Field Evaluation of Selected Highway Construction Temporary Sediment Controls for Storm Water Pollution Prevention Plans

PB98-139116

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Project Number 0-1425

"Evaluation of the Impacts, Performance, and Costs of Storm Water Pollution Prevention Plans as Applied to Highway Construction Activities"

Research performed in cooperation with the Texas Department of Transportation and the U.S. Department of Transportation, Federal Highway Administration.

Technical Report Documentation Page

1. Report No. 1425-2	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle FIELD EVALUATION OF SELECTED HIGHWAY CONSTRUCTION TEMPORARY SEDIMENT CONTROLS FOR STORM POLLUTION PREVENTION	5. Report Date May, 1997 6. Performing Organization Code
7. Author(s) Joseph P. Muscara, Theodore G. Cleveland, Keh-Han Wang	8. Performing Organization Report No.
9. Performing Organization Name and Address Department of Civil & Environmental Engr University of Houston Houston, Texas 77204-4791	10. Work Unit No. (TRAIS) 11. Contract or Grant No. Project 0-1425
12. Sponsoring Agency Name and Address Texas Department of Transportation Research and Technology Transfer Office P.O. Box 5080 Austin, Texas 78763-5080	13. Type of Report and Period Covered Research Report (9/95 - 5/97) 14. Sponsoring Agency Code

15. Supplementary Notes

Project conducted in cooperation with Federal Highway Administration

16. Abstract

A highway construction project in Houston was monitored from pre-construction through the first phase of construction to determine the effectiveness of temporary sediment controls for pollutant control. Nearby receiving waters were also monitored to determine the type and quantity of pollutants that left the site. Nutrients, metals, and general water quality parameters were monitored throughout the investigation period. The receiving-water bodies showed little or no changes in water quality parameters. There was no consistent, quatifiable effect of the use of the temporary sediment controls as pollutant controls as installed at the study site.

17. Key Words Temporary Sediment Control Pollutant control highway construction monitoring	18. Distribution Statement No restrictions. This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of pages 154	22. Price

Form DOT F 1700.7 (8-72) Reproduction of completed page authorized

Disclaimers

This report is derived entirely from the master's thesis of Joseph P. Muscara. The names of the research supervisors are included as report authors for project identification purposes.

NOTICE

Acknowledgements

We want to thank the Texas Department of Transportation for funding this research project, providing the impetus for the research, providing the test site, and assisting us as the project progressed. In particular thanks to Jim Darden, Director of Project Development for District 12, Maureen Wakeland, Area Engineer of the Genoa Area office, and the staff of the Genoa Area Office.

We would like to thank the Hach Company for providing technical support and permission to reproduce selected sections of their documentation.

Abstract

A highway construction project in the Houston area was monitored from pre-construction through the first phase of construction to determine the effectiveness of temporary sediment controls (TSCs) used for pollutant control. Nearby receiving-water bodies were also monitored to determine the type and quantity of pollutants that left the site. Nutrients, metals, and general water quality parameters were monitored throughout the investigation period. The receiving-water bodies showed little or no effects of construction, nor any long term changes in water quality parameters. There was no consistent, quantifiable effect of the use of the temporary sediment controls as installed at the study site.

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List of Abbreviations

BOD_5 - five day biochemical oxygen demand

Cd - cadmium

Cl^- - chloride

COD - carbonaceous oxygen demand

Cu - copper

CWA - Clean Water Act

EPA - Environmental Protection Agency (also US EPA)

Fe - iron

FTU - Formazin turbidity unit

HNO_3 - nitric acid

L - liter

mg - milligram

mL - milliliter

NH_3-N - ammonia nitrogen

Ni - nickel

NO_3^--N - nitrate nitrogen

NO_2^--N - nitrite nitrogen

NPDES - National Pollutant Discharge Elimination System

NTU - nephalometric turbidity unit

NURP - Nationwide Urban Runoff Program

P - phosphorus

PM - permanent monitoring site

Pb - lead

SO_4^{2-} - sulfate

SW3P - Storm Water Pollution Prevention Plan

TSC - temporary sediment control

TxDOT - Texas Department of Transportation

Zn - zinc

μ - mean

Chapter 1 Introduction

Background

The impacts of human activities upon the environment have been recognized for a number of years. In the case of surface-water quality, most attention has been focused upon point sources such as industrial discharge pipes and sewage-treatment plant outfalls. Pollution sources largely overlooked until recently are those classified as "nonpoint sources" of pollution. These sources have been mostly unregulated, mainly because they originate from sources as numerous and diverse as the population itself.

This form of pollution develops as rainfall, snowmelt, or irrigation runoff flows over the land, dissolving or suspending nearly anything in its path. Food production residues, lawn maintenance chemicals, rubber, oil, and grease from automobiles, or metals and chemicals as well as unprotected soils from highway or building construction are some typical nonpoint pollutants (Mitchell, 1996).

Soil disturbance resulting from construction activities accelerates the erosion process and increases the sediment load in runoff, thus adversely affecting receiving waters (TxDOT, 1993). Highway construction activities are usually started with a clearing and grubbing phase where vegetation and other naturally occurring soil-stabilizing materials are removed from the site. These surfaces are then exposed to the erosive forces of wind and precipitation until the site is artificially stabilized or until construction has ceased and the vegetation and naturally occurring soil-stabilizing materials are restored (Barrett et al., 1995a).

Damage incurred from sediment transport and deposition into surface waterways is thought to occur via several mechanisms. Fish spawning areas and benthic (sea bottom) habitats may be buried when the sediment is deposited on the bottom of the waterways. Increased turbidity reduces light transmission, limiting aquatic photosynthesis, consequently reducing aquatic food supply and habitat. Suspended solids might also coat and abrade aquatic organisms, reduce surface water quality and usability, and reduce the capacity of reservoirs or other water carrying systems via deposition. There is also evidence that stormwater sediments also act as a transport mechanism for pollutants (Barrett et al., 1995a).

While the effects of various contaminants upon the health of organisms in the receiving-water bodies, as well as upon the usefulness of the water to humans, are beyond the scope of this project, there is evidence that changes in concentrations of these contaminants can have adverse effects. High concentrations of heavy metals inhibit growth in aquatic life (Buckley, 1994a, Buckley, 1994b). Increases in nutrients cause algal blooms, resulting in an overall oxygen deficiency (Reinert and Hroncich, 1990).

Objectives

This project had two principal objectives. One was to determine the effects of highway construction on the levels of various parameters considered pollutants in affected receiving-water bodies. The other was to develop a methodology to test the effectiveness of the current level of technology of stormwater pollution prevention plans (SW3Ps) as currently used at highway construction sites upon mitigating the levels and effects of these parameters. These results would then be used to help calibrate the sediment and pollutant mobilization and transport models being developed for the Texas Department of Transportation (TxDOT) by other researchers.

Scope and Limitations

The pollution control measures evaluated in this research were only of the type used to prevent or restrain pollutants and/or sediments from entering a receiving-water body. This study was also limited to the erosion and sediment controls used at one particular construction site as described later. There were no evaluations of preventative measures that limit contact between stormwater and potential pollutants. Nor was consideration given to the practices of minimizing erosion potential by limiting the disturbed area, restricting construction traffic, revegetating disturbed areas as soon as possible, etc., that are part of any SW3P including the one under study. This study is limited to the Houston-Galveston area but is hoped to develop a test methodology for geotechnically different areas.

Since many factors can affect the water quality of receiving-water bodies, it is difficult to determine absolutely if highway construction has any effects. Land-use changes, socio-economic changes, and natural changes both in and out of the receiving-water body may affect it. Other ongoing research is underway to help isolate the effects of the highway construction.

Organization

The remainder of this thesis will review literature and the history of the problem in Chapter 2, define and develop the methodology in Chapter 3, present the results of the analysis in Chapter 4, and conclude with a summary of the results, conclusions, and recommendations in Chapter 5. The appendices include the Hach procedures used in the lab analyses with the corresponding USGS methods (both described in Chapter 3), the results from the tests of standards performed on the Hach DR/2000, raw data from the field and laboratory analyses on each sample collected, and statistical data reduction for the various sample types as summarized in Chapter 4.

Chapter 2 Literature Review

Prior to 1960, water-quality effects of stormwater pollution received little attention, with most stormwater concerns related to drainage problems. Initial work in the area of stormwater pollution tended towards the type and amount of pollutants involved or methods to reduce the pollutant load. In Detroit, an early investigation into the pollutional effects of stormwater overflowing from a properly designed combined sewer system were evaluated by Palmer (1950). This study determined that the combination of the low quality of urban stormwater and its dilution effect on wastewater in the sewer system resulted in sewage overflows that were not significantly more polluting than stormwater alone.

An attempt to characterize urban runoff in Cincinnati was reported by Weibel et al., (1964). This paper evaluated effects of regulated stream flow on water quality and water uses in controlling water pollution not susceptible to other means of abatement. Mean concentrations of constituents in urban land runoff versus time were analyzed, and stormwater runoff loads and sanitary sewage loads were compared. This study concluded, among other items, that there appeared to be a relationship between increased rainfall and increased loadings of suspended solids. They also noted some evidence of a "first flush," where a larger amount of solids and loadings were picked up by the initial flow of runoff.

The Federal Government recognized the possible negative impacts of stormwater runoff as early as 1964. The U. S. Public Health Service expressed concern about pollutants in urban runoff and concluded that there may be significant water quality problems associated with stormwater runoff (US EPA, 1983a). Section 62 of the Water Quality Act of 1965 (Public Law 89-234) authorized the Federal government to make grants for the purpose of "assisting in the development of any project which will demonstrate a new or improved method of controlling the discharge into any water of untreated or inadequately treated sewage or other waste from sewerage which carry stormwater or both stormwater and sewage or other waste . . . ." The Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-500) demonstrated a heightened national awareness of the state of the nation's surface waters and thus the Congressional intent that national water quality goals be established. This act made significant strides in improvement of surface water quality from improvements in point source discharges. However, as reduction of pollutants from point sources were made, the negative effects that might be caused by nonpoint sources such as stormwater runoff became more prominent.

Research in this area was limited in the information provided about the amount of improvement attainable or the need to improve the water quality of the receiving-water body. Additional questions existed regarding uncertainties associated with the local nature and extent of urban runoff water quality problems, the effectiveness of management and control measures, and the affordability of such measures in terms of benefits derived. These unknowns were so significant and the associated control cost estimates were so high that Congress deleted Federal funding for the treatment of separate stormwater discharges in the Clean Water Act of 1977 (Public Law 95-217).

They stated that there was not enough information about urban runoff loads, impacts, and controls to justify major investments in physical control systems.

This lack of information led the EPA to develop the Nationwide Urban Runoff Program (NURP). This program, instead of being a research program, was designed to be a support function where information and methodologies would be provided for water quality planning efforts.

> "The overall goal of NURP was to develop information that would help provide local decision makers, States, EPA, and other interested parties with a rational basis for determining whether or not urban runoff is causing water quality problems and, in the event that it is, for postulating realistic control options and developing water quality management plans, consistent with local needs, that would lead to implementation of least cost solutions. (U. S. EPA 1983b)."

The NURP study defined a water quality problem from urban runoff using a three-level definition as follows: 1) impairment or denial of beneficial uses, 2) water quality criterion violation, and 3) local public perception (U. S. EPA 1983b). This definition provided a framework within which to discuss water quality problems associated with runoff.

The results of this study confirmed that runoff was a transport mechanism for pollutants. Heavy metals, organics, coliforms, nutrients, oxygen demanding substances, and suspended solids were all found to be present in urban runoff.

Geographic location, land use category, topography, population density, and precipitation characteristics all appeared to have little use in predicting urban runoff characteristics (U. S. EPA 1983a). A more recent study, using stormwater samples from various land-use areas in the Dallas - Fort Worth Metroplex, determined that no significant relationship existed between particle size distribution and land use (Pechacek, 1993).

A study in France analyzed the metallic content of urban runoff waters (Lara-Cazenave, 1994). Most metallic pollutants were in the particulate phase at relatively high concentrations (Cd 5 μg/g, Cu 400 μg/g, Pb 700 μg/g, Zn 2000 μg/g). Multiparameter correlations were performed and showed strong links between COD, BOD_5, suspended solids, and Cu and Pb concentrations in the particulate phase.

A Texas Department of Transportation funded study of the impacts of highway construction on water quality in the Edwards aquifer recharge zone included a field monitoring program of water bodies affected by highway construction (Barrett et al., 1995a). This research showed significant increases of suspended solids, turbidity, iron, and zinc between sites upstream and downstream of highway construction. Other constituents showed less significant changes. A correlation between the concentration of iron and that of suspended solids was found, but no permanent change in the water body was found.

In another study supported under the same grant, temporary sediment controls were evaluated at active highway construction sites (Barrett et al., 1995b). Total suspended solids and turbidity reduction was evaluated primarily for sediment control fences, but some data was included for rock filter dams. This study concluded that both the sediment control fences and rock filter dams surveyed showed negligible total suspended solids and turbidity reductions. These results were consistent with the findings of the monitoring of the receiving-water bodies where suspended solids were noted to increase downstream of the highway construction.

The use of stormwater prevention plans in areas such as highway construction are a result of the Water Quality Act of 1987. This act included amendments to the Clean Water Act (CWA) that requires the EPA to develop regulations for nonpoint pollutant sources. The CWA requires those construction sites that disturb 5 or more acres be authorized by a National Pollutant Discharge Elimination System (NPDES) permit as published in the Federal Register, Volume 57, Number 175, Wednesday, September 9, 1992.

Each construction site covered by a permit is required to have a stormwater pollution prevention plan (SW3P). The SW3P must include a site description, the controls that will be used, maintenance of the controls, and inspection plan for the disturbed areas of the site. The controls fall into three categories: erosion and sediment controls, stormwater management, and waste disposal. The erosion and sediment controls have two subcategories, stabilization practices which include preserving existing vegetation, seeding, mulching, and sod stabilization, and structural practices that include the aforementioned sediment control fences and rock filter dams, as well as other temporary structures.

As detailed as the SW3P is required to be, there is no provision for monitoring the effectiveness of the plan. While the plan has been said to cost about two percent of the total engineering costs of the project, the lack of monitoring provides no feedback on the effectiveness of the plan, and thus, the expenses incurred from it. There are good construction engineering reasons for controlling erosion, not the least of which are the costs associated with replacing eroded soils for aesthetic or structural reasons. The Texas Department of Transportation (1993) stated that a "goal of reducing the sediment from disturbed areas by 70-80% with the use of erosion and sedimentation controls is considered realistic and attainable." However, current literature such as the aforementioned study by Barrett et al., (1995b) suggests that the present level of technology does not provide this level of pollutant control.

Chapter 3 Methodology

General Approach

Stormwater and background samples were collected at a test site agreed upon by TxDOT and the University of Houston research team. Figure 1 is a map showing the monitored test site. Five permanent monitoring locations were chosen for ambient sampling. The locations of four of these permanent monitoring sites were based upon storm sewer outfalls along the construction site. The fifth site was selected as an upstream baseline in Mud Lake so that construction would have no effect. Except for the upstream baseline, all permanent monitoring locations had an "upstream" and a "downstream" sampling point.

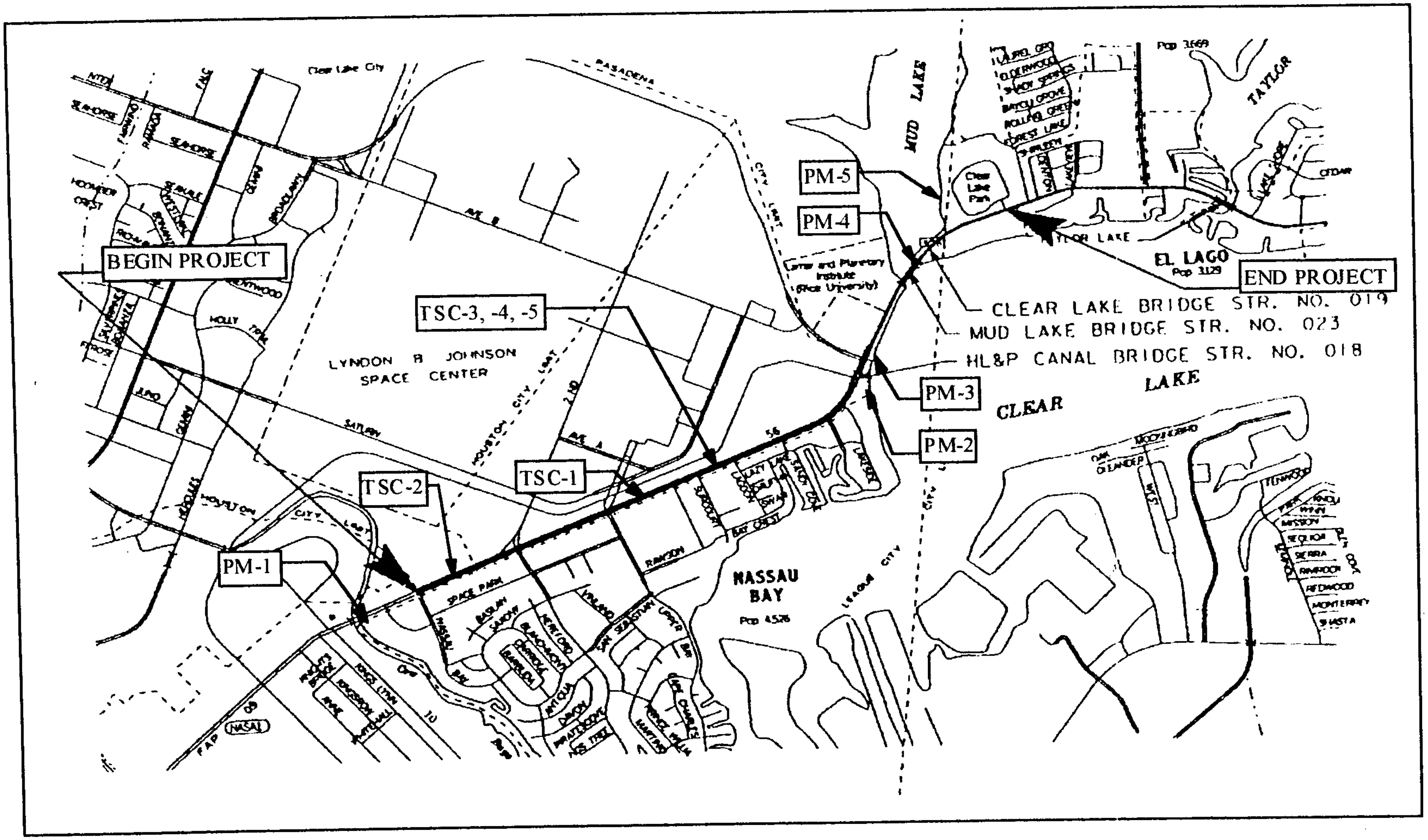

Figure 1: Map of NASA Rd. 1 Test Site with Sampling Points (TxDOT, 1995)

Five temporary sediment controls (TSC) were selected, based upon convenience, safety, storm flows, and type. A representative mix of TSC type was selected so that both rock filter dams and sediment control fences were represented in the study. All temporary sediment controls had an “upstream” and a “downstream” sampling point.

The sampling plan consisted of two types of sampling: ambient and storm influenced. The ambient sampling plan consisted of sampling the permanent monitoring locations regularly, approximately every two weeks. The purpose of these samples was to create a baseline with which to compare the storm influenced samples, as well as possibly determine if there are any long term effects in the receiving-water bodies, as the ambient sampling started before construction influences occurred. Since there were no storm flows when the ambient samples were taken, these samples were taken at the downstream sample points.

During or as soon as possible after a storm event occurred, samples were taken at the permanent monitoring locations and temporary sediment controls, at their respective upstream and downstream points, for storm influenced samples. When samples were taken during a storm, as many locations as possible were sampled upstream and downstream at regular intervals. Since it was difficult to “catch” a storm in progress, all locations were sampled as soon as possible after a storm event. Again, these samples were taken at all upstream and downstream points. Sufficient rainfall was necessary to create flows in storm sewers and upstream and downstream of all TSCs to take samples.

Test Site

The test site selected was a 2.368 mile construction site along NASA Rd. 1 in southern Harris County, Texas. The western end of the project was 0.36 mile east of FM 270, its eastern end was 0.63 mile east of Space Center Blvd., and the total project area was 52 acres, with 35 acres disturbed. The construction activities planned centered on widening the road and thus the work at the site consisted of grading, structures, utility relocation, storm sewers, base, concrete pavement, traffic signals, signing and pavement markings. The soil-disturbing activities included preparing the "right-of-way," grading, excavation and embankment for roadway erosion and sediment control, storm sewers, utility adjustments, and topsoil work for sodding.

The western end of the project drains into Cow Bayou, while the section of the project between 3rd Street and the HL&P Co. cooling canal drains into Clear Lake via a TxDOT drainage outfall. The area of the project between the cooling canal and the Clear Lake bridge west of Clear Lake Park drains into Clear Lake via another TxDOT outfall adjacent to Space Center Blvd. The eastern end of the project drains into Clear Lake by a TxDOT drainage ditch. Figure 1 shows the locations of NASA Rd. 1 and the receiving-water bodies.

The permanent monitoring locations were chosen based upon the locations of these outfalls. Four permanent monitoring locations (PM-1 through PM-4) were designated at the four outfalls described above. The fifth permanent monitoring location (PM-5) was located in Mud Lake as an upstream baseline in a large body of water so that construction would have no effect. Figure 1 shows the relative location of the five permanent monitoring sites on a map of the test site. As it turned out, PM-4 can also be considered a baseline since construction had not progressed to the eastern end of the project during the time surveyed. One permanent monitoring site, PM-2, was lost early during the research period due to construction at that location.

Five temporary sediment controls (TSC-1 through TSC-5) were selected based upon convenience, safety, storm flows, and type. Three TSCs were simple rock filter dams. According to TxDOT's "Storm Water Management Guidelines for Construction Activities," a rock filter dam is a temporary berm constructed of open-graded rock whose purpose is to intercept and slow down sediment laden stormwater runoff from disturbed areas, retain the sediment, and release the water in sheet flow. This runoff should outfall directly to an undisturbed or stabilized area. They are used where there is sheet flow or concentrated flow in a channel above the rock filter dam.

The design guidelines for rock filter dams specify that the drainage area be less than 5 acres, the maximum flow through rate be 60 gal/min/ft, and the rock be 3 to 5 inches in diameter. At this site and for this research, all rock filter dams studied are Type 1, specified as 18 inches in height, 2-foot minimum top width, with water velocities less than 8 ft/sec. These rock filter dams are recommended for the toe of slopes, around inlets, in small ditches, and at dike and swale outlets (TxDOT, 1993).

Figure 2 is a photograph of the first rock filter dam, TSC-1. It was located in the median of NASA Rd. 1 east of 3rd Street to protect a storm sewer inlet. This rock filter dam was at the eastern end of the median, approximately one meter from the median break or crossing. The other two, TSC-3 and TSC-4, were located in the median of NASA Rd. 1 between Surf Court and Lagoon Drive to protect another storm sewer inlet. TSC-3 was similar in construction to TSC-1 and was located approximately two meters to the west of the storm sewer inlet and is shown in Figure 3. TSC-4 was U-shaped, and was built around three sides of the inlet as shown in Figure 4.

Figure 2: Rock Filter Dam TSC-1

Figure 3: Rock Filter Dam TSC-3

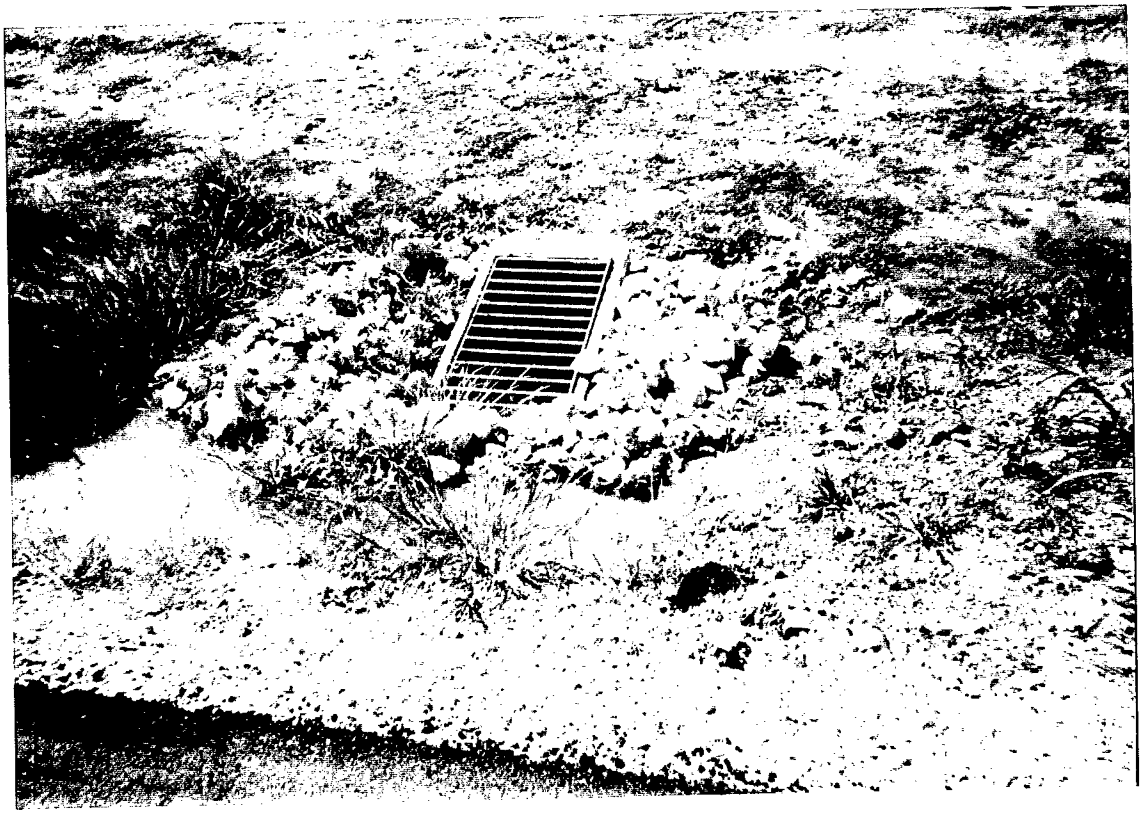

Figure 4: Rock Filter Dam TSC-4

The remaining TSCs were sediment control fences. Like TSC-1, TSC-2 was being used to protect a storm sewer inlet in a median. It was located approximately 1 meter from the western end of the median of NASA Rd. 1 between Kings Park and 2nd Street/Point Lookout. Figure 5 is a photograph of TSC-2. The other sediment control fence (TSC-5) is shown in Figure 6 showing its location relative to TSC-3 and TSC-4. TSC-5 was being used in conjunction with TSC-3 and TSC-4 to protect the storm sewer inlet there and was located about 2 meters to the east of the inlet.

