3-N. As seen in Figure 1, the slope falls off between 1 and 10 ppm NO_3-N but if several standards are utilized, measurements to 1 ppm NO_3-N (4.5 ppm NO_3) are possible. A concentration of 0.1 ppm NO_3-N is not measurable as the electrode drifts erractically.

Well samples may exhibit variable ionic strengths and variable concentrations of potential interferents. Therefore, the buffer solution and reference electrode solution proposed by Milham[11] were used. Ten ml standard nitrate samples were mixed with 10 ml of the electrode buffer solution and the sample stirred during measurement. The single junction reference electrode was filled with saturated potassium sulfate.

Again, the electrode shows a Nernstian response between 10-1000 ppm NO_3-N and a working range of 1-1000 ppm NO_3-N as shown in Figure 2. The slope between 1 and 10 ppm NO_3-N is 37.5 mv or 63 percent of the correct response where as in Figure 1 the slope is only 22 mv or 37 percent of the correct response. Therefore, at the low end the use of the buffer solution and different reference electrode filling solution improves the electrodes response.

The effects of well water and high chloride contents (30 ppm Cl^-) were next investigated. Standard nitrate samples were made up in a very low level NO_3^- well water instead of distilled water and compared with distilled water standards. Further, spiked well water samples with 30 ppm added Cl^- were measured vs distilled water standards.

Again, the buffer solution and K_2SO_4 reference electrode were utilized. Results are shown in Figure 3. There was no difference between measurements of distilled water standards or well water standards. Further the addition of 30 ppm Cl does not affect the NO_3 electrode's response. The displacement in the curves is caused by electrode drift in the intervening four hour time between analyses.

A well sample of known very low nitrate concentration (<.05 ppm NO_3-N) was spiked with nitrate to correspond to 6, 12, and 18 ppm NO_3-N. Results on three separate determinations using the nitrate electrode with the described buffer are shown in Table 1. The $\pm$ error values represent one standard deviation.