Figure 5: Sediment Control Fence TSC-2

Figure 6: Sediment Control Fence TSC-5 (TSC-3 and TSC-4 visible in background)

A sediment control fence is a temporary barrier fence made of geotextile filter fabric that is water permeable and traps water borne sediment and is reinforced with a wire backing. Its purpose is to intercept and detain waterborne sediment from stormwater runoff. They are used during the construction period near the perimeter of a disturbed area to intercept sediment while water percolates through, and they should remain until disturbed area is permanently stabilized. They should not be used where there is a concentration of water in a channel or drainageway or where soil conditions prevent a minimum toe-in depth of 6 inches or installation of support post to a depth of 12 inches. Sediment control fences should be replaced with rock filter dams if concentrated flow occurs after installation (TxDOT, 1993).

The design guidelines for sediment control fences specify that the drainage area be less than 2 acres, the maximum flow through rate be 40 gal/min/ft^2 of frontal area, that they have a 24-inch minimum height and a 6-inch minimum toe-in. Sediment control fences should be placed and constructed in such a manner that runoff will be intercepted, sediment trapped, and surface runoff allowed to percolate through the structure onto an undisturbed or stabilized area (TxDOT, 1993).

Water Sampling and Storage

Samples that were taken from a standing water body (bayou, lake, pond, etc.) were withdrawn from the water body using an Alconox® cleaned, triple tap water rinsed, acid rinsed (HNO_3), triple deionized water rinsed polyethylene sample retriever. An initial sample was withdrawn and used to rinse the sample retriever in order to eliminate any contaminant that might have leached from the container to the sample and to equilibrate the sample to the container. This sample was then poured downstream of the sampling point. A second sample was then withdrawn and poured into the appropriate sample storage container as described below. Both samples were withdrawn from a point in the water body that appeared to be well mixed and representative of the effect of the stormwater runoff on the water body. This point was usually as close as possible to the center of the water body. If this point was too far to be within arm's reach, then a rope was attached to the sample retriever handle. This method of sample collection had the advantage of requiring the presence of the researcher and thus allowing the opportunity to make operational observations during storm events and make modifications to the sampling plan, if necessary. For ambient samples, the samples were analyzed on-site for pH, temperature, and conductivity/total dissolved solids.

The flows upstream and downstream of a temporary sediment control that were collected during or following a storm event were fairly shallow. Therefore, these samples were taken with care being exercised to not scrape any of the underlying material into the container, nor to collect excessive unrepresentative particles such as floating litter. The considerations described above for sampling from a standing water body generally were also applied to sampling at a TSC.

It should be noted here that for all sample times and locations, safety was of the utmost concern. Sample sites were selected based not only on convenience and access, but upon being located a safe distance from traffic flows and construction activities and avoiding risks such as from steep inclines near the standing water.

Depending upon the type of analysis to be performed, the samples were collected and stored in the appropriate type of container. Any sample that was to be analyzed for metals (Fe, Ni, Zn) was stored in a 500 mL or 1000 mL polyethylene container with a Teflon® lined cap. These containers were purchased as precleaned; before any subsequent re-use, they were washed with Alconox®, triple tap water rinsed, rinsed with nitric acid, and then triple rinsed with deionized water. This cleaning method is based upon the work of Laxen and Harrison (1981) and methods described by Hach Company (1992). When it was likely that the sample would not be analyzed for metals within 24 - 48 hours, the sample was acid preserved to pH<2 with nitric acid. This pH level was achieved by adding the acid to the sample container at the laboratory before leaving for the sampling site. These samples were stored at room temperature. These storage techniques are based upon information provided by the Hach Company (1992).

Samples that were analyzed for non-metallic constituents were stored in 500 mL or 1000 mL glass containers that have been washed with Alconox®, triple tap water rinsed, and triple deionized water rinsed. These samples were stored in a portable cooler while on site or in transit, and were stored in a refrigerator in the lab at 4° C until ready for analysis. Again, this storage technique is based upon that described by Hach Company (1992). Before analysis, the sample was gently warmed to room temperature.

All sample containers that were used to collect and store samples from the field were labeled as much as possible before leaving the lab for the collection event. This included sample site (PM or TSC number, upstream or downstream) and an increment number. The increment number was used instead of a time, since it was impossible to determine in advance at what times sampling would occur due to the length of the drive to the test site. The correlation between increment number and sample time was documented in a field notebook. This marking method also allowed reuse of the labeled containers (after appropriate washing) once the samples had been completely analyzed in the laboratory.

All glassware used in the lab was regularly washed with Alconox®, triple tap water rinsed, and triple deionized water rinsed. If the glassware was to be used for metals analysis, it was also acid washed as described above.

Laboratory Analysis

As stated above, all refrigerated samples were gently warmed to room temperature before analysis. If a sample was acid preserved, its pH was raised to a value no higher than pH = 5, since this is the maximum acceptable pH for Zinc analysis (Hach Company, 1992).

The principal technique that was used for constituent analysis is a colormetric method using a Hach DR/2000 spectrophotometer. In most cases, 25 mL of blank is compared to a 25 mL prepared sample in which a reaction has taken place. Generally, sample preparation consists of adding and mixing a premeasured reagent to 25 mL of the sample and allowing the required time for a color reaction to take place. The spectrophotometer measures the amount of light of a particular wavelength that passes through the blank, references this as zero, and measures the same light passing through the reacted sample. Using calibration curves built into the spectrophotometer, a reading is given of concentration of the constituent being analyzed. Although measurement of suspended solids and turbidity does not involve reactions, the method is similar, with a deionized water blank being compared to the sample. Also, the methods for Cl^-, NO_3^--N, and NH_3-N compare the reaction in a deionized water blank to the reacted sample. The Ni method uses a chloroform blank since the sample reaction extracts the Ni complex into a chloroform layer to concentrate the color and thus increase sensitivity (Hach Company, 1992).

The method used by the DR/2000 Spectrophotometer is based upon conversion of the constituent of interest into a substance whose solution or suspension is colored and will absorb radiant energy. Beer's law describes the absorption of all types of electromagnetic radiation. This law is stated mathematically as follows:

$$A = -\log_{10} T = \log P_0 / P = abc, \qquad (1)$$

where A = absorbance,

T = transmittance (0 to 100 percent),

P_0 = radiant power incident upon the sample,

P = radiant power leaving the sample,

a = absorptivity,

b = light-path length in centimeters, and

c = concentration of the absorbing species.

This equation shows that the relation between absorbance and concentration or pathlength is linear. Thus, for a fixed concentration of an absorbing substance, the absorbance varies with path length (Fishman and Friedman, 1989).

Since the constituent measurements are intended only to be used as indicators of water quality problems resulting from runoff at highway construction sites, the laboratory analyses were performed at a survey or screening level. No digestions were performed for metals analyses, only reactive phosphorus (orthophosphate) was measured, and distillation was not performed for ammonia nitrogen. Both the nitrite and sulfate methods are EPA approved, and the reactive phosphorus method is from Standard Methods (Hach Company, 1992). This experimental methodology was agreed upon by the Texas Department of Transportation and the research team at the

University of Houston. Table 1 lists the Hach procedures used, and whether each procedure was EPA approved, adapted from Standard Methods, or was USGS approved and the method number for each, where appropriate. The Hach procedures used and their corresponding USGS procedures are provided in Appendix A.

Table 1: Hach Spectrophotometer Procedures - Sources or Approvals

Procedure	Symbol	Range (mg/L)	Hach Method #	EPA Approved?	Standard Methods	USGS TWRI
Chloride	Cl^-	0 - 20	8113			I-1187-85
Conductivity	cond	0 - 20 mS/cm	8160	yes		
Iron, Total	Fe	0 - 3.00	8008	with digestion - *Federal Register,* 45 (126) 43459 (June 27, 1980)	3500 Fe	
Nickel	Ni	0 - 1.8	8037	with digestion		
Nitrate, MR	NO_3^--N	0 - 4.5	8171			
Nitrite, LR	NO_2^--N	0 - 0.300	8507	*Federal Register,* 44(85) 25505 (May 1, 1979)		I-1540-85
Nitrogen, Ammonia	NH_3-N	0 - 2.50	8038	with distillation	4500 NH_3	I-1520-85
pH	pH	0 - 14	8156	yes	4500 H^+	I-1586-85
Phosphorus, Reactive	P	0 - 2.50	8048	yes	4500 P	I-1601-85
Suspended Solids[1]		0 - 750	8006			
Sulfate	SO_4^{2-}	0 - 70	8051	yes	4500 SO_4^{2-}	I-2823-85
Turbidity[2]	FTU	0 - 450 FTU	8237			
Zinc	Zn	0 - 2.00	8009	with digestion - *Federal Register,* 45(105) 36166 (May 29,1980)	3500 Zn	

[1] Compared to Total Solids, Gravimetric, EPA Approved

[2] FTU equal to NTU using the Formazin turbidity standard

Spectrophotometer Verification

Standard solutions were developed in order to verify the calibration of the Hach DR/2000 Spectrophotometer. These standard solutions were made by adding a known mass of the chemical to be tested to a known volume of deionized water. The solution then had a known concentration that would be used for further computations. This solution was then used at various dilutions to develop curves to correlate predicted versus actual amount of substance present. The dilutions were created by taking a measured volume of mixed standard and adding it to a larger volume of deionized water. Since the volume of standard had a known mass of substance, this mass divided by the new total volume gave the predicted concentration. The concentrations tested were chosen to represent the range of concentrations expected from the actual field samples. The results from these tests are provided in Appendix B.

Data Analysis

The sample data analyses were grouped three ways in order to determine the effects of construction upon stormwater runoff and receiving-water bodies. At each permanent monitoring site, ambient samples were compared to storm influenced samples, and storm influenced upstream versus downstream samples were compared to study dilution effects. To ascertain the effectiveness of temporary sediment controls, samples taken upstream of the TSC were compared with those taken downstream.

Previous research showed that it was likely that there would be a difference in the means of either of the sample types being compared, and that there would also be some differences in the variance. A two-sample t-test assuming unequal variances was selected based on this prior work to compare means of the two sample sets being tested.

A t-test was performed on the data in order to test the following hypotheses: 1) $\mu_{\text{Ambient}} = \mu_{\text{Storm Influenced}}$, and 2) $\mu_{\text{Upstream PM}} = \mu_{\text{Downstream PM}}$. A level of significance of $\alpha = 0.05$ was used. Since there was some risk of rejecting a true hypothesis, the terminology used was that the hypothesis was accepted or rejected, as opposed to using true or false.

The first hypothesis was a typical equality of means test with unknown variance and unequal sample sizes. The t-statistic used for this case was

$$t = \frac{X_1 - X_2}{s_p\sqrt{\left(\frac{1}{N_1}\right)+\left(\frac{1}{N_2}\right)}}, \tag{2}$$

where X_n = mean of sample n,

N_n = number of observations of sample n,

s_p^2 = pooled mean-square estimate of σ^2 given by

$$s_p^2 = \frac{(N_1 - 1)s_1^2 + (N_2 - 1)s_2^2}{N_1 + N_2 - 2},$$

and s_n = variance observed in sample n.

The means for the levels of suspended solids, turbidity, nitrate-nitrogen, nitrite-nitrogen, sulfates, phosphorus, iron, zinc, chloride, ammonia-nitrogen, and nickel were compared in this case. Since it was unknown whether the storm influenced samples would be greater or less than the ambient samples, and it was possible that the runoff would have either a pollutional or a dilutional effect upon the receiving-water bodies, a two-tailed t-test was used to test this hypothesis.

The second hypothesis involved a before and after test, where the sample sizes were equal and naturally paired. The t-statistic used for this case was

$$t = \frac{X - \mu_0}{s/\sqrt{N}}, \tag{3}$$

where X = mean of the differences,

μ_0 = hypothesized mean difference,

s = standard deviation of the differences,

and N = number of paired samples.

Again, a two-tailed t-test was used as before the start of the test it was unknown whether the upstream stormwater runoff would have a pollutional or a dilutional effect upon the receiving-water bodies downstream. The same parameters as listed above were also compared for this case.

The effectiveness of the TSCs tested was determined by calculating the removal efficiency for each of the 11 parameters listed above. This removal efficiency was calculated by

$$\%\text{Reduction} = \frac{\text{UpstreamValue} - \text{DownstreamValue}}{\text{UpstreamValue}}(100\%). \tag{4}$$

Although percent reductions are presented for all available TSC data, in some cases this calculation can be misleading. For instance, if the upstream value was 0.02, and the downstream value was 0.01, this would indicate a 50% reduction. However, depending upon the analysis performed, this difference could be within the measurement error of the procedure. Therefore, additional analysis is presented where it is determined if, for each parameter at each TSC, there appears to be a reduction, an increase, both, or insufficient data to determine.

Chapter 4 Results

A total of 22 sample sets were taken from the period of April 10, 1996, to October 2, 1996. Of these, 13 were ambient, three were post-storm storm-influenced, and six were time-based storm samples. Since there was only one set of time-based storm event samples, each of these individual samples was treated as a separate storm influenced sample.

In this chapter, ambient samples are compared with storm influenced samples for all four permanent monitoring sites, and, for PM-1, PM-3, and PM-4, storm influenced upstream versus downstream samples are compared to study dilution effects. Samples taken upstream of temporary sediment controls are compared with samples taken downstream to evaluate the effectiveness of the TSCs.

The pH, temperature, conductivity, and total dissolved solids of the storm influenced samples were measured in the lab after the samples had begun to chill during transport. Therefore, comparing these parameters to their ambient counterparts is not valid and results from these measurements are not shown here.

The verification test for phosphorus showed that there was a large instrumental error for this parameter. This is likely due to the fact that only reactive phosphorus, also known as orthophosphate, was measured, while phosphorus can exist in several forms in natural waters, depending upon such factors as pH and temperature (Snoeyink and Jenkins, 1980). Therefore, phosphorus results are reported for completeness although the data is considered meaningless.

Except for turbidity, all parameters in the following tables are in the units of mg/L water. Turbidity is in Formazin turbidity units (FTU).

Comparison of Ambient vs. Storm Influenced Samples at Permanent Monitoring Sites

Due to their location and the earth moving activities that took place during the research period, PM-1 and PM-3 should show effects of construction by comparing their ambient samples with storm influenced samples. Using the t-test described previously, the hypothesis tested was $\mu_{\text{Ambient}} = \mu_{\text{Storm Influenced}}$ for each parameter analyzed. Table 2 shows the t-test results from the PM-1 data. As previous research had suggested, suspended solids and turbidity were both increased during storm influenced conditions over ambient. This increase is shown by the t-test hypothesis being rejected and the higher storm influenced means. The storm influenced data also shows a higher variance, indicating a larger spread in the data.

Table 2: t-Test Two Sample Assuming Unequal Variances at PM-1, Ambient vs. Storm Influenced

	Ambient		*Storm Influenced*				
Parameter	Mean	Variance	Mean	Variance	t Stat	t Critical (two tail)	Hypothesis
Sus. Solids	13	153.83	183.5	12216.57	-4.35	2.36	Reject
Turbidity	13.6	97.26	104	3786	-4.12	2.36	Reject
Iron (Fe)	0.23	0.05	0.28	0.03	-0.56	2.09	Accept
Zinc (Zn)	0.017	0.00085	0.0225	0.00034	-0.49	2.13	Accept
Nickel (Ni)	0.024	0.00108	0.0788	0.00127	-3.25	2.14	Reject
SO_4	90.09	23812.7	6.78	171.9	1.78	2.23	Accept
Cl^-	297.73	334858.	30.875	2321.03	1.52	2.23	Accept
Phosphorus	0.085	0.002	0.058	0.0014	1.53	2.09	Accept
NO_3-N	0.354	0.266	0.333	0.035	0.13	2.12	Accept
NO_2-N	0.0047	$7.7*10^{-6}$	0.016	0.00045	-1.57	2.31	Accept
NH_3-N	0.219	0.0213	0.806	0.0838	-5.27	2.23	Reject

Table 3 shows the t-test results from the PM-3 data. This location did not show the increases in parameters in storm influenced samples over ambient conditions as seen at PM-1. In all cases, the t-test hypotheses were accepted, indicating that there was no change between ambient and storm influenced samples.

Table 3: t-Test Two Sample Assuming Unequal Variances at PM-3, Ambient vs. Storm Influenced

	Ambient		*Storm Influenced*				
Parameter	Mean	Variance	Mean	Variance	t Stat	t Critical (two tail)	Hypothesis
Sus. Solids	44.38	908.3	50.67	1590	-0.26	3.18	Accept
Turbidity	43.54	431.44	38	77.33	0.76	2.16	Accept
Iron (Fe)	0.106	0.006	0.093	0.002	0.42	2.26	Accept
Zinc (Zn)	0.015	0.0003	0.01	0	0.92	2.23	Accept
Nickel (Ni)	0.139	0.022	0.05	$8*10^{-4}$	1.68	2.26	Accept
SO_4	1200	177727	1075	102500	0.62	2.36	Accept
Cl^-	5718	8715636	10500	42320000	-1.02	12.7	Accept
Phosphorus	0.148	0.005	0.158	0.004	-0.25	2.45	Accept
NO_3-N	0.423	0.022	0.325	0.002	2.04	2.13	Accept
NO_2-N	0.0076	$6.8*10^{-5}$	0.01	$3.8*10^{-5}$	-0.68	2.36	Accept
NH_3-N	1.153	0.417	1.24	0.269	-0.24	2.78	Accept

It was expected that PM-4 would not show effects of construction, since, for the study period, there were no earth disturbing activities upstream of PM-4. Table 4 shows the t-test results from the PM-4 data. As expected, this location did not show the increases in parameters in storm influenced samples over ambient conditions as seen at PM-1, except for nickel. In all other cases, the t-test hypotheses were accepted, indicating that there was no change between ambient and storm influenced samples.

Table 4: t-Test Two Sample Assuming Unequal Variances at PM-4, Ambient vs. Storm Influenced

	Ambient		*Storm Influenced*				
Parameter	Mean	Variance	Mean	Variance	t Stat	t Critical (two tail)	Hypothesis
Sus. Solids	40.46	279.44	29.67	30.33	1.92	2.20	Accept
Turbidity	43.31	151.7	32.25	85.58	1.92	2.37	Accept
Iron (Fe)	0.085	0.003	0.065	0.001	0.85	2.31	Accept
Zinc (Zn)	0.01	0.00018	0.03	0.0002	-1.85	12.7	Accept
Nickel (Ni)	0.146	0.005	0.065	$5*10^{-4}$	2.81	2.37	Reject
SO_4	1102	187215	1075	114167	0.13	2.36	Accept
Cl^-	6227	5856181	8267	63583333	-0.44	4.30	Accept
Phosphorus	0.146	0.004	0.118	$4*10^{-4}$	1.39	2.13	Accept
NO_3-N	0.431	0.012	0.3	0.047	1.16	2.78	Accept
NO_2-N	0.0069	$9.9*10^{-5}$	0.01	$6.1*10^{-5}$	-0.69	2.45	Accept
NH_3-N	1.055	0.361	1.303	0.382	-0.62	3.18	Accept

Table 5 shows the t-test results from the PM-5 data. As planned, this location did not show the increases in parameters in storm influenced samples over ambient conditions. In all cases, the t-test hypotheses were accepted, indicating that there was no change between ambient and storm influenced samples.

Table 5: t-Test Two Sample Assuming Unequal Variances at PM-5, Ambient vs. Storm Influenced

Parameter	*Ambient* Mean	*Ambient* Variance	*Storm Influenced* Mean	*Storm Influenced* Variance	t Stat	t Critical (two tail)	Hypothesis
Sus. Solids	42.31	354.4	53.33	745.3	-0.66	4.30	Accept
Turbidity	48.69	295.4	55	817	-0.37	4.30	Accept
Iron (Fe)	0.092	0.003	0.128	0.017	-0.54	3.18	Accept
Zinc (Zn)	0.0055	$8.7*10^{-5}$	0.01	0.0002	-0.43	12.7	Accept
Nickel (Ni)	0.128	0.007	0.035	0.002	2.08	3.18	Accept
SO_4	1129	257481	802	357683	0.98	2.57	Accept
Cl^-	5036	6596545	6614	113211352	-0.25	4.30	Accept
Phosphorus	0.134	0.01	0.168	0.017	-0.47	2.78	Accept
NO_3-N	0.508	0.064	0.5	0.07	0.05	3.18	Accept
NO_2-N	0.0067	0.00013	0.023	0.0005	-1.40	3.18	Accept
NH_3-N	0.795	0.062	1.443	0.108	-3.179	3.182	Accept

Table 6 summarizes the results of the ambient versus storm influenced hypothesis tests for PM-1, PM-3, PM-4, and PM-5.

Table 6: Summary of Results of t-Tests for Permanent Monitoring Sites, Ambient vs. Storm Influenced

Parameter	PM-1	PM-3	PM-4	PM-5
Sus. Solids	Reject	Accept	Accept	Accept
Turbidity	Reject	Accept	Accept	Accept
Iron (Fe)	Accept	Accept	Accept	Accept
Zinc (Zn)	Accept	Accept	Accept	Accept
Nickel (Ni)	Reject	Accept	Reject	Accept
SO_4	Accept	Accept	Accept	Accept
Cl^-	Accept	Accept	Accept	Accept
Phosphorus	Accept	Accept	Accept	Accept
NO_3-N	Accept	Accept	Accept	Accept
NO_2-N	Accept	Accept	Accept	Accept
NH_3-N	Reject	Accept	Accept	Accept

Comparison of Storm Influenced Upstream vs. Downstream Samples at Permanent Monitoring Sites During Storm Events

The following three tables show the results from the t-test on the upstream versus downstream sample data. Except for the case of nickel at PM-1, the hypothesis used was accepted. For these tests, the hypothesis was $\mu_{Upstream} = \mu_{Downstream}$. This result suggests that, during a storm event, the runoff flowing into the receiving-water body is indiscernible from the water in the water body.

Table 7: t-Test Two Sample Assuming Unequal Variances at PM-1, Upstream vs. Downstream

Parameter	*Upstream* Mean	Variance	*Downstream* Mean	Variance	t Stat	t Critical (two tail)	Hypothesis
Sus. Solids	183.5	12216	172	11537	0.19	2.36	Accept
Turbidity	104	3786	108.8	2736	-0.16	2.36	Accept
Iron (Fe)	0.286	0.032	0.28	0.029	0.45	2.36	Accept
Zinc (Zn)	0.0225	0.00034	0.04	0.0002	-1.94	2.36	Accept
Nickel (Ni)	0.079	0.001	0.06	$7*10^{-4}$	2.45	2.36	Reject
SO_4	4.875	159	1	3.43	0.96	2.36	Accept
Cl^-	30.9	2321	12.9	9.3	1.01	2.36	Accept
Phosphorus	0.513	0.001	0.068	0.002	-2.15	2.36	Accept
NO_3-N	0.325	0.04	0.35	0.037	-0.79	2.36	Accept
NO_2-N	0.016	0.0005	0.019	0.0006	-2.11	2.36	Accept
NH_3-N	0.806	0.084	0.801	0.102	0.217	2.36	Accept

Table 8: t-Test Two Sample Assuming Unequal Variances at PM-3, Upstream vs. Downstream

Parameter	*Upstream*		*Downstream*		t Stat	t Critical (two tail)	Hypothesis
	Mean	Variance	Mean	Variance			
Sus. Solids	65.5	1861	166.5	38920	-0.92	12.7	Accept
Turbidity	41.3	49.3	74.33	4280	-0.93	4.30	Accept
Iron (Fe)	0.093	0.003	0.12	0.022	-0.49	4.30	Accept
Zinc (Zn)	0.01	0	0.025	$5*10^{-5}$	-3	12.7	Accept
Nickel (Ni)	0.05	$8*10^{-4}$	0.065	0.002	-1	12.7	Accept
SO_4	983.3	103333	267	93333	2.75	4.30	Accept
Cl^-	10500	42320000	5085	32240450	9.26	12.7	Accept
Phosphorus	0.143	0.0044	0.023	0.001	2.53	4.30	Accept
NO_3-N	0.3	$2.8*10^{-17}$	0.5	0.03	-2	4.30	Accept
NO_2-N	0.012	$3.03*10^{-5}$	0.04	0.002	-1.32	4.30	Accept
NH_3-N	1.24	0.269	0.51	0.016	3.03	4.30	Accept

Table 9: t-Test Two Sample Assuming Unequal Variances at PM-4, Upstream vs. Downstream

Parameter	*Upstream* Mean	 Variance	*Downstream* Mean	 Variance	t Stat	t Critical (two tail)	Hypothesis
Sus. Solids	29.5	60.5	19.5	112.5	0.77	12.7	Accept
Turbidity	28.33	36.33	20.33	6.3	1.92	4.30	Accept
Iron (Fe)	0.057	0.002	0.023	$3.33*10^{-5}$	1.64	4.30	Accept
Zinc (Zn)	0.03	0.0002	0.02	0	1.00	12.7	Accept
Nickel (Ni)	0.065	0.00045	0.06	0.0008	1	12.7	Accept
SO_4	1016.7	150833	533	85833	3.71	4.30	Accept
Cl^-	8267	63583333	4160	$2.2*10^7$	2.17	4.30	Accept
Phosphorus	0.113	$4*10^{-4}$	0.093	0.004	0.49	4.30	Accept
NO_3-N	0.2	0.01	0.233	0.003	-1	4.30	Accept
NO_2-N	0.01	$6.53*10^{-5}$	0.008	$4.3*10^{-6}$	0.68	4.30	Accept
NH_3-N	1.30	0.382	0.313	0.005	3.13	4.30	Accept

Table 10 summarizes the results of the upstream versus downstream hypothesis tests for PM-1, PM-3, and PM-4.

Table 10: Summary of Results of t-Tests for Permanent Monitoring Sites, Upstream vs. Downstream

Parameter	PM-1	PM-3	PM-4
Sus. Solids	Accept	Accept	Accept
Turbidity	Accept	Accept	Accept
Iron (Fe)	Accept	Accept	Accept
Zinc (Zn)	Accept	Accept	Accept
Nickel (Ni)	Reject	Accept	Accept
SO_4	Accept	Accept	Accept
Cl^-	Accept	Accept	Accept
Phosphorus	Accept	Accept	Accept
NO_3-N	Accept	Accept	Accept
NO_2-N	Accept	Accept	Accept
NH_3-N	Accept	Accept	Accept

Comparison of Storm Influenced Upstream vs. Downstream Samples at Temporary Sediment Controls

To evaluate the effectiveness of individual TSCs, samples were taken upstream and downstream of each TSC tested. The analysis of these samples was then used to determine if there was any change in water quality due to the presence of the TSC.

The following tables present the results of this analysis, and the percent reduction observed. Where the values of percent reduction are negative, this indicates an observed percent increase downstream of the TSC. While it is unlikely that the TSCs themselves contributed to these increases, observations of the TSCs during and after storm events indicated several sources of problems. These observations will be discussed in the following section. Figures 7 through 10 present the percent reduction results from Tables 11 and 12 graphically.

Due to the sparsity and variance of the data collected, it was felt that a statistical analysis of this data would have been inappropriate. However, some general conclusions were drawn and are described below.

Table 11: Comparison of TSC-1 Upstream vs. Downstream

Collection Date	Site	Type	SS	Turb	NO_3^--N	NO_2^--N	SO_4^{2-}	P	Fe	Zn	Cl^-	NH_3-N	Ni
6/25/96 10:30	TSC 1 Up	Storm Influenced	440	263	0.7	0.051	0.00	0.00	0.30	0.10	17.2	1.92	0.14
6/25/96 10:30	TSC 1 Dn	Storm Influenced	400	203	0.6	0.050	0.00	0.00	0.08	0.20	23.0	1.73	0.02
		% Reduction	*9%*	*23%*	*14%*	*2%*	*0%*	*0%*	*73%*	*-100%*	*-34%*	*10%*	*86%*
6/25/96 11:00	TSC 1 Up	Storm Influenced	310	198	0.7	0.074	0.00	0.01	0.15	0.04	20.7	1.80	0.02
6/25/96 11:00	TSC 1 Dn	Storm Influenced	283	174	0.8	0.078	0.00	0.19	0.16	0.01	19.3	1.84	0.13
		% Reduction	*9%*	*12%*	*-14%*	*-5%*	*0%*	*-1800%*	*-7%*	*75%*	*7%*	*-2%*	*-550%*
6/25/96 11:15	TSC 1 Up	Storm Influenced	366	205	0.8	0.096		0.04	0.05	0.09	23.9	2.27	0.15
6/25/96 11:15	TSC 1 Dn	Storm Influenced	270	155	0.7	0.091		0.00	0.08	0.05	15.4	1.78	0.11
		% Reduction	*26%*	*24%*	*13%*	*5%*		*100%*	*-60%*	*44%*	*36%*	*22%*	*27%*
6/25/96 11:30	TSC 1 Up	Storm Influenced	430	184	0.7	0.093		0.10	0.08	0.08	22.1	1.52	0.13
6/25/96 11:30	TSC 1 Dn	Storm Influenced	225	137	0.7	0.085		0.08	0.00	0.01	14.6	1.83	0.12
		% Reduction	*48%*	*26%*	*0%*	*9%*		*20%*	*100%*	*88%*	*34%*	*-20%*	*8%*
6/25/96 11:45	TSC 1 Up	Storm Influenced	1320	450	0.4	0.003		0.10	0.60	0.06	16.6	4.46	0.30
6/25/96 11:45	TSC 1 Dn	Storm Influenced		154	0.8	0.081		0.11	0.03	0.08	19.1	1.75	0.13
		% Reduction		*66%*	*-100%*	*-2600%*		*-10%*	*95%*	*-33%*	*-15%*	*61%*	*57%*
6/25/96 12:00	TSC 1 Up	Storm Influenced	380	168	0.4	0.045		0.00	0.06	0.04	8.2	1.81	0.09
6/25/96 12:00	TSC 1 Dn	Storm Influenced	280	144	0.6	0.065		0.12	0.05	0.05	10.8	1.50	0.12
		% Reduction	*26%*	*14%*	*-50%*	*-44%*		*0%*	*17%*	*-25%*	*-32%*	*17%*	*-33%*
8/9/96	TSC 1 Up	Storm Influenced	36	25	0.6	0.017	0	0.10	0.06	0.06	1.5	0.28	0.11
8/9/96	TSC 1 Dn	Storm Influenced	30	23	0.3	0.014	0	0.10	0.04	0.04	1.6	0.23	0.03
		% Reduction	*17%*	*8%*	*50%*	*18%*	*0%*	*0%*	*33%*	*33%*	*-7%*	*18%*	*73%*
8/22/96	TSC 1 Up	Storm Influenced	55	47	0.6	0.122	0	0.00	0.01	0.04	23.1	0.37	0.05
8/22/96	TSC 1 Dn	Storm Influenced	99	43	0.5	0.108	0	0.00	0.01	0.02	5.4	0.28	0.05
		% Reduction	*-80%*	*9%*	*17%*	*11%*	*0%*	*0%*	*0%*	*50%*	*77%*	*24%*	*0%*

Table 12: Comparison of Upstream vs. Downstream for TSC-2, TSC-3, TSC-4, and TSC-5

Collection Date	Site	Type	SS	Turb	NO_3^--N	NO_2^--N	SO_4^{2-}	P	Fe	Zn	Cl^-	NH_3-N	Ni
8/9/96	TSC 2 Up	Storm Influenced	685	366	1.6	0.066	13	0.00	0.60	0.01		2.5	0.08
8/9/96	TSC 2 Dn	Storm Influenced	960	o/r	2.4	0.026	23	0.00	0.70	0.01		1.68	0.12
		% Reduction	*-40%*		*-50%*	*61%*	*-77%*	*0%*	*-17%*	*0%*	*0%*	*33%*	*-50%*
8/22/96	TSC 2 Up	Storm Influenced	396	264	4.1	0.261	25	0.00	0.37	0.01	30	1.72	0.04
8/22/96	TSC 2 Dn	Storm Influenced	334	232	4.3	0.283	43	0.00	0.26	0.01	40	1.50	0.05
		% Reduction	*16%*	*12%*	*-5%*	*-8%*	*-72%*	*0%*	*30%*	*0%*	*-33%*	*13%*	*-25%*
8/22/96	TSC 3 Up	Storm Influenced	396	305	1.2	0.050	0	0.00	0.55	0.02	50	1.85	0.04
8/22/96	TSC 3 Dn	Storm Influenced	394	303	1.0	0.043	0	0.00	0.50	0.00	30	1.71	0.00
		% Reduction	*1%*	*1%*	*17%*	*14%*	*0%*	*0%*	*9%*	*100%*	*40%*	*8%*	*100%*
8/22/96	TSC 4 Up	Storm Influenced	328	205	0.8	0.170	13	0.04	0.28	0.04	40	1.66	0.00
8/22/96	TSC 4 Dn	Storm Influenced	371	235	0.8	0.071	0	0.00	0.44	0.01	50	1.69	0.01
		% Reduction	*-13%*	*-15%*	*0%*	*58%*	*100%*	*100%*	*-57%*	*75%*	*-25%*	*-2%*	*0%*
8/22/96	TSC 5 Up	Storm Influenced	286	201	0.7	0.122	16	0.00	0.34	0.02	50	1.38	0.02
8/22/96	TSC 5 Dn	Storm Influenced	329	199	0.7	0.183	20	0.00	0.27	0.09	50	1.50	0.02
		% Reduction	*-15%*	*1%*	*0%*	*-50%*	*-25%*	*0%*	*21%*	*-350%*	*0%*	*-9%*	*0%*

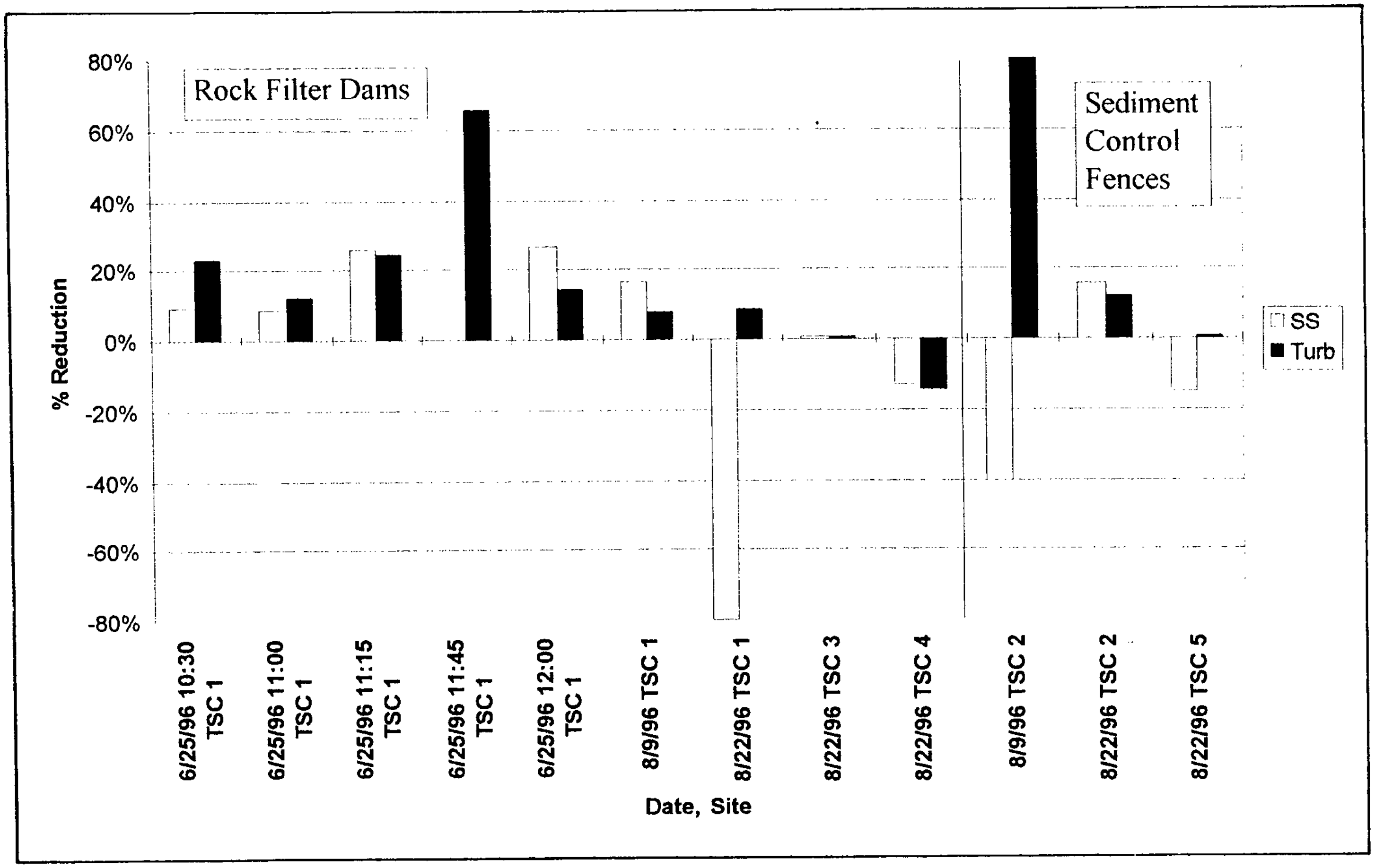

Figure 7: Suspended Solids and Turbidity - Percent Reductions at TSCs

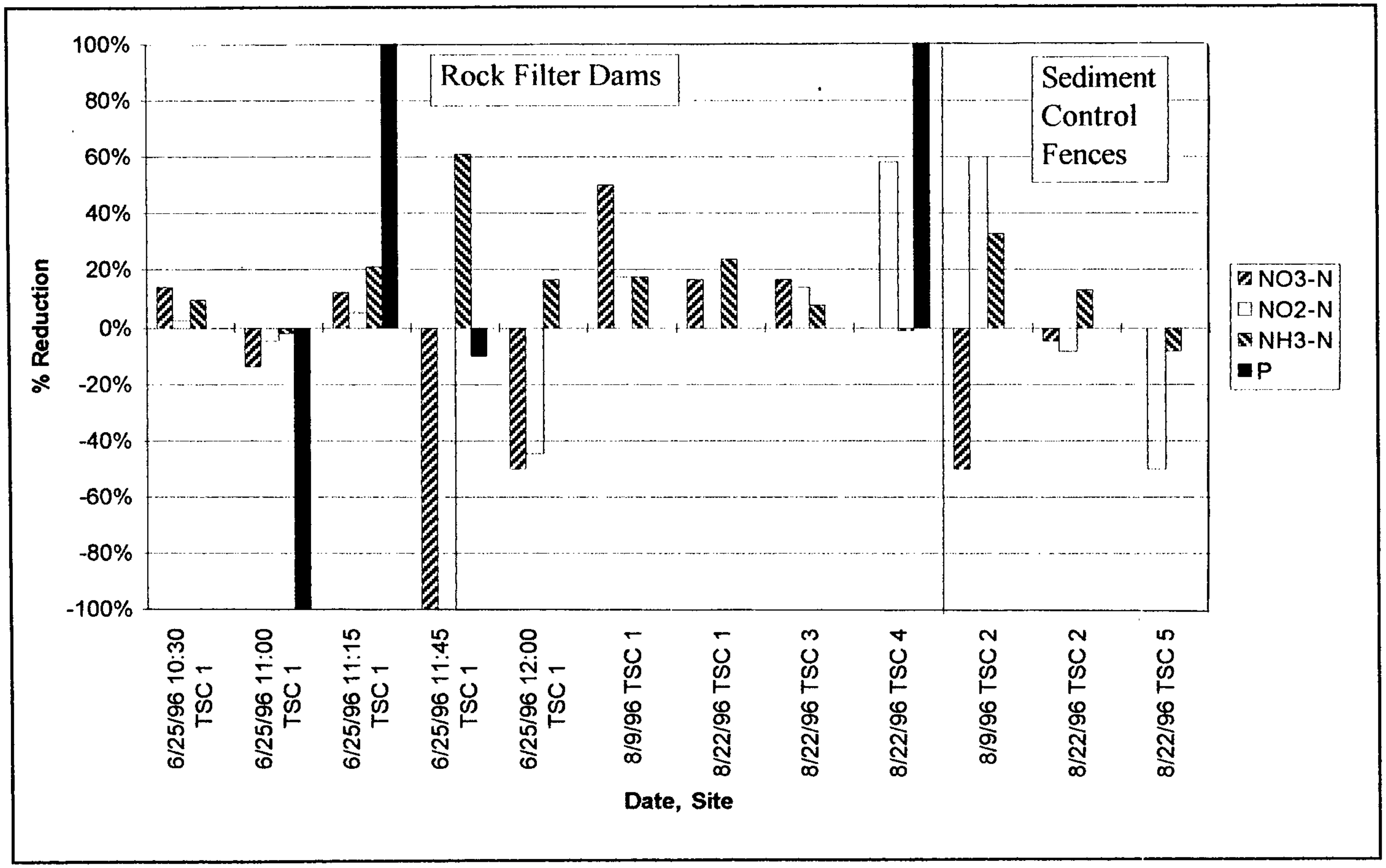

Figure 8: Nutrient Parameters - Percent Reductions at TSCs

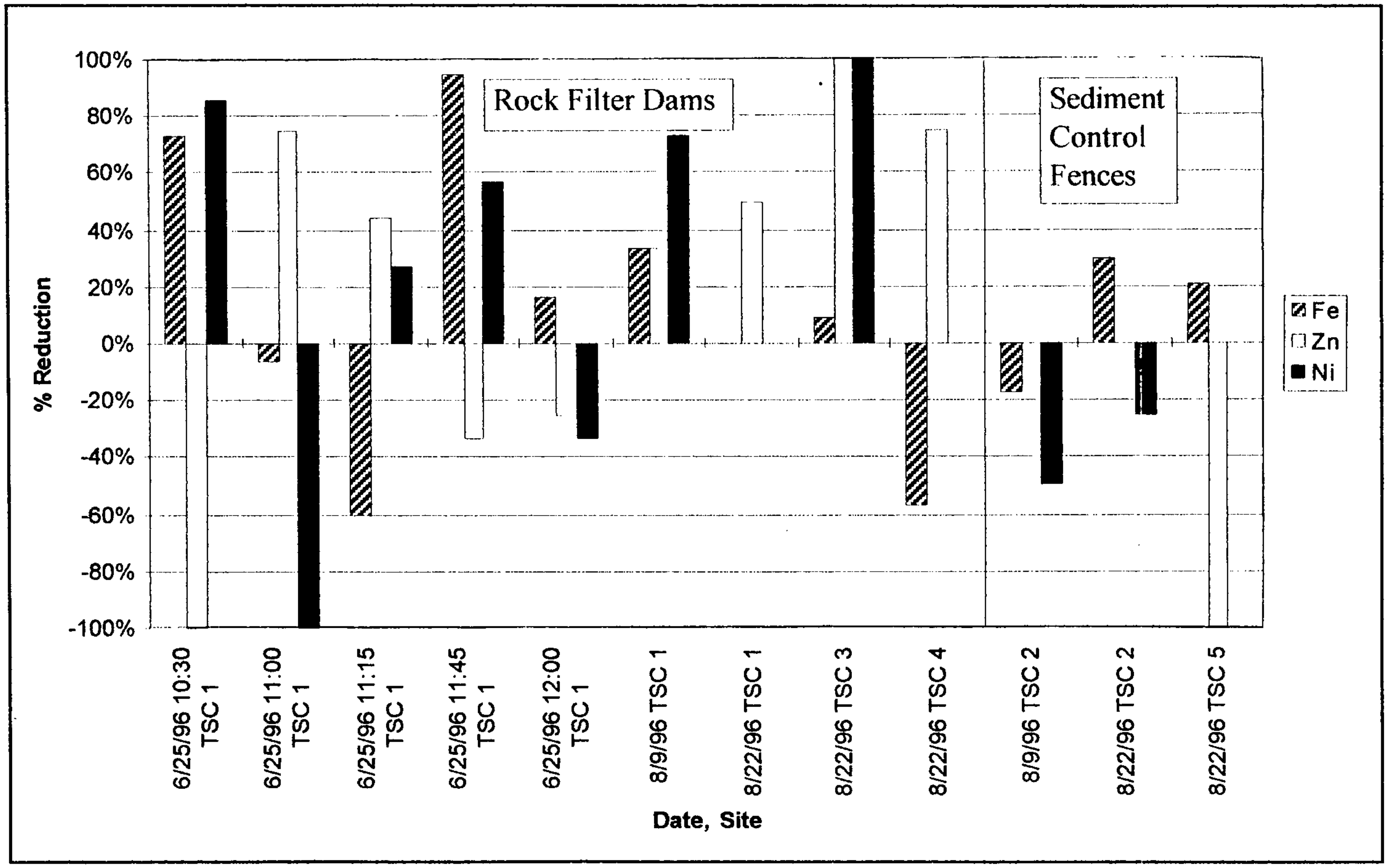

Figure 9: Metals - Percent Reduction at TSCs

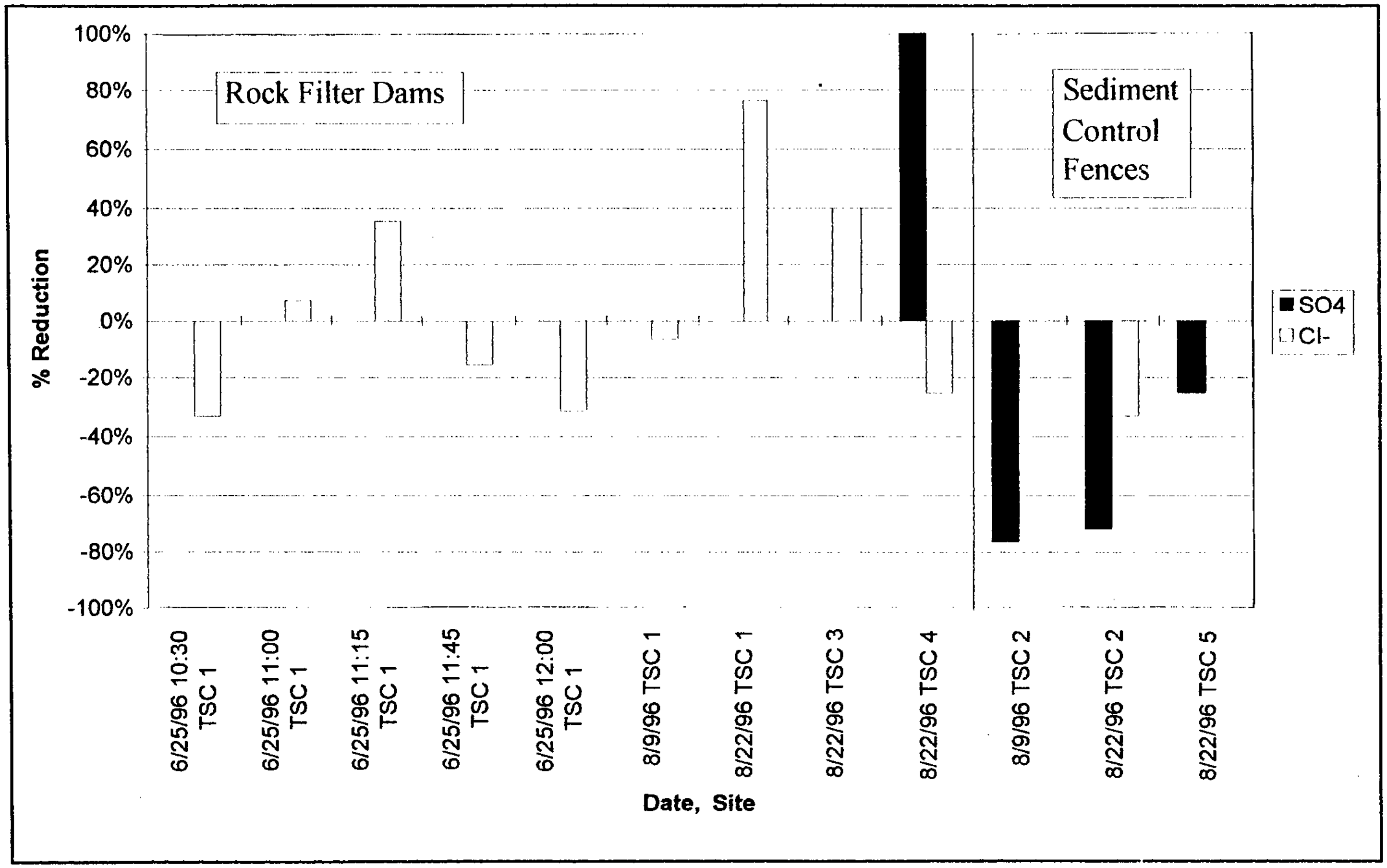

Figure 10: Sulfates and Chlorides - Percent Reduction at TSCs

Suspended Solids

Suspended solids showed the most consistent reduction from TSCs when the TSCs are judged as correctly implemented. For the June 25 storm event, TSC-1 exhibited reduction in nearly all cases as seen in Table 11, except for the 11:45 AM sample, where the short, intense rainfall in the period caused a large amount of soil disturbance (see next section "*Observations of Structural Control Installation and Use*").

Table 12 shows that the other two rock filter dams, TSC-3 and TSC-4, did not show suspended solids reductions for the samples taken there. Rock filter dam TSC-3 showed no change between upstream and downstream values, while TSC-4 showed an increase of suspended solids. This increase is interesting, since the downstream sample was taken inside the rock filter dam at the sewer inlet, where there was no soil downstream to disturb.

The sediment control fences, TSC-2 and TSC-5, did not show consistency in suspended solids reduction. TSC-2 showed a significant increase for the event of August 9, and a minor decrease for the event of August 22. The other sediment control fence, TSC-5, showed an increase of suspended solids concentration downstream.

It should be noted that the values of suspended solids concentrations measured were consistently high enough to form judgments of whether there was an increase or decrease without consideration of measurement error.

Turbidity

The results from the turbidity analyses are similar to those of the suspended solids, and serve to verify those observations. Again, TSC-1 generally showed reductions for the June 25 event, except for the 11:45 AM sample. The remaining rock filter dams, TSC-3 and TSC-4, showed no change and an increase, respectively.

For the sediment control fences, TSC-2 showed an unmeasurable increase for the event of August 9, and a decrease for the event of August 22, while TSC-5 showed no change for the event sampled.

Again, these values were high enough to form judgments of the occurrence of an increase or reduction of turbidity at the TSCs without consideration of measurement error.

Nitrate-Nitrogen (NO_3^--N)

It was more difficult to determine the effectiveness of the TSCs upon nitrates, since most results were close enough to be within measurement error. For TSC-1 this inability to discriminate was particularly true, although there was an instance of a percent increase during the June 25 event. The other rock filter dams showed negligible effects on nitrates.

For one event, TSC-2 showed a percent increase of nitrate-nitrogen, but the other data for TSC-2 and for TSC-5 showed a negligible effect.

Nitrite-Nitrogen (NO_2^--N)

Again, for TSC-1, several sample events showed no measurable effect upon nitrites, but others had both increases and decreases beyond measurement error. The other rock filter dams, TSC-3 and TSC-4, did show some reductions that were distinct and observable.

The sediment control fences also showed observable changes in nitrite-nitrogen. However, TSC-2 showed a reduction for one event and an increase for another, while TSC-5 showed an increase.

Sulfates (SO_4^{2-})

High turbidity in the storm influenced samples prevented many measurements of sulfates for most cases. In some of the remaining cases, there were no sulfates measured in upstream or downstream samples. In the one case where there were sulfates measured at a rock filter dam, TSC-4 showed a 100% reduction. All measurements of sulfates at sediment control fences showed observable increases in sulfates.

Phosphorus (P)

In several cases, phosphorus was not indicated by analysis of upstream or downstream samples. For TSC-1, results ranged from slight decreases to increases of

100% or larger. Rock filter dam TSC-4 showed a 100% reduction in one case. There was no phosphorus measured at any sediment control fence.

Iron (Fe)

For TSC-1, there were reductions of iron up to 100%, with the worst case being little or no effect. The other rock filter dams showed a possible reduction for TSC-3, and a definite increase for TSC-4. The sediment control fences showed an increase in iron for one case (TSC-2 on August 9) and reductions for the other two.

Zinc (Zn)

The analysis for zinc at TSC-1 showed measurable reductions in several cases, ranging from 33% to 88%. There were some cases showing no measurable effect. Both of the other rock filter dams also showed reductions in zinc. The sediment control fence TSC-2 showed no effect upon zinc, while TSC-5 showed a large increase of zinc downstream.

Chloride (Cl^-)

The chloride analyses results for TSC-1 split between percent increase and reduction. Only two cases showed no measurable effect. The other rock filter dams also split between percent increase and reduction. One result of the sediment control fence was unmeasurable due to turbidity (TSC-2 on August 9) and the other results split between increase and reduction as well. Since chloride is a dissolved ion, the amount measured should not change significantly. This result suggests a large scatter in the data.

Ammonia Nitrogen (NH_3-N)

Ammonia nitrogen was found to be reduced in most cases by the rock filter dam TSC-1. The other rock filter dams showed a reduction in the case of TSC-3, and no effect for TSC-4. Ammonia nitrogen was reduced by TSC-2, but increased at the other sediment control fence TSC-5.