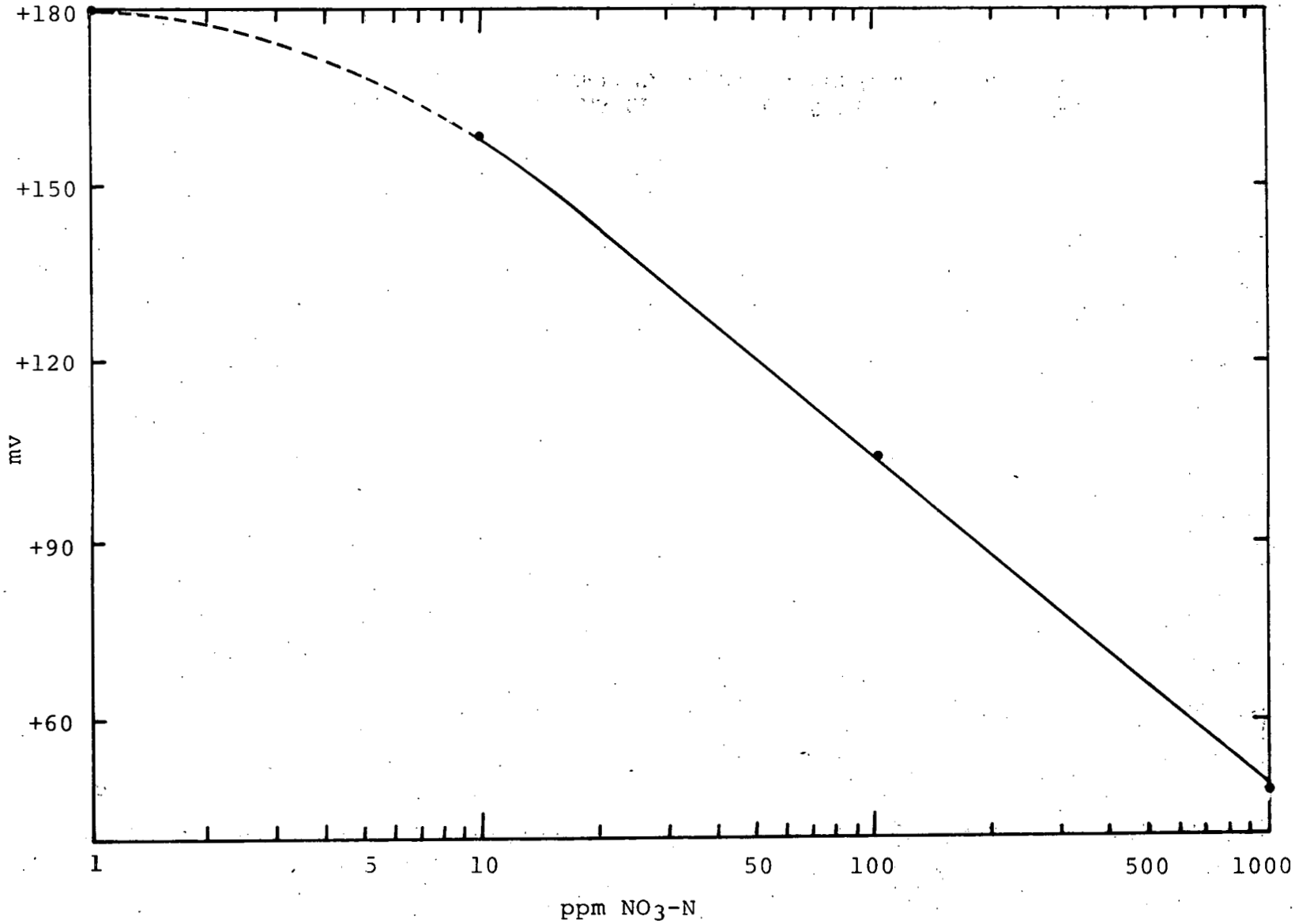

FIGURE 1. NO_3^- ELECTRODE USING 4M KCl IN REFERENCE ELECTRODE AND DISTILLED WATER NO_3^- STANDARDS

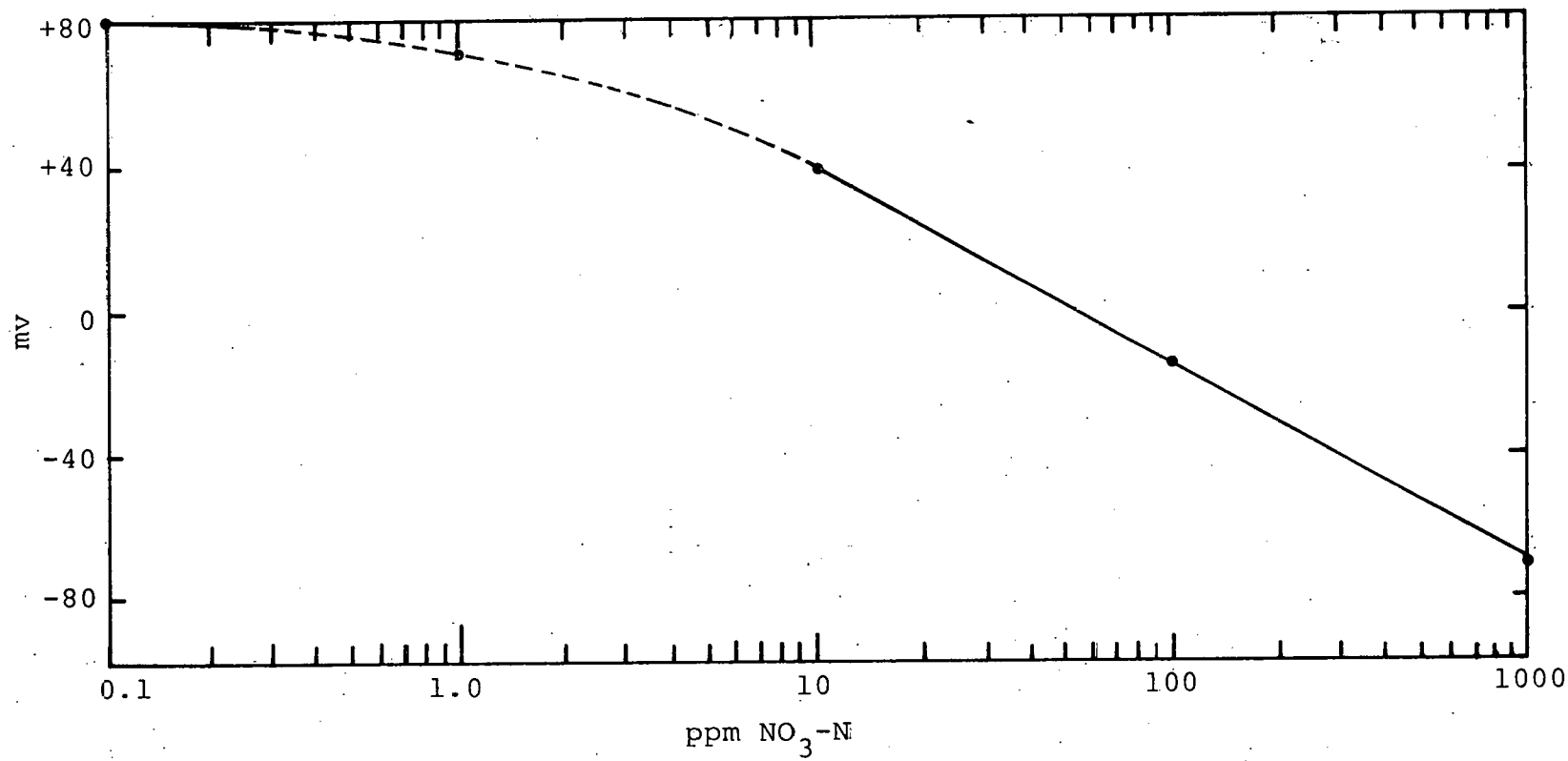

FIGURE 2. NO_3^- ELECTRODE RESPONSE USING 10 ML BUFFER +10 ML SAMPLE AND SATURATED K_2SO_4 IN REFERENCE ELECTRODE

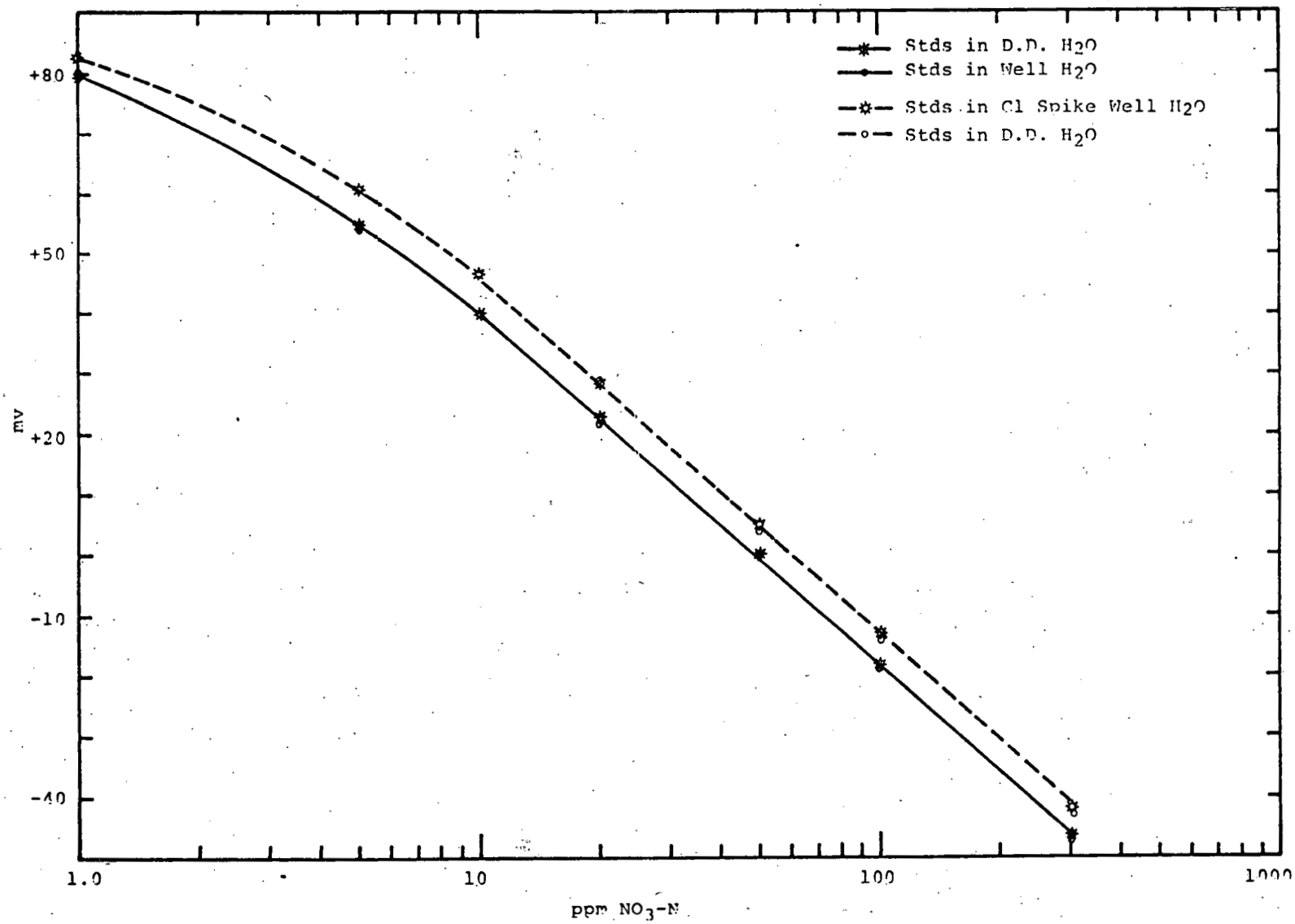

FIGURE 3. NO_3^- ELECTRODE RESPONSE IN VARIOUS SOLUTIONS

TABLE 1

NO_3^- RECOVERY FROM WELL WATER

Sample	ppm NO_3-N Added	ppm NO_3-N (Meas.)	Percent Recovery
1	0	<1	
2	6	5.5 ± 0.5	92%
3	12	10.8 ± 1.0	90%
4	18	18 ± 1.1	100%

A well sample from a contaminated well which had been sampled four months previously, filtered through 0.45 μ filter and stored in the dark at 4°C was also measured. Six vertical water layers had been sampled and analyzed by a simplified cadmium reduction method with prepackaged reagents from the Hach Chemical Company, Ames, Iowa. The comparison of the NO_3^- electrode with the Hach kit results from four months previous are shown in Table 2. The precision for the electrode represents one standard deviation.

TABLE 2

COMPARISON OF ELECTRODE AND COLORIMETRIC RESULTS

Sample	Electrode NO_3-N ppm	Hach Kit NO_3-N ppm	Percent Difference (E-HK)/Ave
1	17.0 ± 1.0	15.1	+12%
2	3.6 ± .3	3.3	+ 7%
3	5.8 ± .4	4.8	+19%
4	15.8 ± .5	15.1	+ 5%
5	7.0 ± .5	6.6	+ 6%
6	4.2 ± .2	4.3	- 2%

The results show that both methods give values in close agreement even after the four month storage. This indicates biological consumption of nitrates in the well water was minimal.

It thus appears that the NO_3^- specific ion electrode in conjunction with the use of a buffer solution is capable of measuring NO_3^- concentrations as low as 1 ppm NO_3-N (4.4 ppm NO_3^-) precisely and accurately. The precision (1 standard deviation) in almost all cases shown in Tables 1 and 2 was better than ±10 percent. The recovery of known spikes was 90-100 percent.

The method is quick. The total time for dilution with buffer solution and electrode response is less than five minutes per sample. The method would be a good screening device to determine low nitrate well samples from higher nitrate samples. The dynamic range of the electrode response of 1-1000 ppm NO_3-N is excellent.

Copper-Cadmium Reduction Procedure

The basic procedure utilized during this study originates as the EPA recommended procedure[15] except cadmium powder <100 mesh was substituted for the granulated form recommended. Because the powder causes a slower flow rate, the design was modified and is shown in Figure 4.

Before experiments were started using the column, the colorimetric part of the procedure was checked using standard solutions of $NaNO_2$ in distilled water. 50 ml standards were used and the standard curve shown in Figure 5 was obtained. The standard curve is not linear but is quite stable and readily reproduced. The use of the ammonium chloride-EDTA buffer solution in a ratio of 3:1 did not change the standard NO_2-N curve. After establishing the adequacy of the colorimetric portion of the procedure, NO_3^- reductions through the column were performed. Initial studies on the flow rate of solution through the column showed a flow rate of 16 mls/min gave the best reproducibility. Flow rates of 8 mls/min and below were erratic. Flow rates above 16 mls/min could not be checked as this was the maximum obtainable through the powdered cadmium during experimentation.

Nitrate and nitrite standards run through the column were compared with nitrite standards run directly. The nitrate and nitrite standards run through the cadmium column show good agreement at the low concentrations and deviations near 10 percent at the high concentrations. Both standards show an apparent loss of nitrite-N upon percolation through the column compared with NO_2-N standards run directly as shown in Figure 6. All the samples were 25 mls standard plus 75 mls NH_4Cl-EDTA buffer solution. The concentrations are based on the 25 ml sample size.

The low nitrate well water and three spikes shown in Table 1 were analyzed by the cadmium reduction method and compared to the electrode data. Results including precision of the data are shown in Table 3.