Nickel (Ni)

While there was generally some reduction of nickel at TSC-1, there were cases where it increased. In one case, it increased five times downstream over the upstream concentration. Rock filter dam TSC-3 showed a reduction downstream, but TSC-4 showed no effect. The sediment control fences showed an increase for one case at TSC-2, and no effect for the other case nor at TSC-5.

Observations of Structural Control Installation and Use

During or after storm events, when stormwater flows were present, the opportunity was taken to observe the condition and performance of temporary sediment controls at the test site. This included, but was not limited to, the TSCs that were monitored for this thesis (TSC-1 through TSC-5).

Several sediment control fences were observed to be used incorrectly. While these structures were installed per the original SW3P, repeated observations showed that no action by the construction contractor was taken to correct obvious deficiencies during the research period. Sediment control fences were installed in drainage ditches that had flows during storm events that flowed over the top of the fence. Sediment control fences being used in the median, including TSC-2, were observed to have concentrations of water upstream that frequently flooded the roadway. These fences also had runoff flowing around the end of the fence, defeating the runoff detention function of the fence. The runoff that was passed through or around the fence also flowed over a devegetated area as shown in Figure 11. These deficiencies resulted in downstream runoff that was barely distinguishable from upstream, as described earlier. While TSC-5 did not demonstrate the deficiencies seen at TSC-2 and other sediment control fences, the results described earlier did not show conclusively that TSC-5 was an effective structural control.

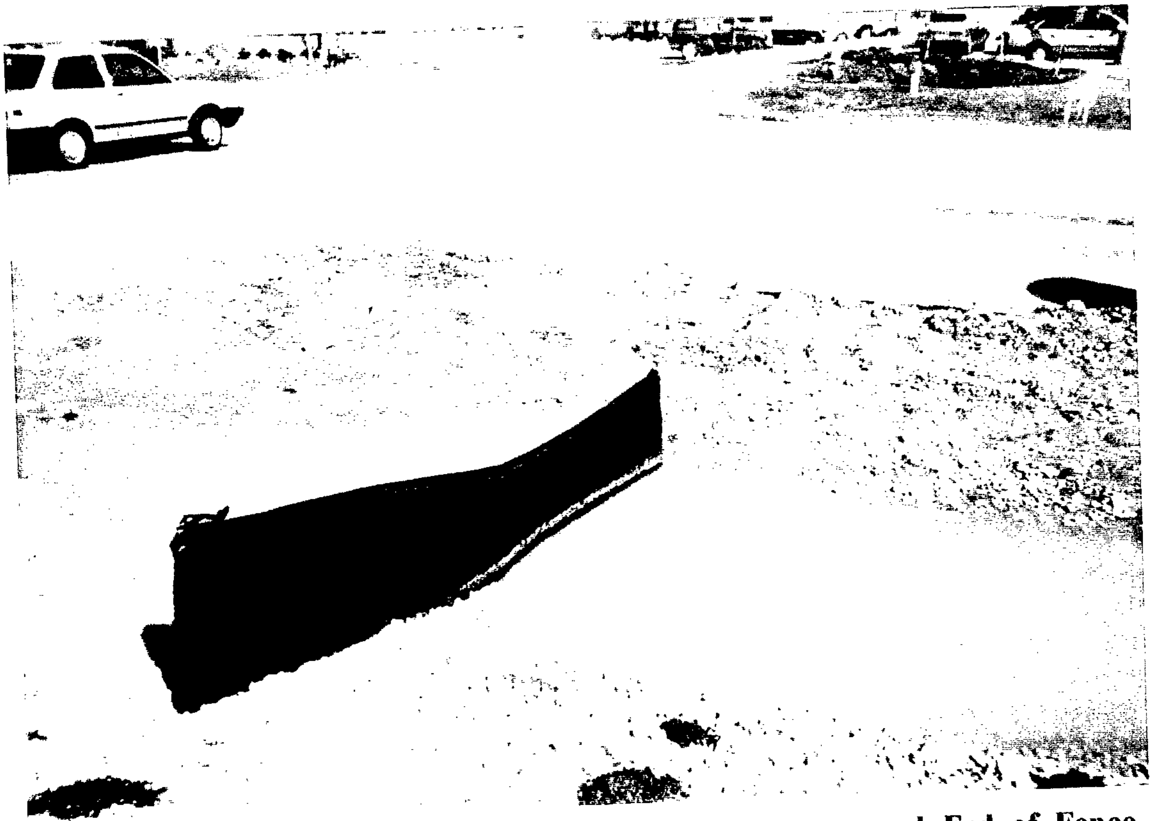

Figure 11: Sediment Control Fence with Runoff Flow around End of Fence Flowing onto Devegetated Area

Observations of the rock filter dams, including TSC-1, TSC-3, and TSC-4 also did not exhibit the faults seen with many of the sediment control fences, save for occasional roadway flooding. It was apparent that the rock filter dams were better suited to higher flow rates and water velocities than sediment control fences, and should have replaced sediment control fences at several locations.

During the June 25 storm event, the opportunity was taken to observe the effects of the storm and rainfall intensity changes upon the water quality of the runoff at the TSCs. Storm intensity increases increased the size and depth of the detention pond upstream of the TSC. Although this ponding should have improved the downstream water quality by increasing settling time, this effect seemed to be negated by the increased soil disturbance. In some instances, it appeared that the larger detention ponds increased the flow rates through the TSCs, also reducing detention times. In the case of TSC-2, this higher flow rate increased the flow around the sediment control fence. This bypassing caused increased disturbances downstream of the fence, since the soil downstream was also devegetated. It should be noted that this analysis is somewhat subjective, especially since time based storm samples were only taken for one storm event. However, Table 13 shows that the data from this one event indicates that the suspended solids and turbidity results track the rainfall intensity.

Table 13: Time-based Suspended Solids and Turbidity versus Rainfall for 6/25/96 Storm Event

Time	*10:30*	*11:00*	*11:15*	*11:30*	*11:45*	*12:00*
Cumulative Rainfall	0.00	0.25	0.25	0.30	0.58	0.68
Interval Rainfall	0.00	0.25	0.00	0.05	0.28	0.10
Upstream SS	440	310	366	430	1320	380
Downstream SS	400	283	270	225	o/r*	280
Upstream Turbidity	263	198	205	184	450	168
Downstream Turbidity	203	174	155	137	154	144

*o/r - out of range

Chapter 5 Summary and Conclusions

Summary

Due to the requirements of the Federal regulations requiring stormwater pollution prevention plans for highway construction sites greater than five acres, a highway construction site in the Houston area was selected to determine the effects of the highway construction. Samples were taken regularly at selected permanent monitoring sites, and samples were taken there and at temporary sediment controls during or after storm events. These samples were analyzed to determine the effectiveness of temporary sediment controls and to determine effects upon receiving waters at the site. A total of 22 sample sets were taken and analyzed. There were 13 bi-weekly ambient samples, three post-storm influenced samples, and six time-based storm samples.

Conclusions

Generally, there appeared to be no effect of the NASA Rd. 1 highway construction project upon the receiving waters at the test site. The downstream ambient versus storm influenced samples at the permanent monitoring sites showed little or no differences. Even those seen at PM-1, which had the most construction activity in the area, did not appear to be long term changes nor highly toxic with suspended solids and turbidity being among the most marked changes observed. Other research has shown these parameters to increase during a construction period and then return to normal levels after construction has ceased (Barrett et al. 1995a).

Comparing the upstream versus downstream samples at the permanent monitoring sites suggested that the stormwater flowing into the receiving-water body was indiscernible from the water of the water body in the immediate area. Coupled with the fact that in the majority of cases, the ambient versus storm influenced (downstream) samples were statistically the same, these results suggest that the stormwater runoff into the receiving-water bodies should have little or no effect upon the water bodies.

There appeared to be no consistent, quantifiable effect of the use of the temporary sediment controls for pollution reduction. The rock filter dams had a tendency to reduce the presence of the measured parameters, but not in any repeatable, predictable fashion. The sediment control fences were even less predictable, and TSC-2 showed marked inconsistencies between storm events. It was likely that the installation and use of the sediment control fences, where the flow was greater than for what they were designed, was the cause of most of the problems and inconsistencies with these devices.

While the temporary sediment controls had a debatable effect upon runoff water quality, the water quality of the receiving-water bodies where stormwater drained into them did not seem to be affected by the construction activity. Actual long term water quality changes downstream of the site versus upstream were beyond the scope of this segment of the study.

Overall, it appears that the methodology used to evaluate the temporary sediment controls and the effects of construction upon receiving-water bodies is sound. The test methods are relatively simple to use at the prescribed survey or screening level, and could be performed in the field for a limited number of parameters. The sample analysis results can clearly be used to compare upstream versus downstream measurements, and thus, in the case of temporary sediment controls, determine the effectiveness of any particular installation. The methodology also provides a method where the overall effects of construction can be monitored at permanent monitoring sites, provided regular ambient monitoring is performed.

Future Work

There are several areas that became apparent during the course of the research that would provide information and assist in developing further the results presented here. Some of these areas are now in progress by the author or other researchers. The others are under consideration.

Monitoring at the test site during and after construction should continue. Not only would further monitoring confirm the work presented here, but monitoring after construction has ended would confirm that levels did not change throughout the earth disturbing activities. This would also determine if there are any long term effects at receiving-water bodies for all parameters. Part of this continued work should include analysis of properly installed TSCs. This would be useful to determine if, in particular, sediment control fences can be an effective pollution abatement device.

Some aspects that are more involved and in depth than the work presented here might provide additional information that researchers in other areas may find helpful to correlate this project with others. This could include analysis of particle size upstream versus downstream, correlated with contaminant measurements to determine where the temporary sediment controls are useful for settling out particles of particular sizes. This may also show if there is a relationship between particle sizes and contaminant type. A correlation of the soil types and topography at this test site could also provide a comparison to other geotechnical areas. Finally, a controlled experiment at a simulated construction site would not only alleviate the difficulties encountered in traveling to a remote site during a storm event, but would help isolate sources and effectiveness of temporary sediment controls under controlled conditions such as rainfall intensity, slope, installation technique, etc. This controlled experiment could also be used to answer some potentially useful questions, such as the following:

1. Do the temporary sediment controls reduce stormwater flows, and if so, by how much?
2. If there is a decrease in the flow velocity, what is the relationship between this and the sedimentation upstream of the TSC?

3. What is the optimal location of the TSC with respect to storm sewer inlets, immediate topography, etc.?
4. Can the effectiveness of different TSCs be directly compared and this data be used to select the best TSC to be used for individual conditions?

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Appendix A: Hach DR/2000 Procedures Used and Corresponding USGS Methods

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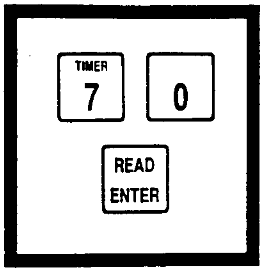
Method 8113

CHLORIDE (0 to 20.0 mg/L Cl^-)

For water and wastewater

Mercuric Thiocyanate Method*



1. Enter the stored program number for Chloride (Cl^-).

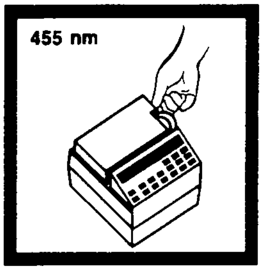
Press: **7 0 READ/ENTER**

The display will show:
DIAL nm TO 455

Note: DR/2000s with software versions 3.0 and greater will display "P" and the program number.

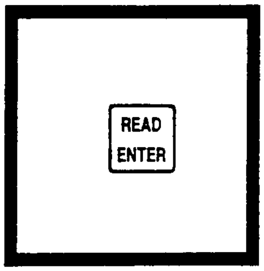
Note: Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.

Note: Samples can be stored for at least 28 days at room temperature in glass or plastic bottles.



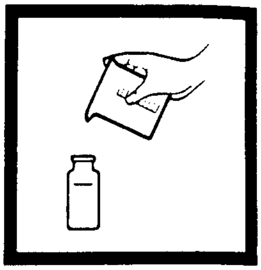
2. Rotate the wavelength dial until the small display shows:
455 nm

Note: Approach the wavelength setting from higher to lower values.



3. Press: **READ/ENTER**

The display will show:
mg/l Cl^-

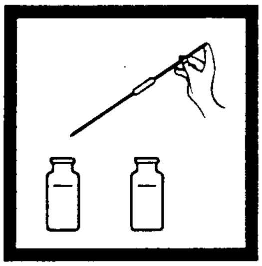


4. Fill a sample cell (the prepared sample) with 25 mL of sample.

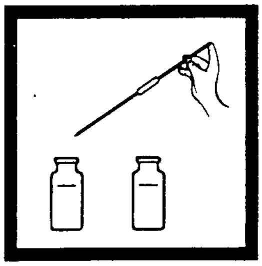
Note: Filter turbid samples through a moderately rapid filter paper before analysis.

Note: For proof of accuracy, use a 10.0 mg/L chloride standard solution (preparation given in the Accuracy Check) in place of the sample.

5. Fill another cell (the blank) with 25 mL of deionized water.

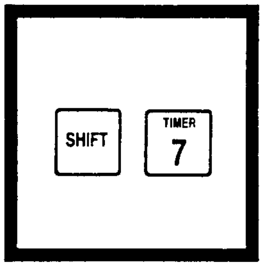


6. Pipet 2.0 mL of Mercuric Thiocyanate Solution into each cell. Swirl to mix.



7. Pipet 1.0 mL of Ferric Ion Solution into each sample cell. Swirl to mix.

Note: An orange color will develop if chloride is present.



8. Press: **SHIFT TIMER**

A two-minute period will begin.

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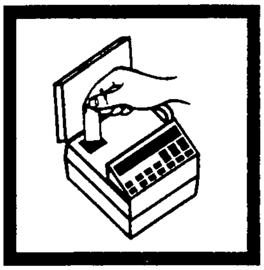
*Adapted from Zall, et. al., *Analytical Chemistry*, 28 (11) 1665 (1956)

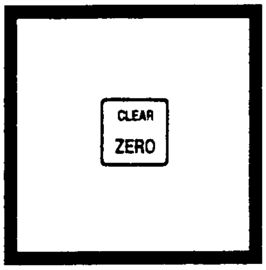


9. When the timer beeps, the display will show:

mg/l Cl⁻

Place the blank into the cell holder. Close the light shield.

Note: The Pour-Thru Cell can be used with this procedure.



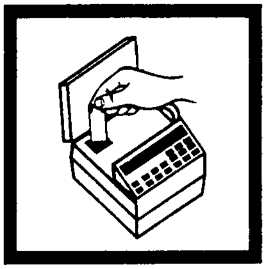
10. Press: **ZERO**

The display will show:

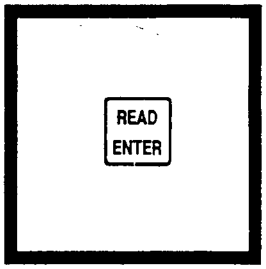
WAIT

then:

0.0 mg/l Cl⁻



11. Place the prepared sample into the cell holder. Close the light shield.



12. Press: **READ/ENTER**

The display will show:

WAIT

then the result in mg/L chloride (Cl⁻) will be displayed.

Note: In the constant-on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the results.

ACCURACY CHECK

Standard Additions Method

a) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of Chloride Standard Solution, 1000 mg/L as Cl⁻, to each of three 25-mL water samples. Mix each thoroughly.

b) Analyze each sample as described above.

c) The chloride concentration should increase 4.0 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see Standard Additions (Section I) for more information.

Standard Solution Method

Prepare a 10.0 mg/L chloride standard solution by diluting 5.00 mL of Chloride Standard Solution, 1000 mg/L to 500 mL with deionized water.

PRECISION

In a single laboratory using a standard solution of 10 mg/L chloride and two lots of reagent with the DR/2000, a single operator obtained a standard deviation of ± 0.3 mg/L chloride.

INTERFERENCES

The pH of the sample after addition of reagents should be about 2. If the sample is strongly acid or alkaline, adjust a portion of sample before testing to a pH of about 7. Use either 5.0 N Sodium Hydroxide Standard Solution or a 1:5 dilution of perchloric acid. Use pH paper, as most pH electrodes will contaminate the sample with chloride.

SUMMARY OF METHOD

Chloride in the sample reacts with mercuric thiocyanate to form mercuric chloride and liberate thiocyanate ion. Thiocyanate ions react with the ferric ions to form an orange ferric thiocyanate complex. The amount of this complex is proportional to the chloride concentration. See *Chemical Procedures Explained*, Appendix A, for more information. Chloride at these levels also can be determined directly using the Chloride Ion Selective Electrode (Cat. No. 44510-71)

REQUIRED REAGENTS

	Cat. No.
Chloride Reagent Set (50 Tests*)	23198-00
Includes: (1) 22122-14, (1) 22121-31	

Description	Quantity Required Per Test	Unit	Cat. No.
Ferric Ion Solution	2 mL	118 mL	22122-14
Mercuric Thiocyanate Solution	4 mL	236 mL	22121-31
Water, deionized	25 mL	3.78 L	272-17

REQUIRED APPARATUS

Pipet, volumetric, 1.0 mL	1	each	515-35
Pipet, volumetric, 2.0 mL	1	each	515-36
Pipet Filler, safety bulb	1	each	14651-00
OR			
Pipet, TenSette, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	1	50/pkg	21856-96

OPTIONAL REAGENTS

Chloride Standard Solution, 1000 mg/L as Cl	473 mL	183-11
Perchloric Acid, ACS, 70%	680 g	757-65
Sodium Hydroxide Standard Solution, 5.0 N	59 mL SCDB	2450-26

OPTIONAL APPARATUS

Filter Paper, folded, moderately rapid, 12.5 cm	100/box	692-57
Flask, erlenmeyer, 125 mL	each	505-43
Flask, volumetric, 500 mL	each	547-49
Funnel, filtering, polypropylene, 75 mm	each	1083-68
pH Paper, 1 to 11 pH	5 rolls/pkg	391-33
Pipet, volumetric, Class A, 5 mL	each	14515-37
Pour-Thru Cell Assembly Kit	each	45215-00

Chloride at these levels can be determined directly using the Chloride Ion Selective Electrode (Cat. No. 44510-71)

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224 toll-free for more information
Outside the U.S.A.—Contact the Hach office or distributor serving you.

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*50 tests equals 25 samples and 25 blanks.

Chloride, colorimetric, ferric thiocyanate

Parameter and Code:

Chloride, dissolved, I-1187-85 (mg/L as Cl): 00940

1. Application

This method may be used to determine dissolved chloride in water containing from 0.1 to 10 mg/L of chloride ion. It is particularly useful for the analysis of low-dissolved- solids-content water when low chloride concentrations must be determined accurately.

2. Summary of method

2.1 Chloride is determined by measurement of the color developed by the displacement of the thiocyanate ion from mercuric thiocyanate by chloride ion in the presence of ferric ion; an intensely colored ferric thiocyanate complex is formed:

$$2Cl^{-1} + Hg(SCN)_2 + 2Fe^{+3} \rightarrow HgCl_2 + 2Fe(SCN)^{+2}$$

2.2 The color is stable for at least 2 h and is proportional to the chloride-ion concentration. The color has a maximum absorbance at 460 nm.

2.3 For additional information see ASTM Method D 512-81, "Standard Methods of Testing for Chloride Ion in Water" (American Society for Testing and Materials, 1984).

3. Interferences

Bromide, iodide, cyanide, thiosulfate, and nitrite interfere. Color, depending upon its spectral absorbance, may interfere with the photometric measurement.

4. Apparatus

4.1 *Spectrometer* for use at 460 nm.

4.2 Refer to manufacturer's manual to optimize instrument.

5. Reagents

5.1 *Chloride standard solution I*, 1.00 mL= 1.00 mg Cl^{-1}: Dissolve 1.648 g primary standard NaCl crystals, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Chloride standard solution II*, 1.00 mL= 0.010 mg Cl^{-1}: Dilute 5.0 mL chloride standard solution I to 500.0 mL with demineralized water.

5.3 *Ferric ammonium sulfate solution*, 22.8 g/L: Dissolve 41.4 g $FeNH_4(SO_4)_2 \cdot 12H_2O$ in 570 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1 L with demineralized water.

5.4 *Mercuric thiocyanate solution*, 3 g/L: Dissolve 3 g $Hg(SCN)_2$ in 1 L 95-percent ethanol (denatured alcohol formula No. 3A is also satisfactory). Stir for 1 h to saturate the solvent; allow undissolved thiocyanate to settle, and then filter through a Pyrex-wool plug or a 0.45-µm membrane filter.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.250 mg of Cl^{-1} (25.0 mL max) into a 50-mL beaker and adjust the volume to 25.0 mL with demineralized water.

6.2 Prepare a demineralized-water blank and at least five standards containing from 0.0025 to 0.250 mg Cl^{-1}, and adjust the volume of each to 25.0 mL.

6.3 Add 2.0 mL $FeNH_4(SO_4)_2$ solution and stir. The samples will be essentially colorless at this point.

6.4 Add 2.0 mL $Hg(SCN)_2$ solution and stir.

6.5 After at least 10 min, but within 2 h, read the absorbance of each standard and sample against the blank at 460 nm, and, when necessary, make corrections for water color.

7. Calculations

7.1 Determine the milligrams chloride from a plot of absorbances of standards containing known amounts of Cl^{-1}.

7.2 Determine the chloride concentration in milligrams per liter as follows:

$$Cl^{-1}\ (mg/L) = \frac{1,000}{mL\ sample} \times mgCl^{-1}$$

8. Report

Report chloride, dissolved (00940), concentrations of less than 10 mg/L to the nearest 0.1 mg/L.

9. Precision

9.1 Data published by the American Society for Testing and Materials (1984) indicate the overall precision of the method to be

$$S_T = 0.054X$$

where

S_T=overall precision, milligrams per liter, and

X=concentration of Cl^{-1}, milligrams per liter.

9.2 Precision for one reference sample expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
6	1.4	33

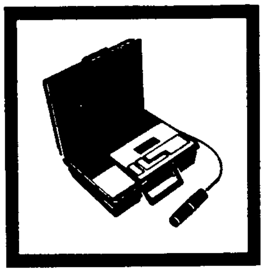
Reference

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 392-400.

Method 8160

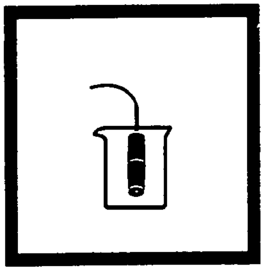
CONDUCTIVITY (0 to 199.9 µS/cm, 0 to 1.99 mS/cm, 0 to 19.9 mS/cm) For water and wastewater

Direct Measurement Method; EPA Approved



1. Prepare the Conductivity Meter for operation as directed in the instrument instruction manual and set the RANGE switch to the highest range.

Note: If the probe has been in storage, soaking may be necessary prior to use to ensure the probe is thoroughly wetted.



2. Immerse the probe in a beaker containing the sample solution. Move the the probe up and down and tap it on the beaker to free any bubbles from the electrode area.

Note: The probe must be immersed beyond the vent holes.

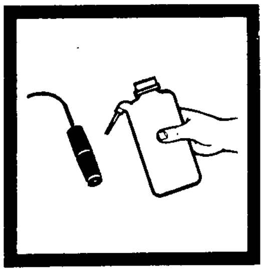
Note: The Hach Model 44600 Portable Conductivity/TDS Meter automatically compensates for sample temperature deviations from 25 °C. If the instrument being used does not have automatic temperature compensation, the sample temperature should be measured and the instrument's temperature control set accordingly.

Select
200 µS/cm
or
2 mS/cm
or
20 mS/cm

3. Select the appropriate range, beginning with the highest range and working down. Read the conductivity of the water sample.

Note: For proof of accuracy, use a Sodium Chloride Standard Solution in place of the sample (see Accuracy Check).

Note: If the reading is in the lower 10% of the range, switch to the next lower range. If the conductivity of the sample exceeds the range of the instrument, the sample may be diluted and the conductivity calculated. Dilution instructions for conductivity tests are included in the instrument manual. (This is not a simple volumetric dilution.)



4. Rinse the probe thoroughly with deionized water after each measurement.

Note: The probe needs to be submerged into several beakers of deionized water to rinse the probe internally.

Note: To display units as TDS press the TDS button. Or, to convert from microsiemens/cm or mg/L sodium chloride or mg/L as calcium carbonate, use Figure 1.

SAMPLING AND STORAGE

Collect samples in clean plastic or glass bottles. Samples should be analyzed as soon as possible after collection but can be stored at least 24 hours by cooling to 4 °C (39 °F) or below. The conductivity meter will compensate for any variation in temperature.

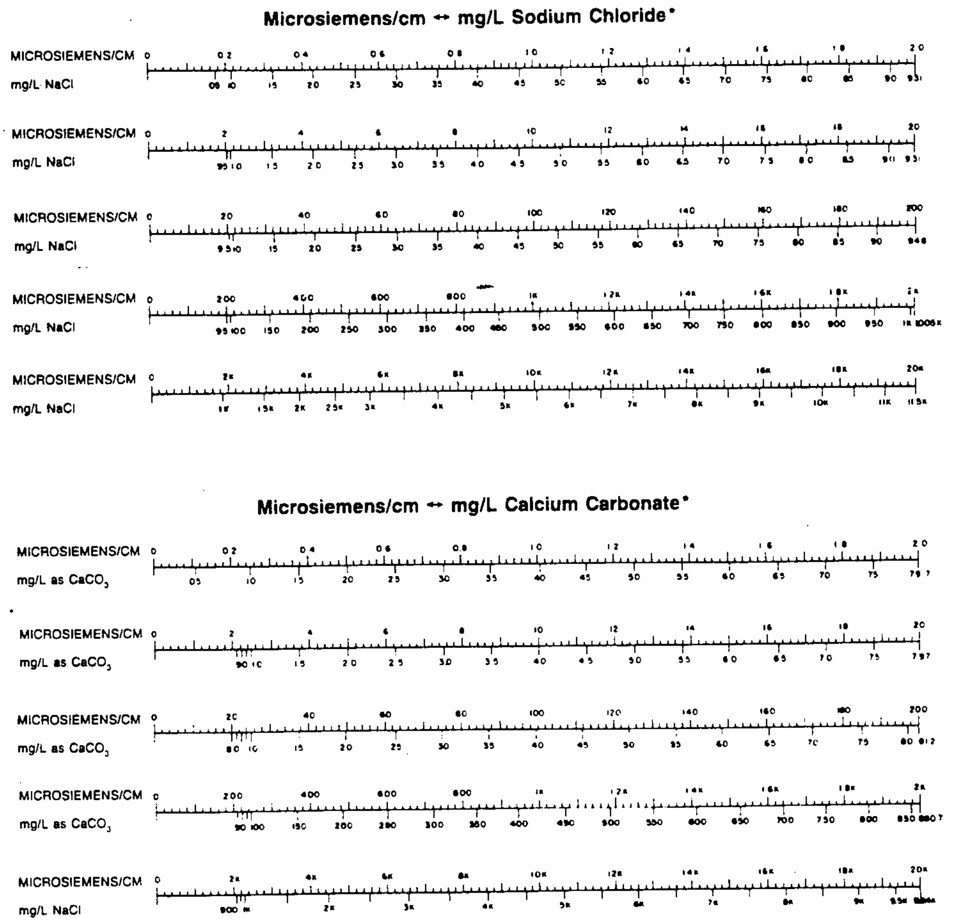
Water samples containing oils, greases or fats will coat the electrodes and affect the accuracy of the readings. Should this occur, the probe should be cleaned with a strong detergent solution and then thoroughly rinsed with demineralized water. Mineral buildup on the probe can be removed with 1:1 Hydrochloric Acid Solution.