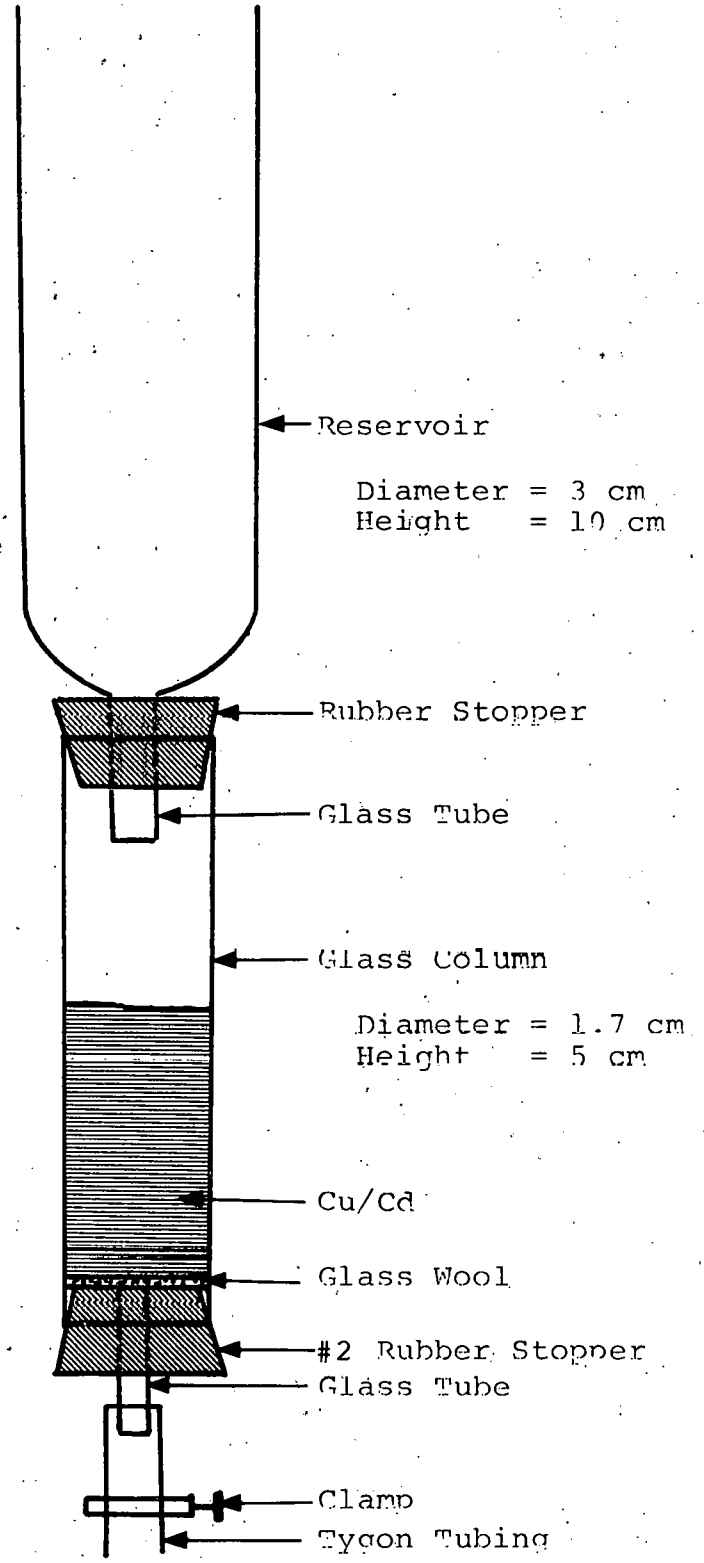

FIGURE 4. PHYSICAL DIMENSIONS OF Cu-Cd REDUCTION COLUMN

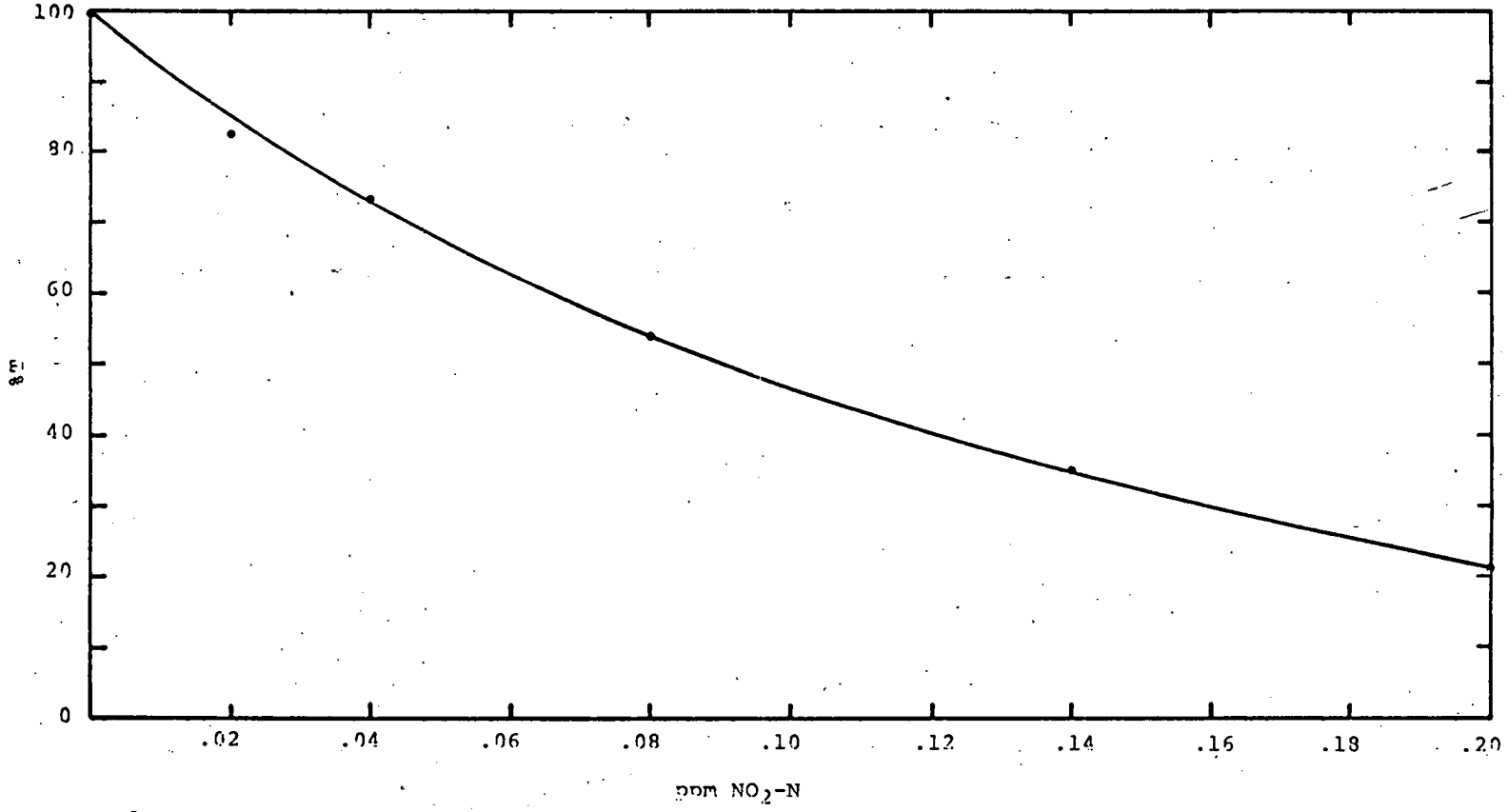

FIGURE 5. STANDARD CURVE FOR NITRITE ANALYZED DIRECTLY AT 540 nm

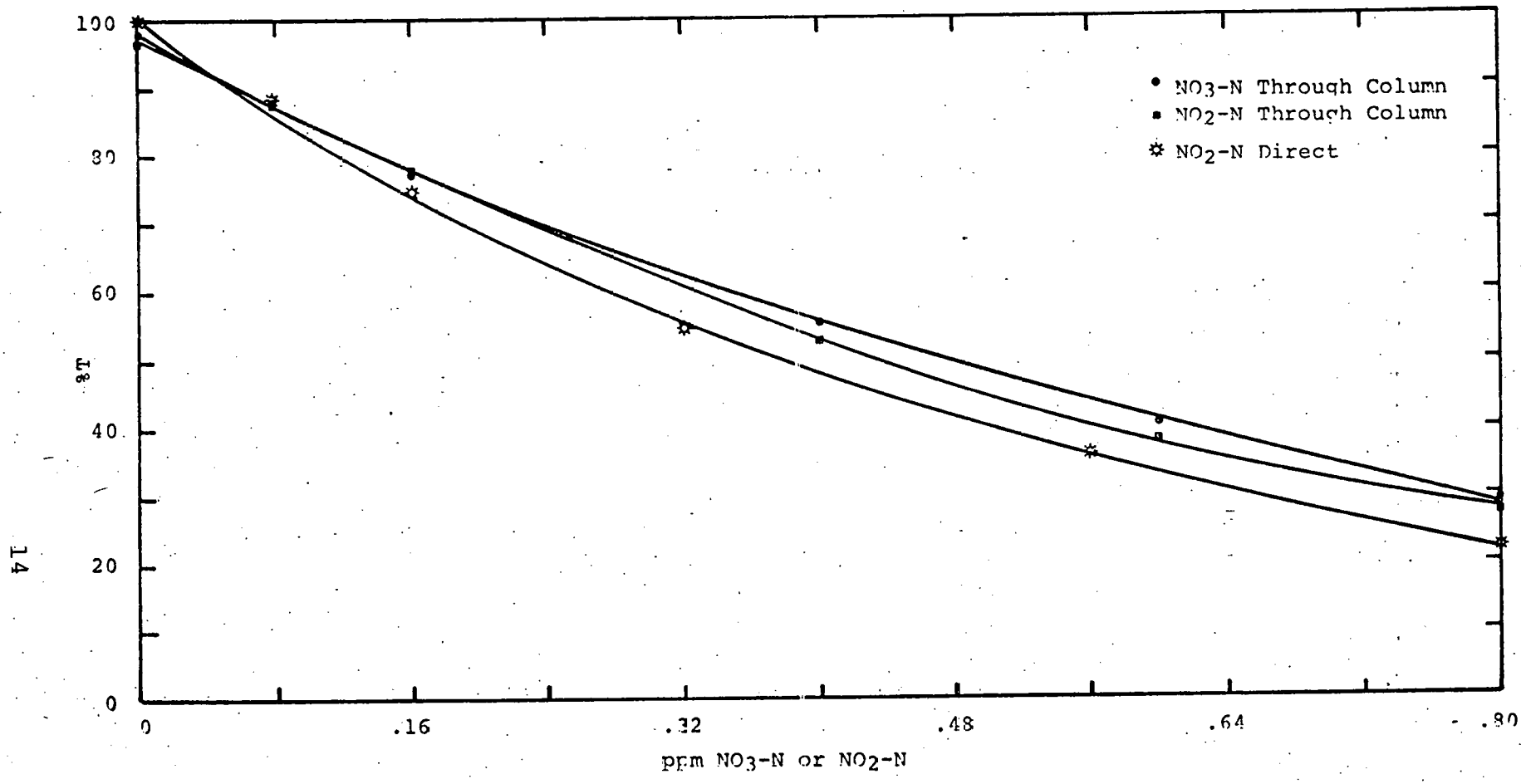

FIGURE 6. NO_3-N AND NO_2-N STANDARD CURVES

TABLE 3

COMPARISON OF CADMIUM REDUCTION AND ELECTRODE METHODS

Sample	NO_3^- Spike ppm-N	REPS	NO_3^- by Cd Reduction ppm-N	Percent Recovery	NO_3^- by Electrode ppm-N	Percent Recovery
1	0	5	0.016 ± .002	-	<1	-
2	6	5	6.84 ± .92	114%	5.5	92%
3	12	5	13.40 ± .10	112%	10.8	90%
4	18	5	20.92 ± .59	116%	18	100%

The cadmium reduction method appears to be biased about 15 percent high. The standard curve used to determine the nitrate concentrations of these samples was run the day before and thus may explain part of the positive bias. Because the standard curve is non-linear and has a small slope, the nitrate concentration is quite sensitive to a few percent change in transmission. Precision for the two lower nitrate concentrations defined by the standard deviation is 13 percent. Precision for the two higher nitrate concentrations is 1-3 percent.

A second well water with 18 ppm NO_3-N was diluted at three levels with deionized distilled water to yield samples of .72 ppm, .29 ppm, and .04 ppm NO_3-N. These samples and distilled water nitrate standards were run at the same time. The sequence of passing the samples through the cadmium column did not appear to effect the results. Thus, a low nitrate sample run after a high nitrate sample does not give erroneously high values therefore the memory effects of the cadmium column are not significant. Results on triplicate analyses of the three diluted well samples are found in Table 4.

TABLE 4

COMPARISON OF MEASURED NO_3^- LEVELS TO CALCULATED VALUES

Calculated NO_3-N ppm	Measured NO_3-N ppm	σ	σ/X (%)
0.72	0.76	±0.06	7%
0.29	0.27	±0.02	9%
0.04	0.04	±0.005	13%

For these samples the cadmium reduction method appears to accurately determine the nitrate levels in the well samples. Precision at the very low value was 13 percent and increased as the higher nitrate samples were analyzed.

To investigate the capacity of the cadmium column to reduce extremely high nitrate bearing samples and to evaluate column memory effects, several high level nitrate in distilled water samples were run through the column followed by deionized distilled water blanks. The samples were then diluted sufficiently to fall on the standard curve shown in Figure 7. The results are presented in Table 5.