CONVERSION

Conductivity readings obtained from the instrument meter can be converted to other units of measure by multiplying by or dividing into a conversion factor. The table that follows provides equations for easy conversions.

Table 1. Conversions

From	To	Equation
mS/cm	µS/cm	mS/cm × 1000
µS/cm	mS/cm	µS/cm × 0.001
µS/cm	µmhos/cm	µS/cm × 1
mS/cm	mmhos/cm	mS/cm × 1
µS/cm	mg/L TDS	µS/cm × 0.5
g/L TDS	mg/L TDS	g/L TDS × 1000
mS/cm	g/L TDS	mS/cm × 0.5
mg/L TDS	g/L TDS	mg/L TDS × 0.001
mg/L TDS	gpg TDS	mg/L TDS × 0.05842
g/L TDS	gpg TDS	g/L TDS × 58.42
µS/cm	ohms cm	1,000,000 ÷ µS/cm
mS/cm	ohms cm	1,000 ÷ mS/cm



*Estimated values—Assumes all ions establishing conducitivity are NaCl or $CaCO_3$, respectively.

FIGURE 1 **CONVERSION SCALES**

INTERFERENCES

When preparing to make conductivity measurements, some considerations should be given to the nature of the sample solution to ensure accurate results. For example, if measuring very low levels of conductivity, it may be necessary to protect the sample from atmospheric gases such as carbon dioxide or ammonia. These gases will dissolve readily in water, causing rapid changes in conductivity. To minimize these effects, the sample can be boiled and then placed in a covered container for cooling.

If the sample contains significant amounts of hydroxide, as can be the case with boiler water, it should be neutralized with Gallic Acid Solution to avoid erroneously high readings. Neutralize by adding four drops of Phenolphthalein Indicator Solution to 50 mL of sample. Add Gallic Acid Solution drop-wise until the pink color completely disappears.

ACCURACY CHECK

Standard Solution Method

Pour a Sodium Chloride Standard Solution with a conductivity in the same range as the sample into a beaker. Perform the conductivity measurement as described above. The conductivity reading should be the same as listed on the Sodium Chloride Standard Solution label if the meter is calibrated properly. Calibration can be performed using this solution. See instrument instruction manual.

SUMMARY OF METHOD

Electrolytic conductivity is the capacity of ions in a solution to carry electrical current and is the reciprocal of the solution resistivity. Current is carried by inorganic dissolved solids, such as chloride, nitrate, sulfate and phosphate anions, as well as such cations as sodium, calcium, magnesium, iron and aluminum. Organic materials like oils, phenols, alcohols and sugars do not carry electrical current well and thus do not have enough conductivity for a useful estimate of concentration.

The determination of conductivity is actually performed by measuring the resistance occurring in an area of the test solution defined by the probe design. A voltage is applied between the two electrodes immersed in the test solution, and the voltage drop caused by the resistance of the solution is used to calculate its conductivity per centimeter. The basic unit of measure for conductivity is the siemens (or mho), the reciprocal of the ohm in the resistance measurement. Because of the ranges normally found in aqueous solutions, millisiemens/cm (10^{-3} S) and microsiemens/cm (10^{-6} S) are used most frequently.

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Conductivity/TDS Meter, portable	1	each	44600-00

OPTIONAL REAGENTS AND APPARATUS

Beaker, poly, 100 mL	each	1080-42
Gallic Acid Solution	59 mL SCDB	14423-26
Hydrochloric Acid Solution, 1:1	500 mL	884-49
Phenolphthalein Indicator Solution, 1 g/L	15 mL* SCDB	1897-36
Sodium Chloride Standard Solution, 1.000 ± 0.010 mS/cm, 500 ± 5 mg/L TDS	118 mL	14400-14
Sodium Chloride Standard Solution, 1.990 ± 0.020 mS/cm, 995 ± 10 mg/L TDS	118 mL	2105-14
Sodium Chloride Standard Solution, 18 ± 0.050 mS/cm, 9,000 ± 25 mg/L TDS	118 mL	23074-14
Sodium Chloride Standard Solution, 180 ± 10 µS/cm, 90 ± 1 mg/L TDS	118 mL	23075-14
Wash bottle, 125 mL	each	620-14
Water, deionized	946 mL*	272-16

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224 toll-free for more information
Outside the U.S.A.—Contact the Hach office or distributor serving you.

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*Contact Hach for larger sizes.

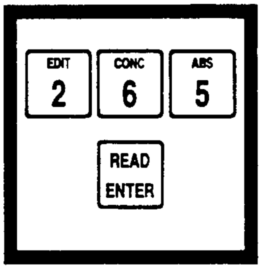
Method 8008

IRON, TOTAL (0 to 3.00 mg/L)

For water, wastewater and seawater

FerroVer Method* (Powder Pillows or AccuVac Ampuls); EPA Approved†—Digestion is required; see Section I.

USING POWDER PILLOWS



1. Enter the stored program number for iron (Fe), FerroVer, powder pillows.

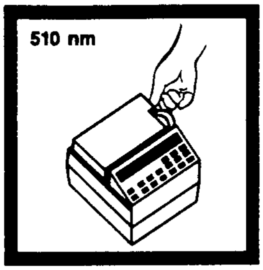
Press: **2 6 5 READ/ENTER**

The display will show:
DIAL nm TO 510

Note: DR/2000s with software versions 3.0 and greater will display "P" and the program number.

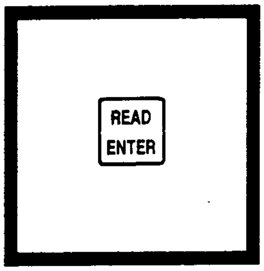
Note: Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.

Note: If samples cannot be analyzed immediately, see Sampling and Storage, below. Adjust pH of stored samples before analysis.



2. Rotate the wavelength dial until the small display shows:
510 nm

Note: Determination of total iron needs a prior digestion; use the mild, vigorous or Digesdahl digestion (Section I).

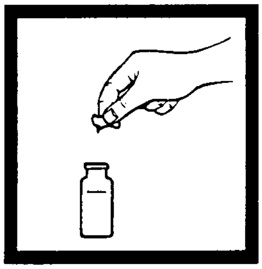


3. Press: **READ/ENTER**

The display will show:
mg/l Fe FV

4. Fill a cell with 25 mL of sample.

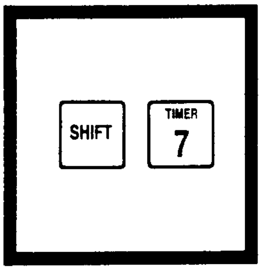
Note: For proof of accuracy, use a 1.0 mg/L iron standard solution (preparation given in the Accuracy Check) in place of the sample.



5. Add the contents of one FerroVer Iron Reagent Powder Pillow to the sample cell (the prepared sample). Swirl to mix.

Note: An orange color will form if iron is present.

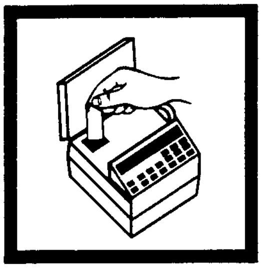
Note: Accuracy is not affected by undissolved powder.



6. Press: **SHIFT TIMER**

A three minute reaction period will begin.

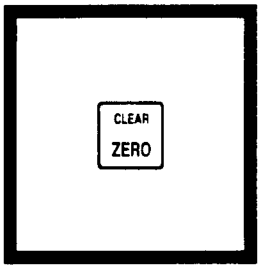
Note: Samples containing visible rust should be allowed to react at least five minutes.



7. When the timer beeps, the display will show:
mg/l Fe FV
Fill another sample cell (the blank) with 25 mL of sample. Place it into the cell holder.

Note: For turbid samples, treat the blank with one 0.2-gram scoop of RoVer Rust Remover. Swirl to mix.

Note: The Pour-Thru Cell can be used with this procedure.



8. Press: **ZERO**

The display will show:
WAIT
then:
0.00 mg/l Fe FV

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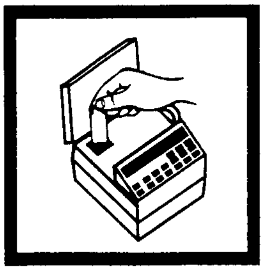
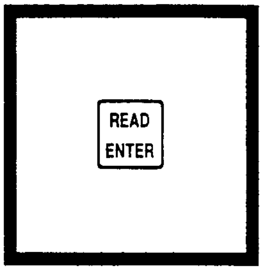
*Adapted from *Standard Methods for the Examination of Water and Wastewater*
†*Federal Register*, 45 (126) 43459 (June 27, 1980)



9. Within thirty minutes after the timer beeps, place the prepared sample into the cell holder. Close the light shield.

Note: If more than five minutes elapse after the timer beeps, ZERO SAMPLE may appear. If so, remove the prepared sample. Insert the blank. Press: ZERO. Insert the prepared sample.

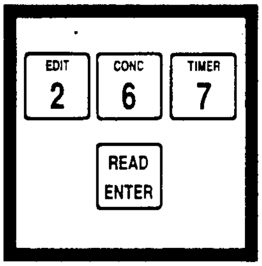


10. Press: **READ/ENTER**

The display will show:
WAIT
then the result in mg/L iron will be displayed.

Note: In the constant-on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.

USING ACCUVAC AMPULS



1. Enter the stored program number for iron (Fe), AccuVac ampuls.

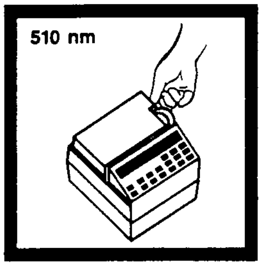
Press: **2 6 7 READ/ENTER**

The display will show:
DIAL nm TO 510

Note: DR/2000s with software versions 3.0 and greater will display "P" and the program number.

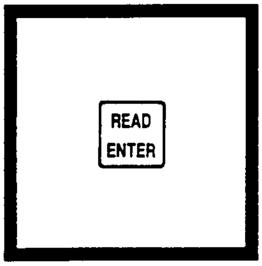
Note: Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.

Note: If samples cannot be analyzed immediately, see Sampling and Storage, below. Adjust pH of stored samples before analysis.



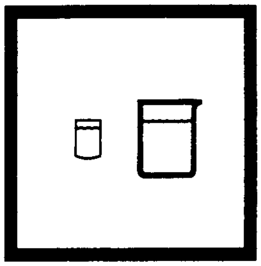
2. Rotate the wavelength dial until the small display shows:
510 nm

Note: Determination of total iron needs a prior digestion; use the mild, vigorous or Digesdahl digestion (Section I).



3. Press: **READ/ENTER**

The display will show:
mg/l Fe FV AV



4. Fill a zeroing vial (the blank) with at least 10 mL of sample. Collect at least 40 mL of sample in a 50-mL beaker.

Note: For proof of accuracy, use a 1.0 mg/L iron standard solution (preparation given in the Accuracy Check) in place of the sample.

SAMPLING AND STORAGE

Collect samples in acid-cleaned glass or plastic containers. No acid addition is necessary if analyzing the sample immediately. To preserve samples, adjust the pH to 2 or less with nitric acid (about 2 mL per liter). Preserved samples may be stored up to six months at room temperature. Adjust the pH to between 3 and 5 with 5.0 N sodium hydroxide Standard Solution before analysis. Correct the test result for volume additions; see Sampling and Storage, Volume Additions (Section I) for more information.

If only dissolved iron is to be determined, filter the sample before acid addition using the labware listed under Optional Apparatus.

ACCURACY CHECK

Standard Additions Method

a) Snap the neck off an Iron Voluette Ampule Standard Solution, 50 mg/L.

b) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard to three 25-mL water samples and mix thoroughly. (For AccuVac Ampuls, use 50-mL beakers.)

c) Analyze each sample as described above. The iron concentration should increase 0.2 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see Standard Additions (Section I) for more information.

Standard Solution Method

Prepare a 1.0 mg/L iron standard by diluting 1.00 mL of Iron Standard Solution, 100 mg/L Fe, to 100 mL with deionized water. Or, use the TenSette Pipet to dilute 1.0 mL of an Iron Voluette Ampule Standard Solution (50 mg/L) to 50 mL in a volumetric flask. Prepare this solution daily.

PRECISION

In a single laboratory, using a standard solution of 1.000 mg/L Fe and two representative lots of reagent with the DR/2000, a single operator obtained a standard deviation of ± 0.006 mg/L.

In a single laboratory, using a standard solution of 1.000 mg/L Fe and two representative lots of AccuVac ampuls with the DR/2000, a single operator obtained a standard deviation of ± 0.009 mg/L Fe.

INTERFERENCES

The following will not interfere below the levels shown:

Chloride	185,000 mg/L
Calcium	10,000 mg/L as $CaCO_3$
Magnesium	100,000 mg/L as $CaCO_3$
Molybdate Molybdenum	50 mg/L as Mo

A large excess of iron will inhibit color development. A diluted sample should be tested if there is any doubt about the validity of a result.

FerroVer Iron Reagent Powder Pillows and AccuVac Ampuls contain a masking agent which eliminates potential interferences from copper.

Samples containing some forms of iron oxide require the mild, vigorous or Digesdahl digestion (Section I). After digestion adjust the pH to between 2.5 and 5 with ammonium hydroxide.

Samples containing large amounts of sulfide should be treated as follows in a fume hood, or well ventilated area: Add 5 mL of hydrochloric acid to 100 mL of sample and boil for 20 minutes. Adjust the pH to between 2.5 and 5 with 5 N sodium hydroxide and readjust the volume to 100 mL with deionized water. Analyze as described above.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see Interferences, pH (Section I).

REAGENT STORAGE

FerroVer Reagent Powder Pillows are stable indefinitely if stored properly. A cool, dry atmosphere is recommended. The reagent can be checked by adding the contents of a pillow to about 25 mL of water containing visual rust (such as a few drops of Rust Suspension). If the orange color does not form, the reagent should be replaced.

SUMMARY OF METHOD

FerroVer Iron Reagent reacts with all soluble iron and most insoluble forms of iron in the sample, to produce soluble ferrous iron. This reacts with the 1,10 phenanthroline indicator in the reagent to form an orange color in proportion to the iron concentration. See *Chemical Procedures Explained,* Appendix A, for more information.

REQUIRED REAGENTS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
FerroVer Reagent Powder Pillows	1 pillow	50/pkg	854-66

REQUIRED REAGENTS (Using AccuVac Ampuls)

FerroVer Iron Reagent AccuVac Ampuls	1 ampul	25/pkg	25070-25

REQUIRED APPARATUS (Using Powder Pillows)

Clippers, for opening powder pillows	1	each	968-00

REQUIRED APPARATUS (Using AccuVac Ampuls)

Adapter, AccuVac vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Sample Cell, 10-mL with screw cap	1	each	21228-00

OPTIONAL REAGENTS

Ammonium Hydroxide, ACS	500 mL	106-49
Hydrochloric Acid Standard Solution, 6 N	500 mL	884-49
Hydrochloric Acid, ACS	500 mL	134-49
Iron Standard Solution, 100 mg/L	118 mL	14175-14
Iron Voluette Ampule Standard, 50 mg/L	16/pkg	14254-10
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	473 mL	2540-11
RoVer Rust Remover	454 g	300-01
Rust Suspension	15 mL DB	1279-36
Sodium Hydroxide Standard Solution, 5.0 N	118 mL MDB	2450-37
Water, deionized	3.78 L	272-17

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052-00
Ampule Breaker Kit	each	21968-00
Clippers, Shears 7-1/4"	each	23694-00
Cylinder, graduated, poly, 25 mL	each	1081-40
Cylinder, graduated, poly, 100 mL	each	1081-42
Filter Discs, glass, 47 mm	100/pkg	2530-00
Filter Holder, membrane	each	2340-00
Filter Pump	each	2131-00
Flask, erlenmeyer, 250 mL	each	505-46
Flask, filtering, 500 mL	each	546-49
Flask, volumetric, Class A, 50 mL	each	14574-41
Flask, volumetric, Class A, 100 mL	each	14574-42
Hot Plate, 3 1/2" diameter, 120 Vac	each	12067-01
Hot Plate, 3 1/2" diameter, 240 Vac	each	1206702
pH Meter, Hach One	each	43800-00
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
Pipet Filler, safety bulb	each	14651-00
Pipet, serological, 2 mL	each	532-36
Pipet, serological, 5 mL	each	532-37
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pour-Thru Cell Assembly Kit	each	45215-00
Spoon, measuring, 0.1 g	each	511-00
Spoon, measuring, 0.2 g	each	638-00

For Technical Assistance, Price and Ordering

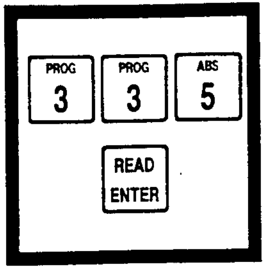
In the U.S.A.—Call 800-227-4224 toll-free for more information
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8037

NICKEL (0 to 1.80 mg/L Ni)

For water, wastewater and seawater

Heptoxime Method*; EPA Approved—Digestion is required; see Section I.



1. Enter the stored program number for nickel (Ni)—heptoxime method.

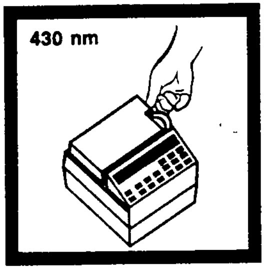
Press: **3 3 5 READ/ENTER**

The display will show:
DIAL nm TO 430

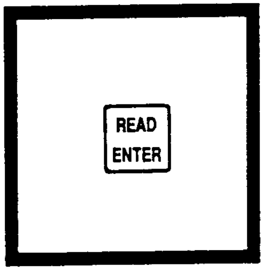
Note: DR/2000s with software versions 3.0 and greater will display "P" and the program number.

Note: Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.

Note: If sample cannot be analyzed immediately, see Sampling and Storage, following these steps. Adjust the pH of stored samples before analysis.

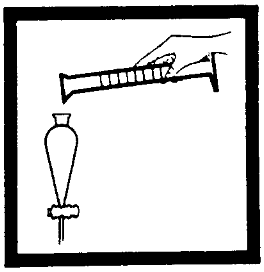


2. Rotate the wavelength dial until display shows:
430 nm



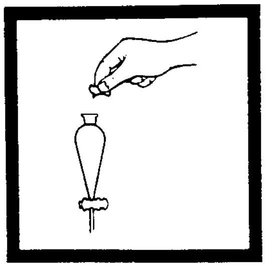
3. Press: **READ/ENTER**

The display will show:
mg/l Ni Hept

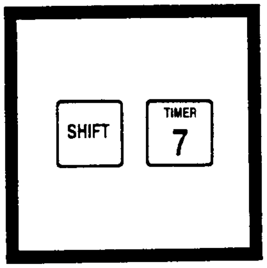


4. Measure 300 mL of sample in a 500-mL graduated cylinder. Pour into a 500-mL separatory funnel.

Note: For proof of accuracy, use a 1.0 mg/L nickel standard solution (preparation given in the Accuracy Check) in place of the sample.

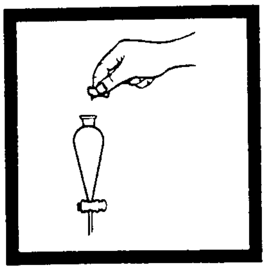


5. Add the contents of one Nickel 1 Reagent Powder Pillow to the funnel. Stopper. Shake to mix.

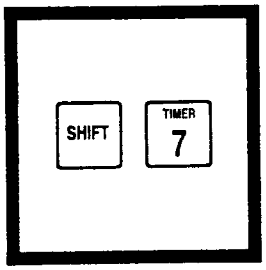


6. Press: **SHIFT TIMER**

A five-minute reaction period will begin.



7. When the timer beeps, add the contents of one Nickel 2 Reagent Powder Pillow to the funnel. Stopper. Shake to mix.



8. Press: **SHIFT TIMER**

A second five-minute reaction period will begin.

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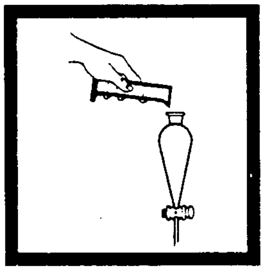
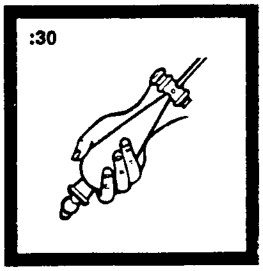
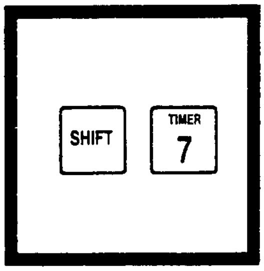
*Adapted from *Chemie Analytique*, 36 43 (1954)



9. When the timer beeps, add 10 mL of chloroform. Stopper. Shake gently. Invert. Open the stopcock to vent.

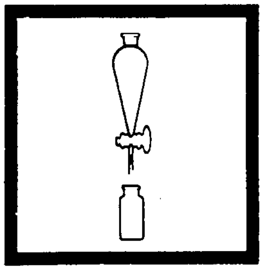


10. Close stopcock. Shake for 30 seconds.



11. Press: **SHIFT TIMER**

A third five-minute reaction period will begin. Shake the funnel several times over the five minute period.

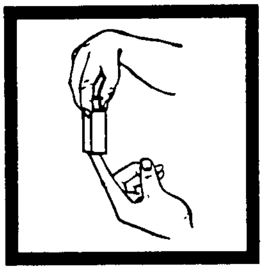


12. When the timer beeps, the display will show:

mg/l Ni Hept

Wait for the layers to separate. Insert a small cotton plug into the delivery tube of the funnel. Drain the chloroform layer into a sample cell (the prepared sample). Stopper.

Note: Use a plug about the size of a pea.

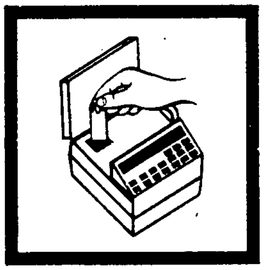


13. Repeat Steps 9 to 12 two additional times with 10-mL portions of chloroform.

Note: The five-minute reaction period is not necessary. Shake with chloroform to separate; then continue. Wait for layers to separate, then continue.

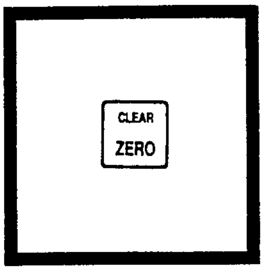
Note: The final volume of extract will be about 25 mL due to the slight solubility of chloroform in water.

Note: Swirl sample cell to mix extracts.



14. Fill a second cell (the blank) with 25 mL of chloroform. Stopper. Place the blank into the cell holder. Close the light shield.

Note: The Pour-Thru Cell cannot be used with this procedure.



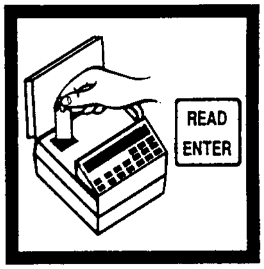
15. Press: **ZERO**

The display will show:

WAIT

then:

0.00 mg/l Ni Hept



16. Place the prepared sample into the cell holder. Close the light shield.

Press: **READ/ENTER**

The display will show:

WAIT

then the result in mg/L nickel will be displayed.

Note: In the constant-on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.

SAMPLING AND STORAGE

Collect samples in acid-washed plastic bottles. Adjust the sample pH to 2 or less with nitric acid (about 5 mL per liter). Preserved samples can be stored up to six months at room temperature. Adjust the sample pH to between 3 and 8 with 5.0 N Sodium Hydroxide Standard Solution just before analysis. Do not exceed pH 8 as this may cause some loss of nickel as a precipitate. Correct the test results for volume additions; see Sampling and Storage, Volume Additions, (Section I) for more information.

ACCURACY CHECK

Standard Additions Method

a) Snap the neck off a Nickel Voluette Ampule Standard Solution, 300 mg/L Ni.

b) Use the TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard to three 300-mL samples.

c) Analyze each sample as described above. The nickel concentration should increase 0.10 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see Standard Additions (Section I) for more information.

Standard Solution Method

Prepare a 1.0 mg/L nickel standard solution by diluting 50.0 mL of a 10 mg/L working standard solution to 500 mL in a volumetric flask. The working stock solution should be prepared daily by diluting 10.00 mL of Nickel Standard Solution, 1000 mg/L as Ni, to 1000 mL with deionized water.

Or, use the TenSette Pipet to add 1.0 mL of a Nickel Voluette Ampule Standard Solution, 300 mg/L Ni, into a 500-mL volumetric flask and dilute to volume with deionized water. This solution is 0.6 mg/L nickel.

PRECISION

In a single laboratory using standard solutions of 0.83 mg/L nickel and two representative lots of reagent with the DR/2000, a single operator obtained a standard deviation of ± 0.022 mg/L nickel.

INTERFERENCES

Cobalt, copper and iron interferences can be overcome by adding one or more additional Nickel 1 Reagent Powder Pillows in Step 5. The tolerance limits of these interferences are shown in the following table:

Tolerance Limits vs. Number of Nickel 1 Reagent Powder Pillows used.

	Tolerance Limit (mg/L)		
Pillows of Nickel 1 Reagent	**Cobalt**	**Copper**	**Iron**
1	1	10	20
2	7	16	65
3	13	22	110
4	18	28	155
5	25	35	200

A preliminary acid digestion is required to determine any suspended or precipitated nickel and to eliminate interference by organic matter. To eliminate this interference or to determine total recoverable nickel perform the EPA approved digestion in Digestion (Section I).

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see Interferences, pH (Section I).