TABLE 5

RESULTS OF HIGH LEVEL NITRATE EFFECTS ON COLUMN

Calculated ppm NO_3-N	Measured ppm NO_3-N	Mean	σ	Recovery %
18	17.5			
	17.2			
	17.2			
	17.2			
	17.5			
	17.5			
	17.3	17.3	0.15	96
0	0.03			
100	105.0			
	104.5			
	104.5			
	101.0			
	104.0	104.0	1.6	104
0	0.10			
0	0.00			
500	550.0			
	615.0			
	560.0			
	560.0	571.0	30.0	114
0	0.26			
	0.01			
1000	1170.0			
	1190.0			
	1190.0			
	1150.0			
	1170.0			
	1190.0			
	1190.0			
	1170.0	1177.0	15.0	118
0	>.80			
	.06			
	.072			
	.008			

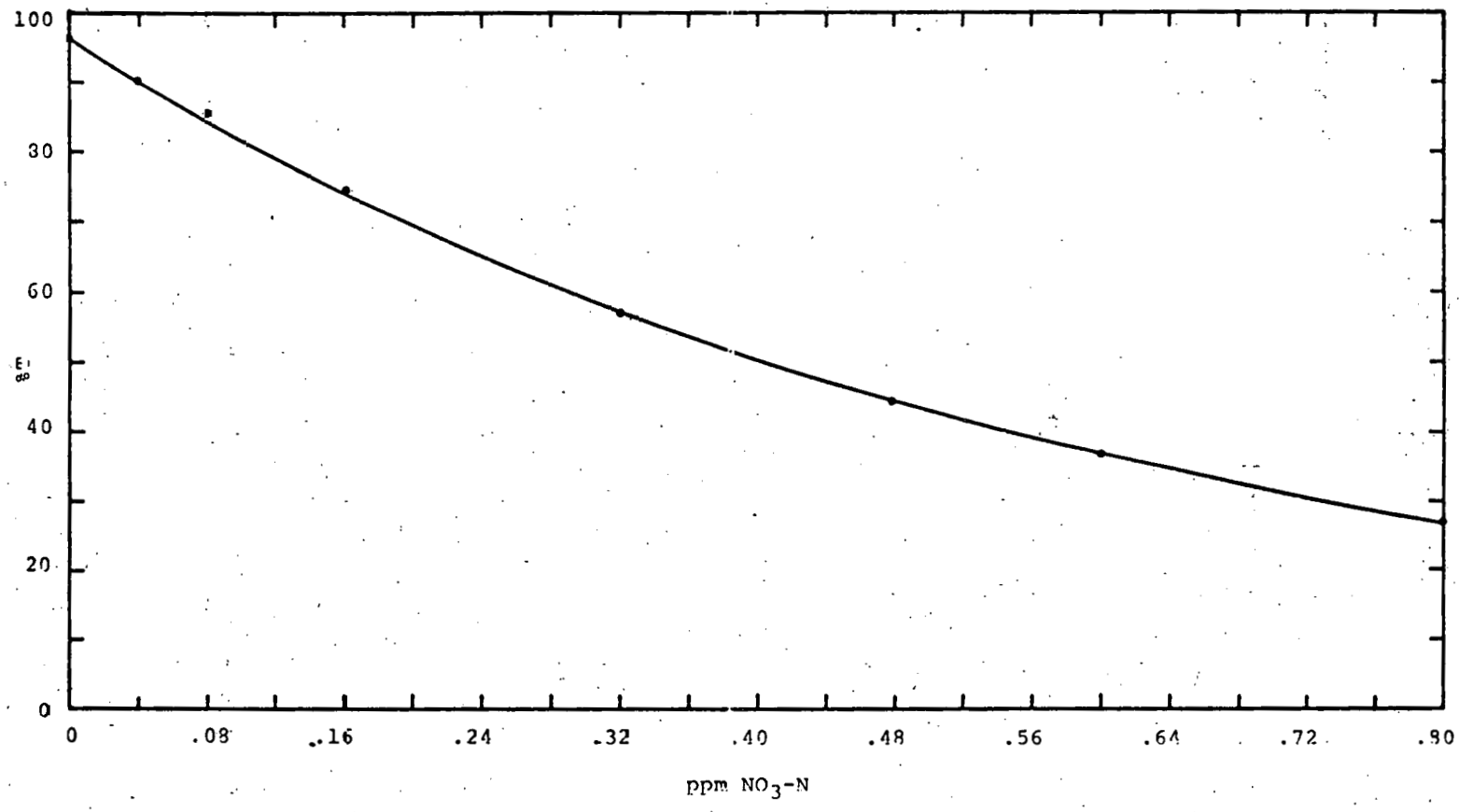

FIGURE 7. Cd REDUCTION COLORIMETRIC NO_3-N STANDARD CURVE

Table 5 shows that the cadmium column has the capacity to reduce nitrate bearing waters as high as 1000 ppm NO_3-N. The apparent positive bias at concentrations above 500 ppm NO_3-N may reflect the large dilution which must be made to the column effluent before color development. For the 500 and 1000 ppm NO_3-N samples, a 1250 and 2500 dilution respectively must be made. Each sample consisted of a 100 ml sample through the column with the first 50 ml discarded.

The blank samples run after each batch of high nitrate samples shows that except for the highest case, a proper blank value is obtained on the second 100 ml sample. Even the first blank run after each batch of high nitrate samples is not grossly contaminated by column memory effects. Precision on these high nitrate level samples is good.

As an alternative to the colorimetric determination of the nitrite in the cadmium column effluent, the direct analysis by NO_x specific ion electrode was evaluated. The nitrate water sample (25 ml) was mixed with the chloride-EDTA buffer (75 ml) and run through the cadmium column. The final 50 ml eluant was mixed with 5 mls NO_x acid buffer and directly read with the electrode. Figure 8 shows a standard curve for nitrate in deionized distilled water. With a solution containing 1 ppm NO_3-N, the NO_x electrode performance deviates from the Nernstian response. Because the NO_3^- electrode can adequately determine nitrate concentrations directly down to 1 ppm NO_3-N, the use of the NO_x electrode does not appear to offer any advantages. For low level nitrate samples (<1 ppm NO_3-N), the cadmium reduction method followed by colorimetric analysis appears to be the best method for Hanford well samples.

The cadmium reduction procedure measures both nitrate and nitrite in the well waters. The nitrite concentrations in the Hanford well samples should be minimal, therefore, no correction on the observed nitrate value is made. Nitrite analyses on ten Hanford well samples were performed by the U.S. Geological Survey, Salt Lake City, Utah in 1975.[16] Eight well samples had less than .005 ppm NO_2-N and two wells had concnetrations of .01 ppm NO_2-N. Thus the procedure of neglecting nitrite corrections should have very little effect on the nitrate concentrations reported for uncontaminated wells.

For convenience, Appendix A contains detailed notes on the procedures followed to analyze nitrates in well waters.