SUMMARY OF METHOD

Nickel ion reacts with heptoxime to form a yellow-colored complex which is then extracted into chloroform to concentrate the color and enable a more sensitive determination. Chelating agents are added to the sample to overcome the interferences caused by cobalt, copper and iron. See *Chemical Procedures Explained*, Appendix A, for more information.

REQUIRED REAGENTS

	Cat. No.
Nickel Reagent Set (50 Tests)	22435-00

Includes: (3) 14458-11, (2) 2123-68, (2) 2124-68

Description	Quantity Required Per Test	Unit	Cat. No.
Chloroform, ACS	55 mL	473 mL	14458-11
Nickel 1 Reagent Powder Pillows	1 pillow	25/pkg	2123-68
Nickel 2 Reagent Powder Pillows	1 pillow	25/pkg	2124-68

REQUIRED APPARATUS

Clippers, for opening powder pillows	1	each	968-00
Cotton balls, absorbent	1	100/pkg	2572-01
Cylinder, graduated, 10 mL	1	each	508-38
Cylinder, graduated, 500 mL	1	each	508-49
Funnel, separatory, 500 mL	1	each	520-49
Ring, support, 4"	1	each	580-01
Stand, support, 127x203 mm	1	each	563-00
Stopper, hollow, poly, Size 0	2	6/pkg	14480-00

OPTIONAL REAGENTS

Nickel Standard Solution, 1000 mg/L Ni	100 mL	14176-42
Nickel Standard Solution, Voluette ampule, 300 mg/L Ni, 10 mL	16/pkg	14266-10
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	473 mL	2540-11
Sodium Hydroxide Standard Solution, 5.0 N	1 L	2450-53
Water, deionized	3.78 L	272-17

OPTIONAL APPARATUS

Flask, erlenmeyer, 500 mL	each	505-49
Flask, volumetric, Class A, 500 mL	each	14574-49
Flask, volumetric, Class A, 1000 mL	each	14574-53
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
Pipet, serological, 1 mL	each	532-35
Pipet, serological, 5 mL	each	532-37
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	pkg/50	21856-96
Pipet, volumetric, Class A, 10.00 mL	each	14515-38
Pipet Filler, safety bulb	each	14651-00
Pipet, volumetric, Class A, 50.00 mL	each	14515-41

For Technical Assistance, Price and Ordering

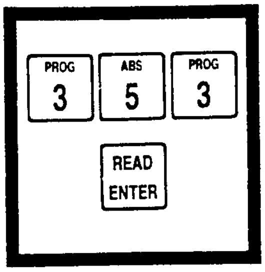
In the U.S.A.—Call 800-227-4224 toll-free for more information
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8171

NITRATE, MR (0 to 4.5 mg/L NO_3^--N) For water, wastewater and seawater*

Cadmium Reduction Method (Using Powder Pillows or AccuVac Ampuls)

USING POWDER PILLOWS



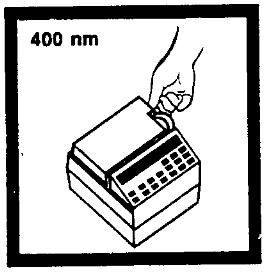
1. Enter the stored program number for medium range nitrate nitrogen (NO_3^--N)–powder pillows.

Press: **3 5 3 READ/ENTER**

The display will show:
DIAL nm TO 400

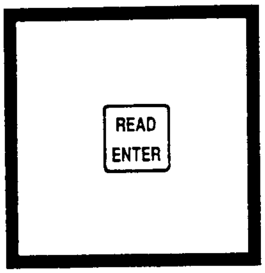
Note: DR/2000s with software versions 3.0 and greater will display "P" and the program number.

Note: Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.



2. Rotate the wavelength dial until display shows:
400 nm

Note: If sample cannot be analyzed immediately, see Sampling and Storage below. Adjust the pH of stored samples before analysis.



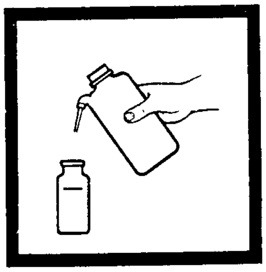
3. Press: **READ/ENTER**

The display will show:
mg/l N NO_3^- M

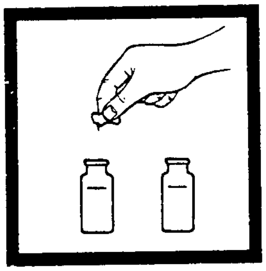
4. Fill a sample cell with 25 mL of sample (the prepared sample).

Note: For proof of accuracy, use a 1.0 mg/L Nitrate Nitrogen Standard Solution listed under Optional Reagents in place of the sample.

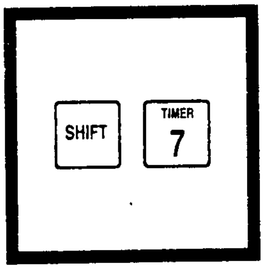
Note: A reagent blank must be determined on each new lot of NitraVer 5. Perform Steps 4 to 12 using deionized water as the sample. Subtract this value from each result obtained with this lot of reagent.



5. Fill another cell with 25 mL of deionized water (the blank).



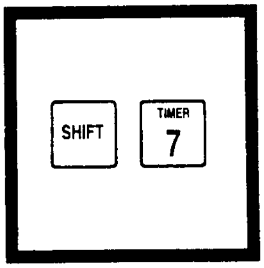
6. Add the contents of one NitraVer 5 Nitrate Reagent Powder Pillow to each cell. Stopper.



7. Press: **SHIFT TIMER**

A one-minute reaction period will begin. Shake until the timer beeps.

Note: Shaking time and technique influence color development. For most accurate results, make successive tests on a solution containing a known amount of nitrate and adjust the shaking time to obtain the correct result. See the Accuracy Check section for more information.



8. When the timer beeps, press: **SHIFT TIMER**

A five-minute reaction period will begin.

Note: A deposit of unoxidized metal will remain after the NitraVer 5 Nitrate Reagent Powder dissolves and will have no effect on test results.

Note: An amber color will develop if nitrate nitrogen is present.

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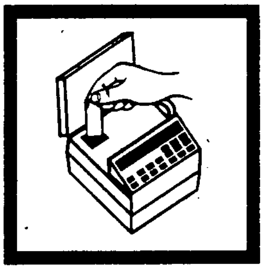
*Seawater requires a manual calibration; see Interferences.

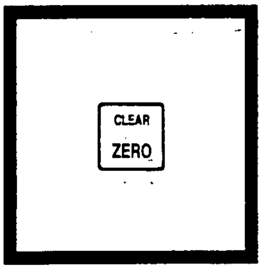


9. When the timer beeps, the display will show:

mg/l N NO_3^- M

Remove the stopper. Place the blank into the cell holder. Close the light shield.

Note: The Pour-Thru Cell can be used if rinsed well with deionized water after use.



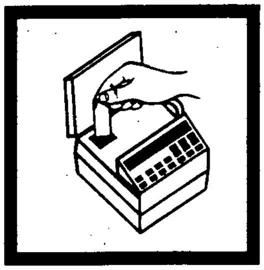
10. Press: **ZERO**

The display will show:

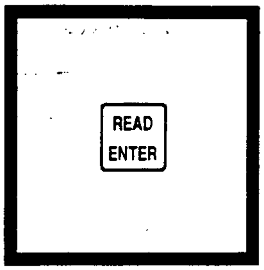
WAIT

then:

0.0 mg/l N NO_3^- M



11. Place the prepared sample into the cell holder. Close the light shield.



12. Press: **READ/ENTER**

The display will show:

WAIT

then the result in mg/L nitrate expressed as nitrogen (NO_3^--N) will be displayed.

Note: In the constant-on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.

Note: The results can be expressed as mg/L nitrate (NO_3^-) by multiplying the mg/L nitrate nitrogen (NO_3^--N) by 4.4.

Note: Rinse the sample cell immediately after use to remove all cadmium particles.

ACCURACY CHECK

Standard Additions Method

a) Measure 25 mL of sample into three cells or 50-mL beakers.

b) Use the TenSette Pipet to add 0.2, 0.4, and 0.6 mL of Nitrate Nitrogen Standard Solution, 100 mg/L as NO_3^--N, to the three samples. Mix well.

c) Analyze each sample as described above. The nitrate nitrogen (NO_3^--N) concentration should increase 0.8 mg/L for each 0.2 mL of standard added.

d) If these increases do not occur, see Standard Additions (Section I) for more information.

Standard Solution Method

A 1.0 mg/L Nitrate Nitrogen Standard Solution is available from Hach. Or, dilute 1.00 mL of Nitrate Nitrogen Standard Solution, 100 mg/L as NO_3^--N, to 100.0 mL with deionized water.

PRECISION

In a single laboratory using standard solutions of 2.0 mg/L nitrate nitrogen (NO_3^--N) and two representative lots of reagent with the DR/2000, a single operator obtained a standard deviation of ± 0.10 mg/L nitrate nitrogen.

In a single laboratory using a standard solution of 1.5 mg/L (NO_3^--N) and two representative lots of AccuVac ampuls with the DR/2000, a single operator obtained a standard deviation of ± 0.03 mg/L nitrate nitrogen.

INTERFERENCES

Compensate for nitrite interference as follows:

a) Add Bromine Water dropwise to the sample in Step 4 until a yellow color remains.

b) Add one drop of Phenol Solution to destroy the color.

c) Proceed with Step 4. Report results as total nitrate and nitrite.

Strong oxidizing and reducing substances will interfere. Ferric iron causes high results and must be absent. Chloride concentrations above 100 mg/L will cause low results. The test may be used at high chloride levels and in seawater, but a calibration must be performed using standards spiked to the same chloride concentration.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see Interferences, pH (Section I).

SUMMARY OF METHOD

Cadmium metal reduces nitrates present in the sample to nitrite. The nitrite ion reacts in an acidic medium with sulfanilic acid to form an intermediate diazonium salt which couples to gentisic acid to form an amber-colored product. See *Chemical Procedures Explained*, Appendix A, for more information.

REQUIRED REAGENTS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
NitraVer 5 Nitrate Reagent Powder Pillows	1 pillow	50/pkg	14034-66

REQUIRED REAGENTS (Using AccuVac Ampuls)

NitraVer 5 Nitrate Reagent AccuVac Ampul	1 ampul	25/pkg	25110-25

REQUIRED APPARATUS (Using Powder Pillows)

Clippers, for opening powder pillows	1	each	968-00
Stopper, rubber, size 2	2	12/pkg	2118-02

REQUIRED APPARATUS (Using AccuVac Ampuls)

Adapter, AccuVac	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Vial, zeroing	1	each	21228-00

OPTIONAL REAGENTS

Bromine Water, 30 g/L	29 mL*	2211-20
Nitrate Nitrogen Standard Solution, 1 mg/L as (NO_3^--N)	473 mL	2046-11
Nitrate Nitrogen Standard Solution, 100 mg/L as (NO_3^--N)	473 mL	1947-11
Phenol Solution	29 mL	2112-20
Sodium Hydroxide Standard Solution, 5.0 N	59 mL*	2450-26
Sulfuric Acid, ACS	500 mL*	979-49
Water, deionized	3.78 L	272-17

OPTIONAL APPARATUS

Cylinder, graduated, 25 mL	each	1081-40
Dropper, for 1-oz bottle	each	2258-00
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
Pipet Filler, safety bulb	each	14651-00
Pipet, serological, 2 mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, 1.0 mL	each	515-35
Pour-Thru Cell Assembly Kit	each	45215-00

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224 toll-free for more information
Outside the U.S.A.—Contact the Hach office or distributor serving you.

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*Contact Hach for larger sizes.

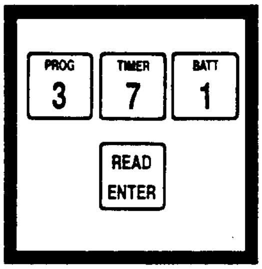
Method 8507

NITRITE, LR (0 to 0.300 mg/L NO_2^--N)

For water, wastewater and seawater

Diazotization Method (Powder Pillows or AccuVac Ampuls), EPA Approved*

USING POWDER PILLOWS



1. Enter the stored program number for low range nitrite nitrogen (NO_2^--N)–powder pillows.

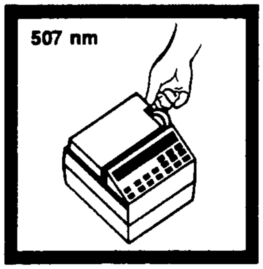
Press: **3 7 1 READ/ENTER**

The display will show:
DIAL nm TO 507

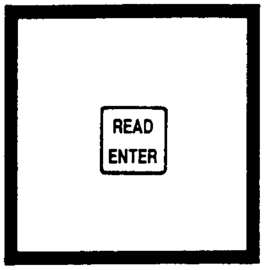
Note: DR/2000s with software versions 3.0 and greater will display "P" and the program number.

Note: Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.

Note: If sample cannot be analyzed immediately, see Sampling and Storage, below.



2. Rotate the wavelength dial until display shows:
507 nm



3. Press: **READ/ENTER**

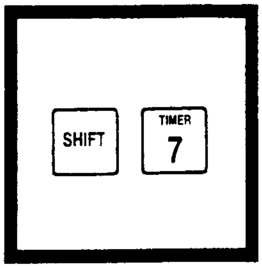
The display will show:
mg/l N NO_2^- L

4. Fill a sample cell with 25 mL of sample.

Note: For proof of accuracy, use a 0.10 mg/L nitrite nitrogen standard solution (preparation given in the Accuracy Check) in place of the sample.

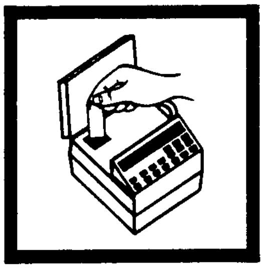
5. Add the contents of one NitriVer 3 Nitrite Reagent Powder Pillow (the prepared sample). Stopper. Shake to dissolve.

Note: A pink color will develop if nitrite nitrogen is present.



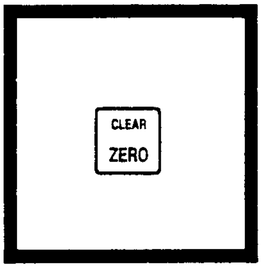
6. Press: **SHIFT TIMER**

A 15-minute reaction period will begin.



7. When the timer beeps, the display will show:
mg/l N NO_2^- L
Fill a second sample cell with 25 mL of sample (the blank). Place the blank into the cell holder.

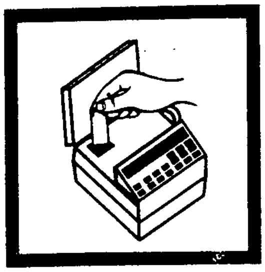
Note: The Pour-Thru Cell can be used with this procedure.



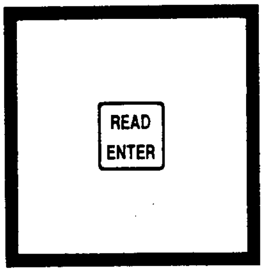
8. Press: **ZERO**

The display will show:
WAIT
then:
0.000 mg/l N NO_2^- L

**Federal Register*, 44(85) 25505 (May 1, 1979)



9. Remove the stopper. Place the prepared sample into the cell holder. Close the light shield.



10. Press: **READ/ENTER**

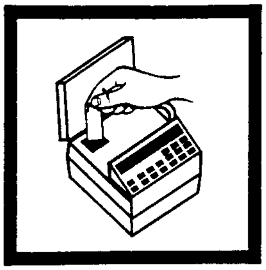
The display will show:

WAIT

then the result in mg/L nitrite expressed as nitrogen (NO_2^--N) will be displayed.

Note: In the constant-on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.

Note: The results can be expressed as mg/L nitrite (NO_2^-) by multiplying the mg/L nitrite nitrogen (NO_2^--N) by 3.3.



9. Place the blank into the cell holder. Close the light shield.

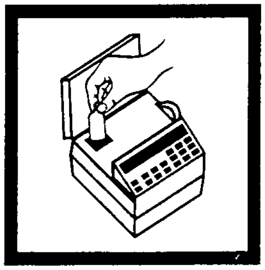
Press: **ZERO**

The display will show:

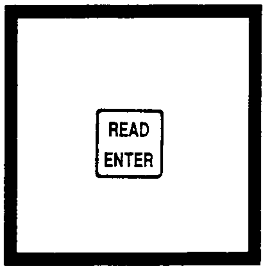
WAIT

then:

0.000 mg/l N NO_2^- L AV



10. Place the AccuVac ampul into the cell holder. Close the light shield.



11. Press: **READ/ENTER**

The display will show:

WAIT

then the result in mg/L nitrite expressed as nitrogen (NO_2^--N) will be displayed.

***Note:** In the constant-on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.*

***Note:** The results can be expressed as mg/L nitrite (NO_2^-) by multiplying the mg/L nitrite nitrogen (NO_2^--N) by 3.3.*

SAMPLING AND STORAGE

Collect samples in clean plastic or glass bottles.

Store at 4 °C (39 °F) or lower if the sample is to be analyzed within 24 to 48 hours. Warm to room temperature before running the test. For longer storage periods, add 4.0 mL of Mercuric Chloride Solution for each liter of sample taken and mix. Sample refrigeration is still required. Do not use acid preservatives.

ACCURACY CHECK

Standard Solution Method

Prepare a nitrite nitrogen standard solution by dissolving 0.493 grams of sodium nitrite, ACS, in 1000 mL of nitrite-free deionized water to give a 100 mg/L nitrite nitrogen (NO_2^--N) standard solution. This solution is not stable and should be prepared daily. Use a TenSette Pipet to dilute 1.00 mL of the stock solution to 1000 mL with nitrite-free deionized water to give a 0.10 mg/L (NO_2^--N) nitrite nitrogen standard solution. Prepare this solution immediately before use.

PRECISION

In a single laboratory using a standard solution of 0.100 mg/L nitrite nitrogen and two representative lots of powder pillow reagent with the DR/2000, a single operator obtained a standard deviation of ± 0.0011 mg/L nitrite nitrogen.

In a single laboratory using a standard solution of 0.100 mg/L nitrite nitrogen and two representative lots of AccuVac ampuls with the DR/2000, a single operator obtained a standard deviation of ± 0.0007 mg/L nitrite nitrogen.

INTERFERENCES

Strong oxidizing and reducing substances interfere. Cupric and ferrous ions cause low results. Ferric, mercurous, silver, bismuth, antimonous, lead, auric, chloroplatinate and metavanadate ions interfere by causing precipitation.

Very high levels of nitrate (100 mg/L nitrate as N or more) appear to undergo a slight amount of reduction to nitrite, either spontaneously or during the course of the test. A small amount of nitrite will be found at these levels.

SUMMARY OF METHOD

Nitrite in the sample reacts with sulfanilic acid to form an intermediate diazonium salt. This couples with chromotropic acid to produce a pink colored complex directly proportional to the amount of nitrite present. See *Chemical Procedures Explained,* Appendix A, for more information.

REQUIRED REAGENTS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
NitriVer 3 Nitrite Reagent Powder Pillows	1 pillow	50/pkg	14065-66

REQUIRED REAGENTS (Using AccuVac Ampuls)

Description	Quantity Required Per Test	Unit	Cat. No.
NitriVer 3 Nitrite Reagent AccuVac Ampul	1 ampul	25/pkg	25120-25

REQUIRED APPARATUS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
Clippers, for opening powder pillows	1	each	968-00
Stopper, hollow, polyethylene, No. 1	1	6/pkg	14480-01

REQUIRED APPARATUS (Using AccuVac Ampuls)

Description	Quantity Required Per Test	Unit	Cat. No.
Adapter, AccuVac Vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Vial, zeroing	1	each	21228-00

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Mercuric Chloride Solution	118 mL	14994-14
Sodium Nitrite, ACS	454 g	2452-01
Water, deionized	3.78 L	272-17

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Balance, analytical	each	22310-00
Flask, volumetric, 1000 mL	each	547-53
Pipet, serological, 10 mL	each	532-38
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, 1.0 mL	each	515-35
Pipet Filler, safety bulb	each	14651-00
Pour-Thru Cell Assembly Kit	each	45215-00

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224 toll-free for more information
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Nitrogen, nitrite, colorimetric, diazotization

Parameter and Code:

Nitrogen, nitrite, dissolved, I-1540-85 (mg/L as N): 00613

1. Application

This method may be used to analyze water containing between 0.01 and 0.6 mg/L of nitrite-nitrogen; samples containing greater concentrations need to be diluted.

2. Summary of method

Nitrite is diazotized with sulfanilamide, and the resulting diazo compound is coupled with N-1-naphthylethylenediamine dihydrochloride to form an intensely colored red compound, which is determined spectrometrically at 540 nm. Sulfanilamide and N-1-naphthylethylenediamine dihydrochloride are combined with a sodium acetate buffer to form a single reagent solution.

3. Interferences

Oxidizing agents interfere by oxidizing nitrite to nitrate. Sulfide also interferes. No other substance commonly occurring in natural water interferes with this method.

4. Apparatus

4.1 Spectrometer for use at 540 nm.

4.2 Refer to manufacturer's manual to optimize instrument.

5. Reagents

5.1 *Color-buffer solution*: Add 105 mL concentrated HCl (sp gr 1.19), 5.0 g sulfanilamide, and 0.5 g N-1-naphthylethylenediamine dihydrochloride to 250 mL demineralized water. Stir until dissolved. Add 136 g $CH_3COONa{\cdot}3H_2O$ or 82 g CH_3COONa and stir until dissolved. Dilute to 500 mL with demineralized water. When 2 mL of this solution is added to 50 mL demineralized water, the resultant solution should have a pH of 1.8. Store the color-buffer solution in the dark and protect from nitrogen oxides that may be in the atmosphere. The solution is stable for several months.

5.2 *Nitrite-nitrogen standard solution I*, 1.00 mL = 0.50 mg NO_2-N: Dissolve 3.038 g KNO_2 in demineralized water and dilute to 1,000 mL. This and the following nitrite standard solution are not stable indefinitely; their concentrations must be checked frequently.

5.3 *Nitrite-nitrogen standard solution II*, 1.00 mL = 0.05 mg NO_2-N: Dilute 100.0 mL nitrite-nitrogen standard solution I to 1,000 mL with demineralized water.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.03 mg NO_2-N (50.0 mL max) into a 100-mL beaker and adjust the volume to 50.0 mL with demineralized water (NOTE 1).

NOTE 1. If the sample has a pH greater than 10 or less than 4 (or greater than 600 mg/L alkalinity or acidity), adjust to approx pH 6 with 3*M* HCl or 2.5*M* NaOH.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 50.0 mL (NOTE 2).

NOTE 2. If the samples were preserved with mercuric chloride fortified with sodium chloride, add an equivalent amount to the blank and standards.

6.3 Add 2.0 mL color-buffer solution and mix.

6.4 Allow the color to develop for at least 15 min and measure the absorbances of the sample and standards against that of the blank.

7. Calculations

7.1 Determine milligrams of nitrite-nitrogen in each test sample from a plot of absorbances of standards.

7.2 Determine the nitrite-nitrogen concentration in milligrams per liter as follows:

$$NO_2\text{-N (mg/L)} = \frac{1{,}000}{\text{mL aliquot}} \times \text{mg } NO_2\text{-N in sample}$$

8. Report

Report nitrogen, nitrite dissolved (00613), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved nitrite-nitrogen for 19 samples within the range of 0.005 to 2.17 mg/L may be expressed as follows:

$$S_T = 0.096X + 0.006$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of nitrite-nitrogen, milligrams per liter.

The correlation coefficient is 0.9094.

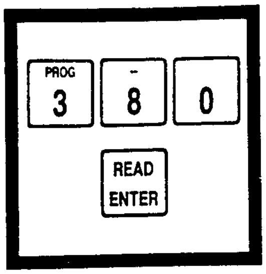
9.2 Precision for dissolved nitrite-nitrogen for five of the 19 samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
11	0.005	100
11	.050	20
14	.556	9
17	1.48	8
10	2.17	12

Method 8038

NITROGEN, AMMONIA (0 to 2.50 mg/L NH_3-N) For water, wastewater*, seawater*

Nessler Method†, EPA Approved—Distillation is required.



1. Enter the stored program number for ammonia nitrogen (NH_3-N).

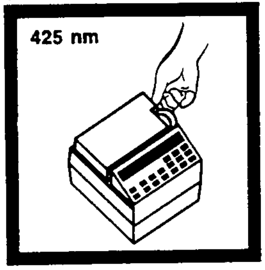
Press: **3 8 0 READ/ENTER**

The display will show:
DIAL nm TO 425

Note: DR/2000s with software versions 3.0 and greater will display "P" and the program number.

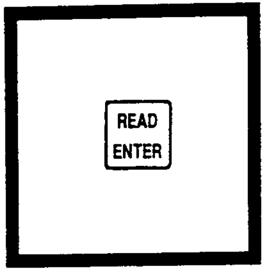
Note: Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.

Note: If samples cannot be analyzed immediately, see Sampling and Storage below. Adjust pH of stored samples before analysis.



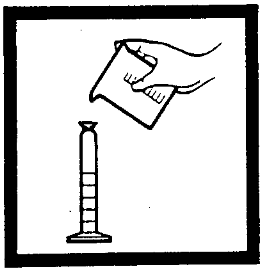
2. Rotate the wavelength dial until the small display shows:
425 nm

Note: This test is sensitive to the wavelength setting. To assure accuracy, run the test using a 1.0 mg/L standard solution and deionized water blank. Repeat Steps 9 to 12 at slightly different wavelengths, setting the dial from higher to lower values, until the correct result is obtained. The wavelength should be 425 ± 2 nm. Always set this wavelength by approaching from high to low values.



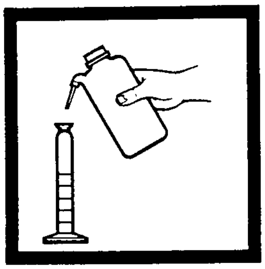
3. Press: **READ/ENTER**

The display will show:
mg/l N NH_3 Ness

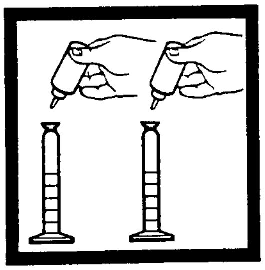


4. Fill a 25-mL mixing graduated cylinder (the prepared sample) to the 25-mL mark with sample.

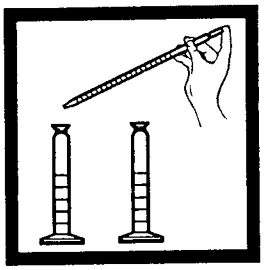
Note: For proof of accuracy, use a 1.0 mg/L Ammonia Nitrogen Standard Solution (listed under Optional Reagents) in place of the sample.



5. Fill another 25-mL mixing graduated cylinder (the blank) with deionized water.



6. Add three drops of Mineral Stabilizer to each cylinder. Invert several times to mix. Add three drops of Polyvinyl Alcohol Dispersing Agent to each cylinder by holding the dropping bottle straight. Invert several times to mix.

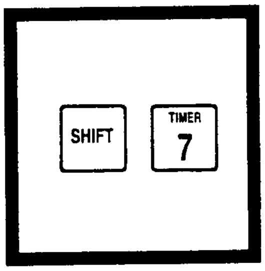


7. Pipet 1.0 mL of Nessler Reagent into each cylinder. Stopper. Invert several times to mix.

Note: Nessler Reagent is toxic and corrosive. Pipet carefully.

Note: A yellow color will develop if ammonia is present. (The reagent will cause a faint yellow color in the blank.)

Note: Use a pipet filler when pipetting.



8. Press: **SHIFT TIMER**

A one-minute reaction period will begin.

Note: Continue with Step 9 while timer is running.

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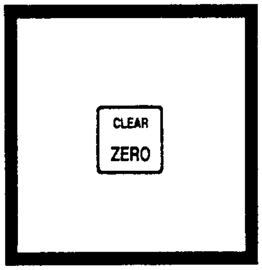
*Requires distillation

†Adapted from *Standard Methods for the Examination of Water and Wastewater*

9. Pour each solution into a sample cell.

Note: The Pour-Thru Cell can be used with this procedure. If the Pour-Thru Cell Assembly Kit is used, periodically clean the cell by pouring a few sodium thiosulfate pentahydrate crystals into the cell funnel. Flush it through the funnel and cell with enough deionized water to dissolve. Rinse out the crystals.



10. When the timer beeps, the display will show:

mg/l N NH_3 Ness

Place the blank into the cell holder. Close the light shield.

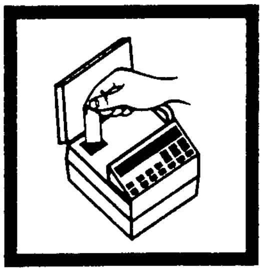
Press: **ZERO**

The display will show:

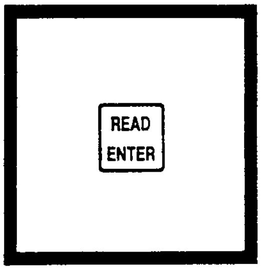
WAIT

then:

0.00 mg/l N NH_3 Ness



11. Place the prepared sample into the cell holder. Close the light shield.



12. Press: **READ/ENTER**

The display will show:

WAIT

then the result in mg/L ammonia expressed as nitrogen (NH_3-N) will be displayed.

Note: Do not wait more than five minutes after reagent addition (Step 7) before performing Step 12.

Note: The results may be expressed as mg/L ammonia (NH_3) or mg/L ammonium (NH_4^+) by multiplying the result by 1.22 or 1.29 respectively.

Note: In the constant-on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.

SAMPLING AND STORAGE

Collect samples in clean glass or plastic bottles. If chlorine is present, add one drop of 0.1 N sodium thiosulfate for each 0.3 mg/L Cl_2 in a 1-liter sample. Preserve the sample by reducing the pH to 2 or less with sulfuric acid (at least 2 mL). Store at 4 °C (39 °F) or less. Preserved samples may be stored up to 28 days. Warm samples to room temperature. Neutralize with 5 N sodium hydroxide before analysis. Correct the test result for volume additions; see Sampling and Storage, Volume Additions, (Section I) for more information.

ACCURACY CHECK

Standard Additions Method

a) Snap the neck off an Ammonium Nitrogen Voluette Ampule Standard Solution, 50 mg/L NH_3-N.

b) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard to three 25-mL samples. Mix each thoroughly.

c) Analyze each sample as described above. The nitrogen concentration should increase 0.20 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see Standard Additions (Section I) for more information.

Standard Solution Method

To check accuracy, use a 1.0 mg/L Ammonium Nitrogen Standard Solution listed under Optional Reagents. Or, this can be prepared by diluting 1.00 mL of solution from a Voluette Ampule Standard For Ammonium Nitrogen to 50.0 mL with deionized water.

PRECISION

In a single laboratory using standard solutions of 1.00 mg/L ammonia nitrogen (NH_3-N) and two representative lots of reagent with the DR/2000, a single operator obtained a standard deviation of ± 0.015 mg/L.

INTERFERENCES

A solution containing a mixture of 500 mg/L $CaCO_3$ and 500 mg/L Mg as $CaCO_3$ does not interfere. If the hardness concentration exceeds these concentration, extra Mineral Stabilizer should be added. Iron and sulfide interfere by causing a turbidity with Nessler Reagent. Residual chlorine must be removed by addition of sodium arsenite solution. Use two drops to remove each mg/L Cl from a 250 mL sample. Sodium thiosulfate can be used in place of sodium arsenite. See Sampling and Storage Section.

Less common interferences, such as glycine, various aliphatic and aromatic amines. organic chloramines, acetone, aldehydes and alcohols may cause greenish or other off colors or turbidity. It may be necessary to distill the sample if these compounds are present.

Seawater samples may be analyzed by addition of 1.0 mL (27 drops) of Mineral Stabilizer to the sample before analysis. This will complex the high magnesium concentrations found in seawater, but the sensitivity of the test will be reduced by 30 percent due to the high chloride concentration. For best results, perform a calibration, using standards spiked to the equivalent chloride concentration, or distill the sample as described below.

DISTILLATION

a) Measure 250 mL of sample into a 250-mL graduated cylinder and pour into a 400-mL beaker. Destroy chlorine, if necessary, by adding 2 drops of Sodium Arsenite Solution per mg/L Cl_2.

b) Add 25 mL of Borate Buffer Solution and mix. Adjust the pH to about 9.5 with 1 N sodium hydroxide solution. Use a pH meter.

c) Set up the general purpose distillation apparatus as shown in the Hach Distillation Apparatus Manual. Pour the solution into the distillation flask. Add a stir bar.

d) Use a graduated cylinder to measure 25 mL of deionized water into a 250-mL erlenmeyer flask. Add the contents of one Boric Acid Powder Pillow. Mix thoroughly. Place the flask under the still drip tube. Elevate so the end of the tube is immersed in the solution.

e) Turn on the heater power switch. Set the stir control to 5 and the heat control to 10. Turn on the water and adjust to maintain a constant flow through the condenser.

f) Turn off the heater after collecting 150 mL of distillate. Immediately remove the collection flask to avoid sucking solution into the still. Measure the distillate to assure 150 mL was collected (total volume 175 mL).

g) Adjust the pH of the distillate to about 7 with 1 N sodium hydroxide. Use a pH meter.

h) Pour the distillate into a 250-mL volumetric flask; rinse the erlenmeyer with deionized water. Add the rinsings to the volumetric. Dilute to the mark. Stopper. Mix thoroughly. Analyze as described above.

SUMMARY OF METHOD

The Mineral Stabilizer complexes hardness in the sample. The Polyvinyl Alcohol Dispersing Agent aids the color formation in the reaction of Nessler Reagent with ammonium ions. A yellow color is formed proportional to the ammonia concentration. See *Chemical Procedures Explained,* Appendix A, for more information.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Nessler Reagent	2 mL	500 mL	21194-49
Mineral Stabilizer	6 drops	59 mL* SCDB	23766-26
Polyvinyl Alcohol Dispersing Agent	6 drops	59 mL* SCDB	23765-26
Water, deionized	25 mL	3.78 L	272-17

REQUIRED APPARATUS

Cylinder, graduated, mixing, tall form, 25 mL	2	each	21190-40
Pipet, serological, 1 mL	2	each	532-35
Pipet Filler, safety bulb	1	each	14651-00

OPTIONAL REAGENTS

Borate Buffer Solution	946 mL	14709-16
Boric Acid Powder Pillows	50/pkg	14817-66
Nitrogen, Ammonia Standard Solution, 1 mg/L NH_3-N	473 mL	1891-11
Nitrogen, Ammonia Standard Solution, Voluette ampule, 50 mg/L NH_3-N	16/pkg	14791-10
Sodium Arsenite Solution, 5 g/L	118 mL MDB	1047-37
Sodium Hydroxide Standard Solution, 5.0 N	118 mL* MDB	2450-37
Sodium Hydroxide Standard Solution, 1.0 N	118 mL* MDB	1045-37
Sodium Thiosulfate Solution, 0.1 N	118 mL* MDB	323-37
Sulfuric Acid, ACS	500 mL*	979-49

OPTIONAL APPARATUS

Beaker, 400 mL	each	500-48
Cylinder, graduated, 25 mL	each	508-40
Cylinder, graduated, 250 mL	each	508-46
Distillation apparatus general purpose accessories	each	22653-00
Distillation heater and support apparatus set, 115 V	each	22744-00
Distillation heater and support apparatus set, 230 V	each	22744-02
Dropper, plastic, 0.5 and 1.0-mL marks	10/pkg	21247-10
Flask, erlenmyer, 250-mL	each	505-46
Flask, volumetric, 50 mL	each	547-41
Flask, volumetric, 250 mL	each	547-46
pH Meter, Hach One	each	43800-00
Pipet, serological, 2 mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, 1 mL	each	515-35
Pour-Thru Cell Assembly Kit	each	45215-00
Thermometer, −20 to 105 °C	each	1877-01

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Outside the U.S.A.—Contact the Hach office or distributor serving you.

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*Contact Hach for larger sizes.

Nitrogen, ammonia, colorimetric, distillation-nesslerization

Parameters and Codes:

Nitrogen, ammonia, dissolved, I-1520-85 (mg/L as N): 00608
Nitrogen, ammonia, total, I-3520-85 (mg/L as N): 00610

1. Application

This method may be used to analyze water and water-suspended sediment containing from 0.01 to 2 mg/L of ammonia-nitrogen. Samples containing more than 2 mg/L need either to be diluted or to be analyzed by an alternative titration procedure.

2. Summary of method

2.1 The sample is buffered to a pH of 9.5 to minimize hydrolysis of organic nitrogen compounds. Ammonia is distilled from the buffered solution, and an aliquot of the distillate then is nesslerized. Essentially, nesslerization is the reaction between potassium mercuric iodide and ammonia to form a red-brown colloidal complex of mercuric ammono-basic iodide:

$$2(HgI_2{\cdot}2KI) + 2NH_3 \rightarrow NH_2Hg_2I_3 + 4KI + NH_4I$$

Concentrations of ammonia are then determined by standard spectrometric measurements. Alternatively, the distillate may be titrated with standard sulfuric acid solution.

2.2 Additional information on the principle of the determination was given by Blaedel and Meloche (1963).

3. Interferences

3.1 Calcium, magnesium, iron, and sulfide interfere with the nesslerization, but the interference of the metals is eliminated by the distillation, and sulfide can be precipitated in the distillation flask by lead carbonate.

3.2 Some organic compounds may distill with the ammonia and form colors with nessler reagent, which cannot satisfactorily be read with the spectrophotometer. Under such conditions, the sample should be titrated with standard sulfuric acid solution.

4. Apparatus

4.1 *Cylinder, graduated, with ground-glass stopper*, 50-mL capacity (Corning No. 3002 or equivalent).

4.2 *Kjeldahl distillation apparatus*, 500-mL flasks.

4.3 *Spectrophotometer*, for use at 425 nm.

4.4 Refer to the manufacturer's manual to optimize instrument.

5. Reagents

5.1 *Ammonia standard solution I*, 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL.

5.2 *Ammonia standard solution II*, 1.00 mL = 0.010 mg NH_3-N: Dilute 10.0 mL ammonia standard solution I to 1,000 mL with ammonia-free water. Prepare fresh daily.

5.3 *Borate buffer solution*: Dissolve 9.54 g $Na_2B_4O_7{\cdot}10H_2O$ in ammonia-free water. Adjust the pH to 9.5 with 1*M* NaOH (approx 15 mL) and dilute to 1 L with ammonia-free water.

5.4 *Boric acid solution*, 20 g/L: Dissolve 20 g H_3BO_3 in 800 mL ammonia-free water and dilute to 1 L.

5.5 *Nessler reagent*—CAUTION: **HgI_2 is a deadly poison, and the reagent must be so marked:** Dissolve 100 g HgI_2 and 70 g KI in a small volume of ammonia-free water. Add this mixture slowly, with stirring, to a cooled solution of 160 g NaOH in 500 mL ammonia- free water and dilute to 1 L. Allow the reagent to stand at least overnight and filter through a fritted-glass crucible.

5.6 *Sodium hydroxide solution,* 1*M*: Dissolve 40 g NaOH in ammonia-free water and dilute to 1 L.

6. Procedure

6.1 Rinse all glassware with ammonia-free water before beginning this determination.

6.2 Free the distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace using nessler reagent—**CAUTION: deadly poison.**

6.3 Pipet a volume of well-mixed sample containing less than 1.0 mg ammonia-nitrogen (250 mL max) into a 500-mL distillation flask, and adjust the volume to approx 250 mL with ammonia-free water (NOTE 1).

NOTE 1. For water-suspended sediment mixtures, rinse the pipet with ammonia-free water to remove adhering particles and combine with sample.

6.4 Add 12.5 mL borate buffer solution, and adjust the pH to 9.5 with 1*M* NaOH, if necessary.

6.5 Immediately distill at a rate of not more than 10 mL or less than 6 mL per min; collect the distillate in a 250-mL volumetric flask containing 25 mL boric acid solution. The tip of the delivery tube must be below the surface of the boric acid solution in the receiving flask.

6.6 Collect approx 200 mL of distillate, dilute to 250 mL with ammonia-free water, and mix.

6.7 Pipet an aliquot of distillate containing less than 0.1 mg ammonia-nitrogen (50.0 mL maximum) into a glass-stoppered, graduated mixing cylinder, and adjust the volume to 50.0 mL with ammonia-free water.

6.8 Prepare a blank of ammonia-free water and a series of standards in glass-stoppered, graduated mixing cylinders. Add 5 mL boric acid solution to each, and adjust the volume of each to 50.0 mL.

6.9 Add 1.0 mL nessler reagent—**CAUTION: deadly poison**—to each blank, standard, and sample. Stopper and invert several times to mix thoroughly.

6.10 Allow the solutions to stand at least 10 min, but not more than 30 min.

6.11 Determine the absorbance of each test sample and standard against the blank.

7. Calculations

7.1 Determine milligrams of ammonia-nitrogen in each sample from a plot of absorbances of standards.

7.2 Determine the ammonia-nitrogen concentration in milligrams per liter as follows:

Ammonia-nitrogen as N, (mg/L) =

$$\frac{1{,}000}{\text{mL sample}} \times \frac{250}{\text{mL aliquot}} \times \text{mg N in aliquot}$$

8. Report

Report nitrogen, ammonia, dissolved (00608), and total (00610), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved ammonia-nitrogen for nine samples within the range of 0.10 to 2.0 mg/L may be expressed as follows:

$$S_T = 0.465X + 0.0001$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of ammonia-nitrogen, milligrams per liter.

The correlation coefficient is 0.8140.

9.2 Precision for dissolved ammonia-nitrogen for four of the nine samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
11	0.104	73
4	.600	33
8	1.51	44
7	2.04	63

9.3 It is estimated that the percent relative standard deviation for total ammonia-nitrogen will be greater than that reported for dissolved ammonia-nitrogen.

Reference

Blaedel, W. J., and Meloche, V. W., 1963, Elementary quantitative analysis: theory and practice (2d ed.): New York, Harper and Row, 826 p.

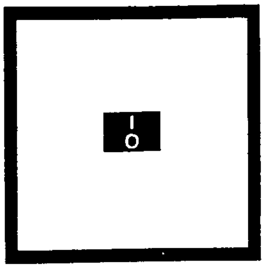
Method 8156

pH

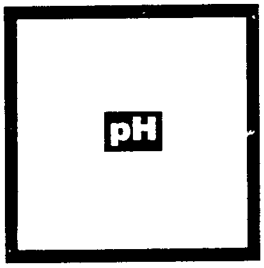
For water and wastewater

Electrode Method with a Portable Hach One Meter; EPA Approved

Two-Standard Calibration in Automatic Mode With Temperature Probe



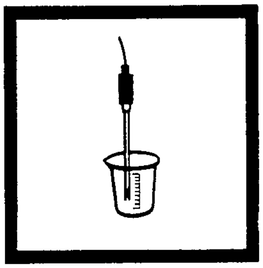
1. Press the POWER key. The display will light.



2. Press the pH key.

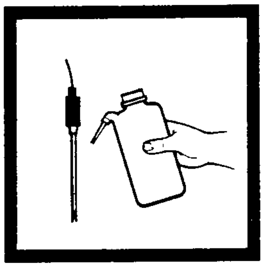
3. Press the AUTO/MANUAL key. The AUTO indicator will light. The S1 and pH indicators will flash. Zeros will appear in the display.

Note: Hach buffers are available as powder pillows or as solutions. They are color-coded for added convenience.



4. Place the electrode into a pH 4.01 buffer solution and press the Dispenser Button. For best accuracy, allow 30 seconds to elapse before performing Step 5. The temperature display will show the actual solution temperature if the temperature probe is connected.

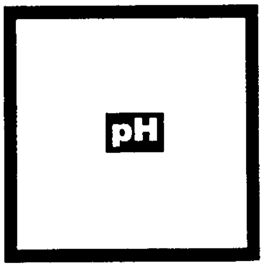
5. Press the STANDARD key and wait until the pH indicator stops flashing. The S2 indicator will begin flashing. The actual pH value will appear in the display based on the default or last calibration. Please disregard.



6. Rinse the electrode with deionized water and blot dry with a paper towel. Place the electrode into a pH 7.00 buffer solution and press the Dispenser Button. For best accuracy, wait 30 seconds before performing Step 7.

7. Press the STANDARD key. S2 will stop flashing. Wait until the pH indicator stops flashing. The actual pH value will appear in the display based on the default or last calibration. Please disregard.

Note: Pressing any key other than the pH key at this point will nullify the calibration values just entered and the meter will revert to the previous calibration.

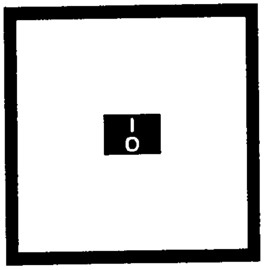


8. Press pH key. Rinse the electrode with deionized water or a portion of the sample to be measured and blot dry with a paper wipe. Place the electrode into the sample and press the Dispenser Button. The meter now measures pH.

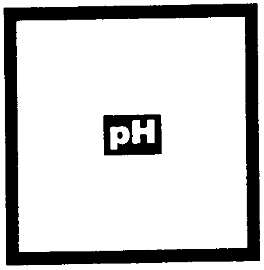
9. To review, press the REVIEW key to show the offset voltage in the upper display and the electrode slope in the lower display. Press the REVIEW key to return to measuring pH. In the automatic buffer recognition mode, buffer solutions pH 4.01, 7.00 and 10.00 may be used in any sequence.

Note: For other calibrations or for more complete operation instructions, refer to the instrument manual.

Sample pH Measurement (Calibration is required.)

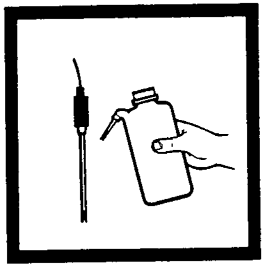


1. Press the POWER key to turn the meter on.



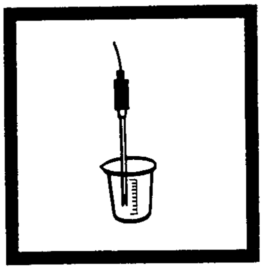
2. Press the pH key. The pH indicator will light.

Note: Be sure there are no air bubbles trapped inside the tip of the electrode or dispense tubing.



3. Rinse the electrode thoroughly with deionized water or a portion of the sample to be measured and blot with a paper towel. Place the electrode in the sample.

Note: If sample cannot be analyzed shortly after sampling, see Sampling and Storage following these steps.



4. Press the Dispenser Button once to dispense electrolyte. Stir at a moderate rate either with a magnetic stirrer or with the electrode. When the Probe Indicator stops flashing (indicating a stable condition), read the sample pH.

SAMPLING AND STORAGE

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Cool to 4 °C (39 °F) and determine within six hours. If samples cannot be analyzed within six hours, report the actual holding time with the results.

INTERFERENCES

Acid error is negligible. Sodium error, usually present in alkaline solutions, is low, even at pH values as high as 11.

SUMMARY OF METHOD

The Hach One Combination pH Electrode responds to the hydrogen ion concentration (activity) by developing an electrical potential at the glass/liquid interface. At a constant temperature, this potential varies linearly with the pH of the solution being measured. The electrode has a free-diffusion junction which eliminates clogging problems. For more information, see Appendix A, Chemical Procedures Explained.

REQUIRED REAGENTS AND APPARATUS

Description	Unit	Cat. No.
Select one:		
Hach One pH Meter	each	43800-00
Hach One Laboratory pH/mV Meter	each	44701-00
Hach One pH/ISE Meter	each	44700-00

OPTIONAL REAGENTS

Buffer Powder Pillows, pH 4, red	50/pkg*	22269-66
Buffer Powder Pillows, pH 7, yellow	50/pkg*	22270-66
Buffer Powder Pillows, pH 9	50/pkg*	14107-66
Buffer Powder Pillows, pH 10, blue	50/pkg*	22271-95
Buffer Solution, pH 4, red	473 mL*	22834-11
Buffer Solution, pH 7, yellow	473 mL*	22835-11
Buffer Solution, pH 10, blue	473 mL*	22836-11
Reference Electrode Solution Cartridge	each	21950-01
Water, deionized	946 mL*	272-16

OPTIONAL APPARATUS

Electromagnetic stirrer and electrode holder, 115 Vac	each	45300-01
Electromagnetic stirrer and electrode holder, 230 Vac	each	45300-02
Thermometer, armored, -20 to 105 °C	each	1877-01
Clippers, for opening pillows	each	968-00
Beaker, poly, 50 mL	each	1080-41
Cylinder, mixing, graduated, 50 mL	each	1896-41
Hach One Combination pH Electrode, U.S. Standard Connector (for use with any pH Meter)	each	44300-00
Hach One Combination pH Electrode, BNC Connector (for use with any pH meter)	each	44300-01
Hach One Combination pH Electrode, (for use with Hach One Meters only)	each	44200-21
pH Half-cell Electrode, glass, BNC Connector	each	44490-71
Hach One Reference Half-cell Electrode	each	44250-00
Stainless Steel Temp-Probe, for Hach One Meters	each	43976-00
Stir Bar, 22.2 × 4.76 mm (7/8 × 3/16")	each	45315-00

RELATED LITERATURE—Ask for your copy by literature code number.

Title	Literature Code No.
pH Measurement by Illingworth	6061

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224 toll-free for more information
Outside the U.S.A.—Contact the Hach office or distributor serving you.

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*Contact Hach for larger sizes.

pH, electrometric, glass-electrode

Parameters and Codes:

pH lab, I-1586-85 (units): 00403
pH lab, automated, I-2587-85 (units): 00403

1. Application

This method may be used to determine the pH of any natural or treated water and any industrial or other wastewater.

2. Summary of method

2.1 See the introduction to electrometry in this chapter for the principles of pH-meter operation. See also Barnes (1964), Bates (1964), and Willard and others (1965).

2.2 This procedure may be automated with commercially available instrumentation.

3. Interferences

3.1 The determination is not affected by the presence of color or turbidity, or of organic or colloidal material. Oxidizing and reducing substances do not impair the accuracy of method.

3.2 The pH measurement is temperature dependent, and a significant error results if the temperatures of the buffers and samples differ appreciably. However, a variation of less than 5 °C has no significant effect except in the most exacting work.

3.3 For samples having abnormally high sodium levels, corrections may be necessary. This correction varies with the type of electrodes used; hence, see the manufacturer's instructions for the necessary computations.

4. Apparatus

4.1 *pH meter,* with glass and reference electrodes or combination pH electrode.

4.2 Several types of pH meters are available, including digital and expanded-scale models. Unless a different type is needed for special purposes, an ordinary laboratory, line-operated, pH meter—capable of a reproducibility of 0.05 of a pH unit—is adequate.

4.3 A new glass electrode or one that has dried completely may require several hours of soaking in water or buffer solution before it produces stable, reliable readings. The tip of the glass electrode must be kept immersed in water when not in use. Although the glass tip is reasonably durable, it can be damaged, and should never be cleaned or wiped with an abrasive or dirty tissue or cioth.

5. Reagents

Standard buffer solutions, pH 4.00, 7.00, and 9.00: These buffers should cover the range of pH of the samples to be measured. If samples of pH less than 4.00 or greater than 9.00 are to be analyzed, additional buffers will be required. Ready-made buffer reagents are satisfactory.

6. Procedure

6.1 After an appropriate warmup period, standardize the instrument with the buffer solutions, bracketing the pH values of the samples. Samples and buffers must be at the same temperature.

6.2 With a minimum of aeration or agitation, measure the pH of samples in accordance with the manufacturer's instructions.

7. Calculations

The pH is read directly from the meter.

8. Report

Report pH values (00403) to the nearest 0.1 pH unit.

9. Precision

9.1 Precision for pH for five of the 36 samples expressed in terms of standard deviation is as follows:

Number of laboratories	Mean (pH units)	Relative standard deviation (pH units)
27	6.21	0.26
59	7.14	.32
33	7.52	.15
48	8.00	.21
60	8.54	.15

9.2 Using automated instrumentation, analysis of two test samples by a single laboratory for 25 replicates of each resulted in mean values of 7.58 and 8.07 pH units and standard deviations of 0.05 and 0.03 pH units, respectively.

References

Barnes, Ivan, 1964, Field measurement of alkalinity and pH: U.S. Geological Survey Water-Supply Paper 1535-H, 17 p.

Bates, R. G., 1964, Determination of pH—theory and practice: New York, John Wiley and Sons, 435 p.

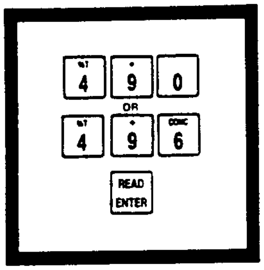
Willard, H. H., Merritt, L. L., Jr., and Dean, J. A., 1974, Instrumental methods of analysis (5th ed.): New York, D. Van Nostrand, 860 p.

Method 8048

PHOSPHORUS, REACTIVE (0 to 2.50 mg/L PO_4^{3-}) For water, wastewater, seawater

(also called: Orthophosphate) PhosVer 3 (Ascorbic Acid) Method* (Powder Pillows or AccuVac Ampuls), EPA Approved

USING POWDER PILLOWS



1. Enter a stored program number for reactive phosphorus–powder pillows.

Press: **4 9 0 READ/ENTER** for units of mg/L PO_4^{3-}

OR

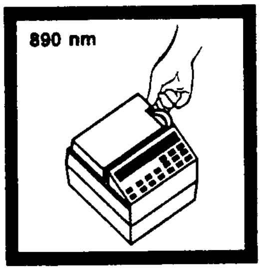
Press: **4 9 6 READ/ENTER** for units of mg/L P

The display will show:

DIAL nm TO 890

Note: DR/2000s with software versions 3.0 and greater will display "P" and the program number.