CONCLUSIONS

- Based on a literature review and subsequent laboratory studies, two methods appear satisfactory for determining nitrate concentrations in Hanford well waters: the nitrate specific ion electrode and the cadmium reduction-colorimetric method.

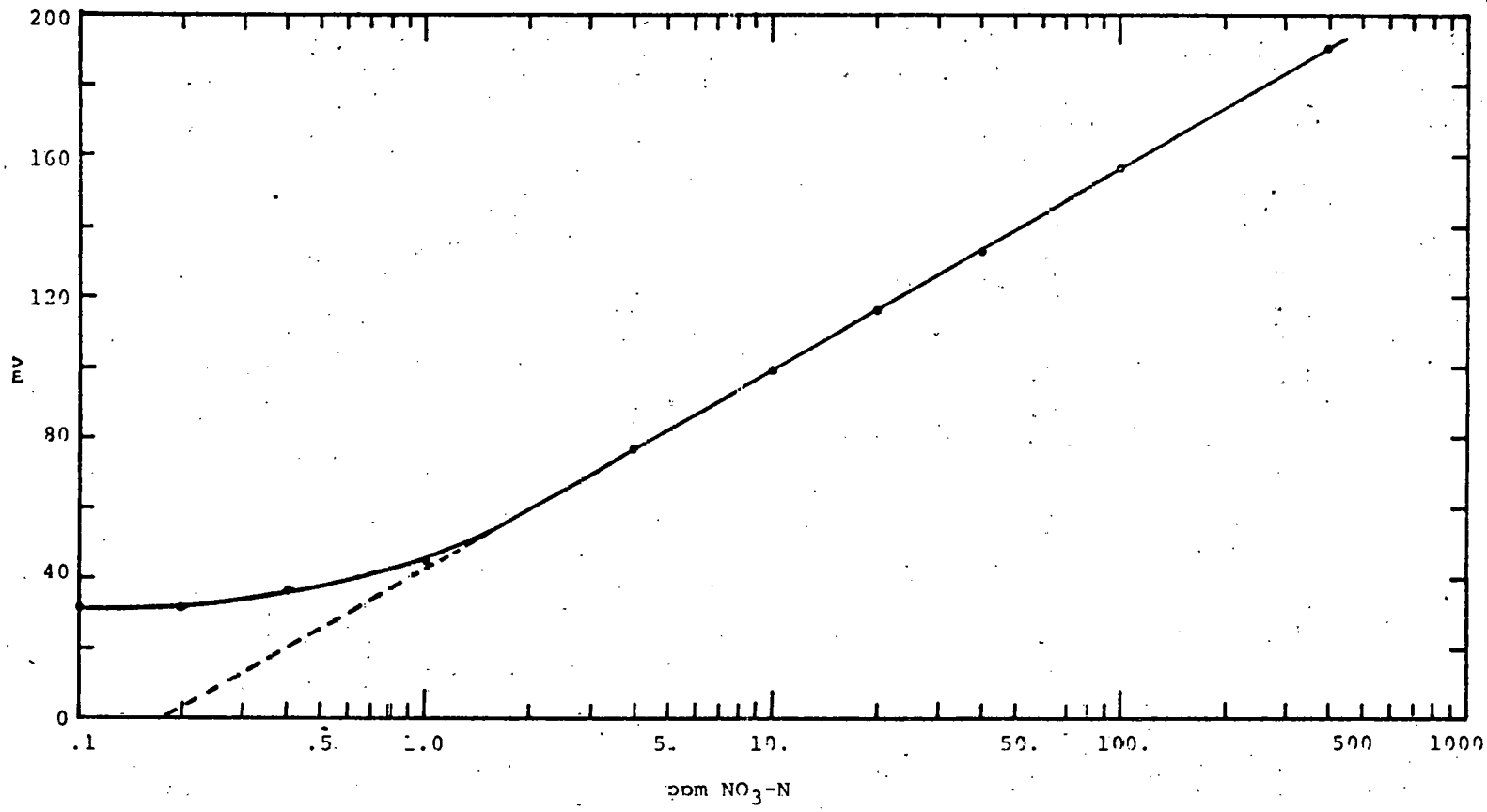

FIGURE 8. NO_x ELECTRODE RESPONSE TO Cd COLUMN REDUCED NITRATE

- The working range of the nitrate ion specific electrode utilizing a buffer solution to minimize ionic strength differences and interferences is 1-1000 ppm NO_3-N (4.4-4400 ppm NO_3^-).

- Accuracy as defined by recovery experiments and precision (± one standard deviation) appear to be 90-100 percent and ±5 to 10 percent respectively for the electrode.

- The electrode shows a tendency to drift such that standard samples must be monitored about once every half to one hour. The standard curve between 1-10 ppm NO_3-N is not Nernstian, but is reproducible.

- The cadmium reduction-colorimetric procedure described can be used on water samples with concentrations between 0-.80 ppm NO_3-N (0-3.2 ppm NO_3^-) with a detection limit of 0.02 ppm NO_3-N (0.1 ppm NO_3^-).

- The standard curve is not linear and for the higher portion of the standard curve the low slope makes the measured concentration quite sensitive to small shifts in the standard curve. Standard curves should be generated with each batch of samples.

- Precision of the colorimetric procedure at the low end of the working range is approximately 13 percent, and, at the high end, between 5-10 percent. Accuracy as defined by recovery was 93-116 percent for spiked water samples between 0-100 ppm NO_3-N.

- The NO_x electrode measures nitrite directly. After cadmium reduction, nitrate water samples as low as 1 ppm NO_3-N may be determined by this method. Because the nitrate specific ion electrode can directly measure the nitrate concentration down to 1 ppm NO_3-N, the use of the NO_x electrode does not appear to offer advantages.

- Preliminary results on aging filtered well waters at 4°C in the dark show no losses of nitrate after four months. Further studies are planned to verify this.

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APPENDIX A

PROPOSED PROCEDURES FOR NITRATE ANALYSIS BY SPECIFIC ION ELECTRODE AND CADMIUM-REDUCTION COLORIMETRIC METHODS

NITRATE ANALYSIS BY SPECIFIC ION ELECTRODE (NO_3^-)

Equipment Requirements:

a. NO_3^- specific ion electrode

b. Reference electrode single junction filled with saturated potassium sulfate.

c. Expanding scale millivolt meter capable of ±0.5 mv readings. A typical research pH meter is adequate but a recording millivolt meter is very convenient.

Solutions:

a. Standard NO_3^- solutions.

Stock 1000 ppm NO_3-N. 7.218g KNO_3 (oven dried) in deionized water diluted to 1000 ml. Preserve with 2 mls chloroform per liter and the solution is stable for at least six months.

b. Standard curve solutions.

1 ppm NO_3-N	= .20 ml stock → 200 mls deionized water
2.5 ppm	= .50 ml stock → 200
5 ppm	= 1.00 ml stock → 200
7.5 ppm	= 1.50 ml stock → 200
10 ppm	= 2.00 ml stock → 200
25 ppm	= 5.00 ml stock → 200
50 ppm	= 10.00 ml stock → 200
100 ppm	= 20.00 ml stock → 200

optional for Hanford groundwaters:

250 ppm	= 50.00 ml stock → 200 ml
500 ppm	= 100.00 ml stock → 200 ml

c. Electrode buffer solution.

.01 M	Aluminum Sulfate	$Al_2(SO_4)\cdot 18H_2O$	6.66 g/l
.01 M	Silver Sulfate	Ag_2SO_4	3.12 g/l
.02 M	Boric Acid	H_3BO_3	1.24 g/l
.02 M	Sulfamic Acid (Amino Sulfonic acid)	NH_3SO_3H	

pH to 3 with .1 M H_2SO_4 (3 mls conc. H_2SO_4/l)

Procedure

1. Take 25 ml of the well water sample or nitrate standard and mix it with 25 ml of the buffer solution.

2. Place the mixture on the stirrer, insert the electrodes and stir at a low speed avoiding turbulence and bubble formation.

3. Record the millivolt reading when it becomes constant. High concentration nitrate samples should take less than one minute to attain equilibrium. Low nitrate samples at the 1 ppm NO_3-N detection limit should take 5-10 minutes.

4. The standard curve is generated by using semi-logarithmic plotting with the millivolts on the linoar ordinate and the nitrate concentration of the logarithmic abscissa.

5. For the most accurate results unknown samples should be bracketed by the closest standard solutions above and below the sample value. By interpolation, the unknown value can be obtained if one is on the linear portion of the standard curve. Points on the standard curve should be checked for drift about every half hour to hour.

6. The electrode is temperature sensitive so all standards and samples should be at the same temperature.

7. Electrode maintenance as suggested by the manu facturer should bc followed.

NITRATE ANALYSIS BY THE CADMIUM REDUCTION METHOD

Equipment Requirements:

a. Reduction column (glass column filled with copperized cadmium 1.7 cm dia by 5 cm height) with a reservoir capable of holding 100 mls (see Figure 4). Granulated cadmium or coarse cadmium powder is cleaned with 6N HCl (50 percent HCl, 50 percent water) by shaking overnight. The cadmium is washed copiously with distilled water. Cadmium is then treated with portions of 2 percent copper sulfate solution (20g $CuSO_4 \cdot 5H_2O$/1) in ratios of 1g Cd/4 mls copper sulfate solution for five minutes or until the blue color partially fades, decant and repeat with fresh copper sulfate until a brown colloidal precipitate forms.

Wash the copper-cadmium with distilled water at least ten times to remove all the precipitated copper. After packing the column with copper-cadmium, entrapped air is removed by saturation with distilled water. The column is treated with 500 ml of chloride-EDTA solution (7.8 g/l NH_4Cl and 1.02 g/l disodium ethylenediamine tetracetate adjusted to pH 8.5 with concentrated ammonium hydroxide) at a flow rate of 7-10 ml/min.

The column is then activated with 300 mls of nitrate-chloride-EDTA (75 ml of 1 mg/l NO_3-N and 225 ml chloride-EDTA) at a flow rate of 16 ml/min. The chloride-EDTA solution is 13 g/l ammonium chloride, 1.7 g disodium ethylenediamine tetracetate, pH to 8.5 with concentrated ammonium hydroxide.

b. Spectrophotometer (540 nm wavelength is used)

Solutions:

a. Standard NO_3^- solutions.

Stock 1000 ppm NO_3-N 7.218g KNO_3 (oven dried) in deionized water diluted to 100 ml. Preserve with 2 mls chloroform per liter and the solution is stable for at least six months.

b. Standard curve solutions.

Make a 20 ppm NO_3-N working standard (2 ml stock nitrate stock to final volume of 100 ml).

0.00 = 0 mls 20 ppm NO_3-N standard to 100 mls
0.05 = .25 mls 20 ppm NO_3-N standard to 100 mls
0.10 = .50 mls 20 ppm NO_3-N standard to 100 mls
0.20 = 1.00 mls 20 ppm NO_3-N standard to 100 mls
0.30 = 1.50 mls 20 ppm NO_3-N standard to 100 mls
0.40 = 2.00 mls 20 ppm NO_3-N standard to 100 mls
0.50 = 2.50 mls 20 ppm NO_3-N standard to 100 mls
0.60 = 3.00 mls 20 ppm NO_3-N standard to 100 mls
0.80 = 4.00 mls 20 ppm NO_3-N standard to 100 mls

c. Chloride-EDTA solution;

13 g/l NH_4Cl
1.7 g/l Na-EDTA
pH 8.5 with conc. NH_4OH

d. Color reagent:

10 g sulfanilamide
1 g N(1-naphthyl)-ethylene-diamine-dihydrochloride
100 ml conc. phosphoric acid
dilute to 1 liter

Procedure

1. Filter the nitrate water sample through 0.45μ membrane.

2. If the pH of the sample is below 5 or above 9, ajust between 5 and 9 with conc. HCl or conc. NH_4OH.

3. To 25.0 ml of sample or a dilute aliquot, add 75 ml of ammonium chloride-EDTA solution.

4. Pour the sample onto the column and collect sample at a rate of 7-16 ml/min. For this experiment 16 ml/min is deemed best.

5. Discard the first 25 ml, collect the rest of the sample.

6. Add 2.0 ml of the color reagent to 50.0 ml of sample. Allow 10 minutes for color development. Within two hours measure the percent transmission or absorbance at 540 nm.

7. If the concentration of the sample exceeds the range of the standard curve, the remainder of the reduced sample may be used to make an appropriate dilution and re-run of the color development. Standards in distilled water are treated in the same fashion (Steps 2-6).

8. Periodically at least one nitrite standard should be compared to a reduced nitrate standard at the same concentration to verify the efficiency of the reduction column.

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