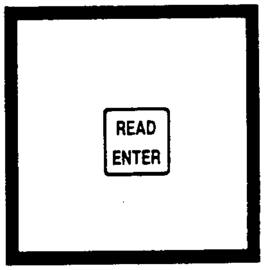
Note: Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.



2. Rotate the wavelength dial until the small display shows:

890 nm

Note: For instruments with software versions that do not have stored program method 496, refer to Instrument Setup following these steps.



3. Press: **READ/ENTER**

The display will show:

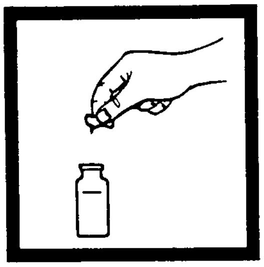
mg/l PO_4^{3-} PV

OR

mg/l P PV

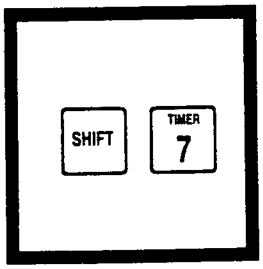
4. Fill a sample cell with 25 mL of sample.

Note: For proof of accuracy, use a 1.0 mg/L Phosphate (0.33 mg/L P) Standard Solution listed under Optional Reagents in place of the sample.



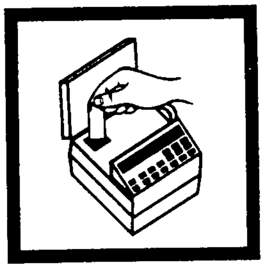
5. Add the contents of one PhosVer 3 Phosphate Powder Pillow to the cell (the prepared sample). Swirl immediately to mix.

Note: A blue color will form if phosphate is present.



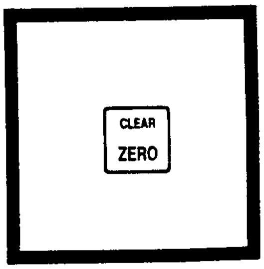
6. Press: **SHIFT TIMER**

A two-minute reaction period will begin.



7. Fill another sample cell (the blank) with 25 mL of sample. Place it into the cell holder.

Note: The Pour-Thru Cell can be used with this procedure.



8. When the timer beeps, the display will show:

mg/l P PV

Press: **ZERO**

The display will show:

WAIT

then:

0.00 mg/l PO_4^{3-} PV

OR

0.00 mg/l P PV

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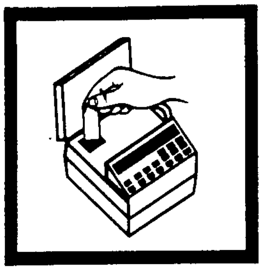
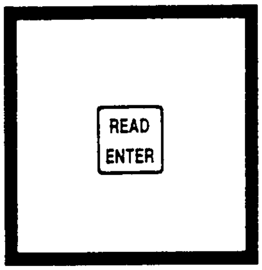
*Adapted from *Standard Methods for the Examination of Water and Wastewater*



9. Place the prepared sample into the cell holder. Close the light shield.

Note: Run a reagent blank for this test. Use deionized water in place of the sample in Step 4. Subtract this result from all test results run with this lot of PhosVer.



10. Press: **READ/ENTER**

The display will show:

WAIT

then the results in mg/L PO_4^{3-} or mg/L P will be displayed.

Note: mg/L PO_4^{3-} results can be expressed as mg/L phosphorus by dividing by 3 or as mg/L phosphorus pentoxide (P_2O_5) by multiplying by 0.75.

Note: In the constant-on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.

With the new methods 496 and 494 successfully entered, block access to the now obsolete methods 491 and 493.

Press:

SHIFT CONFIG METH

%T 4 + 9 BATT 1 READ ENTER

Within 3 seconds, press:

SHIFT PROG 3 CONFIG METH

Press:

SHIFT CONFIG METH

%T 4 + 9 PROG 3 READ ENTER

Within 3 seconds, press:

SHIFT PROG 3 CONFIG METH

Access to methods 491 and 493 are now blocked.

SAMPLING AND STORAGE

Collect samples in plastic or glass bottles that have been cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use commercial detergents containing phosphate for cleaning glassware used in phosphate analysis. Most reliable results are obtained when samples are analyzed as soon as possible after collection. If prompt analysis is impossible, preserve samples up to 24 hours by storing at or below 4 °C. For longer storage periods, add 4.0 mL of Mercuric Chloride Solution to each liter of sample taken and mix. Use of mercuric chloride is discouraged whenever possible for health and environmental considerations. Sample refrigeration is still required. Samples preserved with mercuric chloride must have a sodium chloride level of 50 mg/L or more to prevent mercury interference. Samples low in chloride should be spiked with 0.1 g sodium chloride per liter of sample.

ACCURACY CHECK

Standard Additions Method

a) Snap the neck off a Phosphate Voluette Ampule Standard Solution, 50 mg/L PO_4.

b) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of standard, respectively, to three 25-mL water samples. Mix each thoroughly. (For AccuVac Ampuls use 50-mL beakers.)

c) Analyze each sample as described above. The phosphate concentration should increase 0.2 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see Standard Additions (Section I of the DR/2000 Procedures Manual or *Water Analysis Handbook*) for more information.

INTERFERENCES

Large amounts of turbidity may cause inconsistent results in the phosphate tests because the acid present in the powder pillow may dissolve some of the suspended particles and because of variable desorption of orthophosphate from the particles. For highly turbid or colored samples, add the contents of one Phosphate Pretreatment Powder Pillow to 25 mL of sample. Mix well. Use this solution to zero the instrument.

The PhosVer 3 Phosphate Reagent Powder Pillows should be stored in a cool, dry environment.

The following may interfere when present in concentrations exceeding these listed below:

Aluminum	200 mg/L
Chromium	100 mg/L
Copper	10 mg/L
Iron	100 mg/L
Nickel	300 mg/L
Silica	50 mg/L
Silicate	10 mg/L
Zinc	80 mg/L

Arsenate and hydrogen sulfide do interfere.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see Interferences, pH (Section I of the DR/2000 Procedures Manual or *Water Analysis Handbook*).

PRECISION

In a single laboratory using a standard solution of 1.00 mg/L PO_4^{3-} and two lots of reagents with the DR/2000, a single operator obtained a standard deviation of ± 0.01 mg/L PO_4^{3-}.

In a single laboratory using a standard solution of 1.00 mg/L PO_4^{3-} and two representative lots of AccuVac ampuls with the DR/2000, a single operator obtained a standard deviation of ± 0.02 mg/L PO_4^{3-}.

SUMMARY OF METHOD

Orthophosphate reacts with molybdate in an acid medium to produce a phosphomolybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color. Refer to *Chemical Procedures Explained*, Appendix A, for more information.

REQUIRED REAGENTS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
PhosVer 3 Phosphate Reagent Powder Pillows	1 pillow	100/pkg	2125-99

REQUIRED REAGENTS (Using AccuVac Ampuls)

PhosVer 3 Phosphate Reagent AccuVac Ampuls	1 ampul	25/pkg	25080-25

REQUIRED APPARATUS (Using Powder Pillows)

Clippers, for opening powder pillows	1	each	968-00

REQUIRED APPARATUS (Using AccuVac Ampuls)

Adapter, AccuVac Vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Cap, ampul, blue	1	25/pkg	1731-25
Vial, zeroing	1	each	21228-00

OPTIONAL REAGENTS

Hydrochloric Acid Standard Solution, 6.0 N (1:1)	500 mL	884-49
Mercuric Chloride Solution, 10 g/L	118 mL	14994-14
Phosphate Pretreatment Powder Pillows	50/pkg	14501-66
Phosphate Standard Solution, 1 mg/L as PO_4	473 mL	2569-11
Phosphate Standard Solution, Voluette ampul, 50 mg/L as PO_4, 10 mL	16/pkg	171-10
Sodium Chloride, ACS	454 g	182-01
Sodium Hydroxide Standard Solution, 5.0 N	118 mL* MDB	2450-37
Water, deionized	3.78 L	272-17

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052-00
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, Hach One	each	43800-00
Pipet, 2 mL serological	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Filler, safety bulb	each	14651-00
Spoon, measuring, 0.1 g	each	511-00

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224 toll-free for more information
Outside the U.S.A.—Contact the Hach office or distributor serving you.

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*Larger sizes available.

Phosphorus, orthophosphate, colorimetric, phosphomolybdate

Parameter and Code:

Phosphorus, orthophosphate, dissolved, I-1601-85 (mg/L as P): 00671

1. Application

This method may be used to analyze most water and wastewater containing between 0.02 and 0.4 mg/L of orthophosphate-phosphorus. Samples containing greater concentrations need to be diluted.

2. Summary of method

2.1 As far as is known, the phosphomolybdate method is specific for the orthophosphate form of phosphorus. Weak tests are reported with pyrophosphate and polyphosphates, but these positive tests may well result from orthophosphate contamination of the material.

2.2 Orthophosphate is converted to phosphomolybdate by acidified ammonium molybdate reagent:

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21H^{+1} \rightarrow$$

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4^{+1} + 12H_2O$$

2.3 When phosphomolybdate is reduced with ascorbic acid in the presence of antimony (Murphy and Riley, 1962), an intense blue complex is developed that absorbs light at 882 nm. The reduction is not instantaneous, nor is the developed blue color stable. The full color develops in 6 to 10 min and fades gradually thereafter.

3. Interferences

3.1 Barium, lead, and silver interfere by forming a precipitate. Silica produces a pale-blue color that is additive to the phosphate color, and may require correction. The effect of silica is somewhat dependent on the reagents; therefore, an appropriate silica correction should be determined for each batch of reagents. Nitrite interferes but can be oxidized to nitrate with hydrogen peroxide before analysis. Residual chlorine must be removed by boiling the sample.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L. Mercuric chloride-preserved samples are fortified with a minimum of 65 mg/L NaCl to overcome this interference.

3.3 Arsenic as arsenate (AsO_4^{-3}) produces a color similar to that of phosphate (Murphy and Riley, 1962) and may cause a positive interference. Arsenic concentrations as much as 100 µg/L do not interfere. Greater concentrations were not investigated.

4. Apparatus

Spectrometer for use at 700 or 882 nm.

5. Reagents

5.1 *Antimony tartrate-ammonium molybdate solution*: Dissolve 0.13 g antimony potassium tartrate, $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$, in about 700 mL demineralized water contained in a 1-L volumetric flask. Add 5.6 g ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and shake flask until dissolved. *Cautiously*, add 70 mL concentrated H_2SO_4 (sp gr 1.84) while swirling the contents of the flask. Cool and dilute to volume. Mix thoroughly by repeated inversion and swirling. This solution is stable for at least 1 year if stored in a polyethylene bottle away from heat.

5.2 *Combined reagent solution*: Dissolve 0.50 g ascorbic acid in 100 mL antimony tartrate-ammonium molybdate solution. This reagent is stable for at least 1 week if stored at 4 °C; otherwise prepare fresh daily.

5.3 *Phosphate standard solution I*, 1.00 mL = 0.050 mg P: Dissolve 0.2197 g KH_2PO_4, dried overnight over H_2SO_4, in demineralized water and dilute to 1,000 mL.

5.4 *Phosphate standard solution II*, 1.00 mL = 0.001 mg P: Dilute 20.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.020 mg P (50.0 mL max) into a 100-mL beaker, and adjust the volume to 50.0 mL.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 50.0 mL (NOTE 1).

NOTE 1. If the samples were preserved with mercuric chloride fortified with sodium chloride, add an equivalent amount to the blank and standards.

6.3 Add 10 mL combined reagent solution to each sample, blank, and standard, and mix.

6.4 After 10, but before 30, min measure absorbance of each sample and standard against that of the blank at either 882 or 700 nm.

7. Calculations

7.1 Determine the milligrams of phosphorus in each sample from a plot of absorbances of standards.

7.2 Determine the phosphorus concentration in milligrams per liter as follows:

$$\text{P (mg/L)} = \frac{1{,}000}{\text{mL sample}} \times \text{mg P in sample}$$

8. Report

Report phosphorus, orthophosphate, dissolved (00671), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved orthophosphate-phosphorus for nine samples within the range of 0.000 to 1.70 mg/L may be expressed as follows:

$$S_T = 0.114\,X + 0.004$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of orthophosphate-phosphorus, milligrams per liter.

The correlation coefficient is 0.9067.

9.2 Precision for dissolved orthophosphate-phosphorus for five of the nine samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
11	0.000	0
12	.008	62
15	.406	11
11	1.02	8
14	1.70	13

Reference

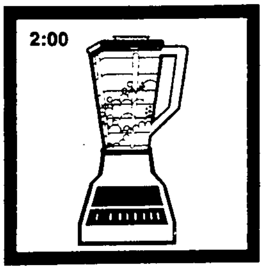
Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chimica Acta, v. 27, p. 31-6.

Method 8006

SUSPENDED SOLIDS (0 to 750 mg/L)

For water and wastewater

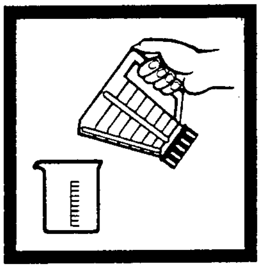
(also called: Nonfilterable Residue) Photometric Method*



1. Blend 500 mL of sample in a blender at high speed for exactly two minutes.

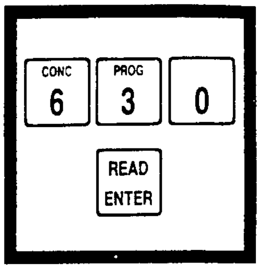
Note: If sample cannot be analyzed immediately, see Sampling and Storage, following these steps.

Note: Obtain blender locally. All other apparatus is available from Hach.



2. Pour the blended sample into a 600-mL beaker.

3. Stir the sample and immediately pour 25 mL of the blended sample into a sample cell (the prepared sample).



4. Enter the stored program number for nonfilterable residue.

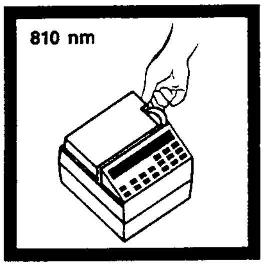
Press: **6 3 0 READ/ENTER**

The display will show:

DIAL nm TO 810

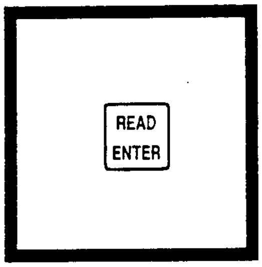
Note: DR/2000s with software versions 3.0 and greater will display "P" and the program number.

Note: Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 6. Proceed with Step 7.



5. Rotate the wavelength dial until the small display shows:

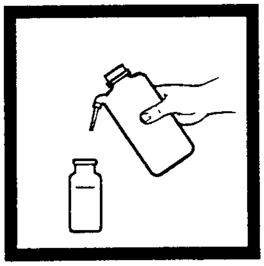
810 nm



6. Press: **READ/ENTER**

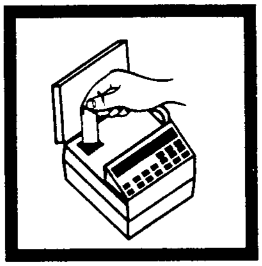
The display will show:

mg/l SUSP.SOLIDS



7. Pour 25 mL of tap or deionized water into a sample cell (the blank).

Note: Remove gas bubbles in the tap water by swirling or tapping the bottom of the cell on a table top.



8. Place the blank into the cell holder. Close the light shield.

Note: The Pour-Thru Cell cannot be used with this procedure.

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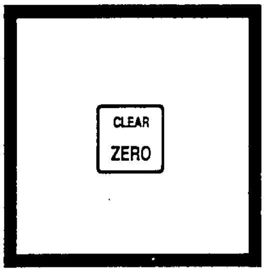
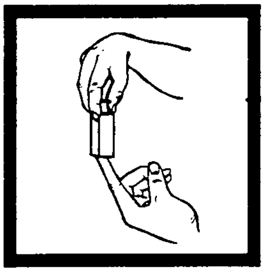
*Adapted from *Sewage and Industrial Wastes*, 31, 1159 (1959)

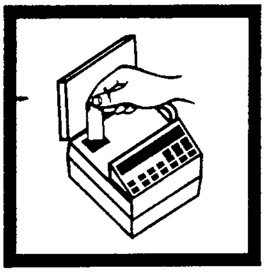


9. Press: **ZERO**

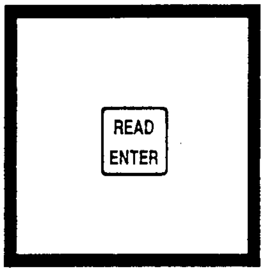
The display will show:
WAIT
then:
0. mg/l SUSP.SOLIDS



10. Swirl the prepared sample cell to remove gas bubbles and uniformly suspend any residue.



11. Place the prepared sample cell into the cell holder. Close the light shield.



12. Press: **READ/ENTER**

The display will show:
WAIT
then the result in mg/L nonfilterable residue will be displayed.

Note: In the constant-on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.

SAMPLING AND STORAGE

Collect samples in clean plastic or glass bottles. Analyze samples as soon as possible after collection. They can be stored seven days by cooling to 4 °C (39 °F).

INTERFERENCES

Calibration for this test is based on parallel samples using the gravimetric technique on sewage samples from a municipal sewage plant. For most samples, this calibration will provide satisfactory results. When higher accuracy is required, it is recommended that parallel spectrophotometer and gravimetric determinations be run using portions of the same sample. The new calibration should be made on your particular sample using a gravimetric technique as a basis.

SUMMARY OF METHOD

The photometric method of determining suspended solids is a simple, direct measurement which does not require the filtration or ignition and weighing steps called for in gravimetric procedures. The stored program has been calibrated using samples from a municipal sewage treatment plant. The EPA specifies the gravimetric method for solids determinations, while the photometric method is often used for checking in-plant processes.

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Beaker, 600 mL, poly	1	each	1080-52
Blender	1	each	purchase locally
Cylinder, 500 mL graduated, poly	1	each	1081-49
Pipet, serological, 25 mL	1	each	2066-40
Pipet Filler, safety bulb	1	each	14651-00

OPTIONAL APPARATUS

Stirring rod, glass	3/pkg	1770-01

For Technical Assistance, Price and Ordering

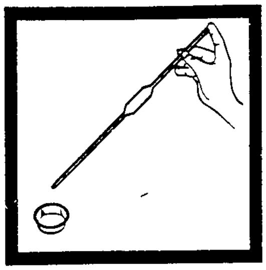
In the U.S.A.—Call 800-227-4224 toll-free for more information
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8271

TOTAL SOLIDS

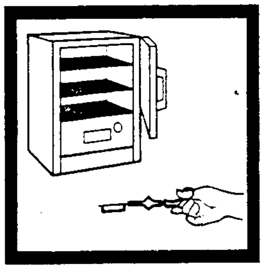
For wastewater

Gravimetric Method, EPA Aprroved



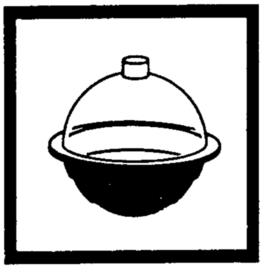
1. Mix sample. Add 50-ml to a preweighed (to nearest 0.1 mg) aluminum dish.

Note: If volatile solids are to be measured, ignite the aluminum dishes for 1 hour at 550 °C prior to use.

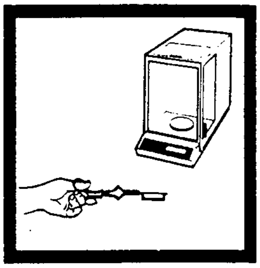


2. Evaporate sample in an oven at 103-105 °C.

Note: Drying will take approximately 6 hours. The oven should be preheated to ensure adequate drying. Highly mineralized water may require prolonged drying.

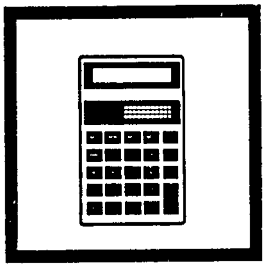


3. Take dish out of oven and allow to cool to room temperature in a desiccator.



4. Weigh the dish to the nearest 0.1 mg using an analytical balance.

Note: Repeat drying (approximately 15 minutes) at 103-105 °C until results do not differ by more than 0.4 mg. Successive weighings that are identical for some wastewater samples are unlikely due to slow organic volatilization.



5. Calculations:

$$\text{mg/L Total Solids} = \frac{(A - B) \times 1000}{\text{sample volume in ml}}$$

WHERE

A = weight (mg) of sample + dish

B = weight (mg) of dish

REQUIRED APPARATUS

Description	Unit	Cat. No.
Balance, analytical	each	22310-00
Cylinder, 50 ml	each	508-41
Desiccant, indicating Drierite	each	20887-01
Desiccator, without stopcock	each	14285-00
Desiccator Plate, ceramic	each	14284-00
Dish, aluminum (63 × 17.5 mm)	100/pkg	21640-00
Furnace, muffle	each	14296-00
Oven, laboratory, 120V, 60 Hz	each	14289-00
Pipet, serological, 25 ml	each	2066-40
Tongs	each	569-00

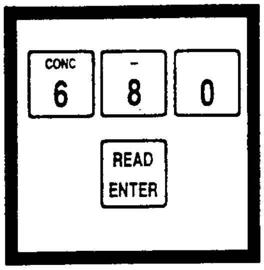
Method 8051

SULFATE (0 to 70 mg/L)

For water, wastewater and seawater

SulfaVer 4 Method* (Powder Pillows or AccuVac Ampuls), EPA Approved

USING POWDER PILLOWS



1. Enter the stored program number for sulfate (SO_4^{2-})-powder pillows.

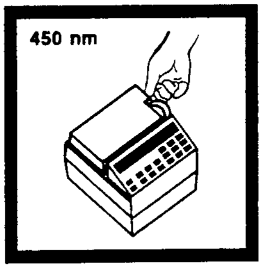
Press: **6 8 0 READ/ENTER**

The display will show:
DIAL nm TO 450

Note: DR/2000s with software versions 3.0 and greater will display "P" and the program number.

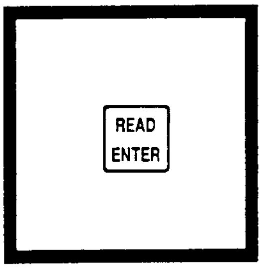
Note: Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.

Note: If samples cannot be analyzed immediately, see Sampling and Storage following these steps.



2. Rotate the wavelength dial until the small display shows:
450 nm

Note: For best results prepare an instrument calibration for each new lot of SulfaVer 4 Sulfate Reagent Powder Pillows; see Calibration following these steps.



3. Press: **READ/ENTER**

The display will show:
mg/l SO_4^{2-}

4. Fill a sample cell with 25 mL of sample.

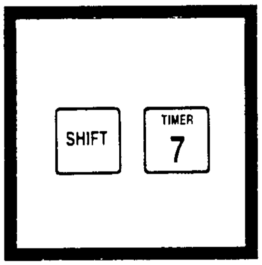
Note: Filter highly colored or turbid samples. Use filtered sample here and in Step 7. Use labware listed under Optional Apparatus.

Note: For proof of accuracy, use a 50 mg/L SO_4^{2-} standard solution (preparation given in the Accuracy Check) in place of the sample.

5. Add the contents of one SulfaVer 4 Sulfate Reagent Powder Pillow to the sample cell (the prepared sample). Swirl to dissolve.

Note: A white turbidity will develop if sulfate is present.

Note: Accuracy is not affected by undissolved powder.



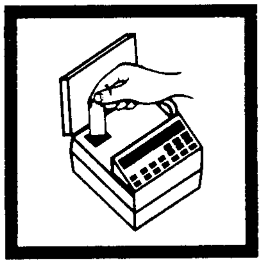
6. Press: **SHIFT TIMER**

A five minute reaction period will begin.

Note: Allow the cell to stand undisturbed.

7. When the timer beeps, the display will show:
mg/l SO_4^{2-}

Fill a second sample cell (the blank) with 25 mL of sample.



8. Place the blank into the cell holder. Close the light shield.

Note: The Pour-Thru Cell cannot be used with this procedure.

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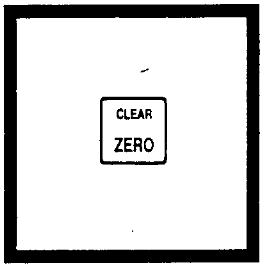
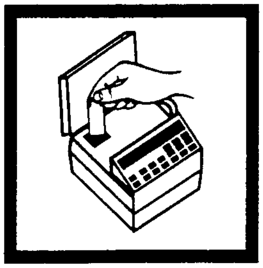
*Adapted from *Standard Methods for the Examination of Water and Wastewater*

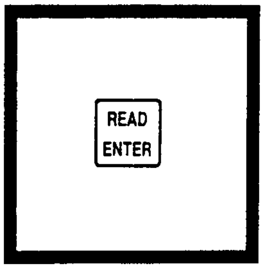


9. Press: **ZERO**

The display will show:
WAIT
then:
0. mg/l SO$_4^{2-}$



10. Within five minutes after the timer beeps, place the prepared sample into the cell holder. Close the light shield.



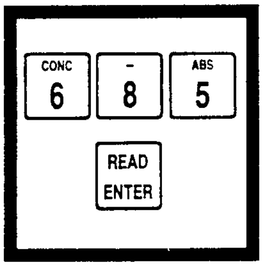
11. Press: **READ/ENTER**

The display will show:
WAIT
then the result in mg/L SO$_4^{2-}$ will be displayed.

Note: Clean the sample cells with soap and a brush.

Note: In the constant-on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.

USING ACCUVAC AMPULS



1. Enter the stored program number for sulfate (SO$_4^{2-}$)–AccuVac Ampuls.

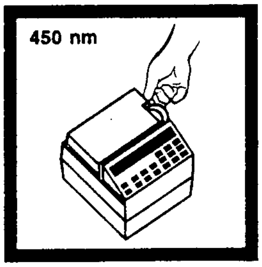
Press: **6 8 5 READ/ENTER**

The display will show:
DIAL nm TO 450

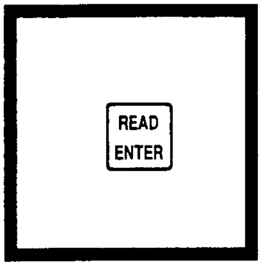
Note: DR/2000s with software versions 3.0 and greater will display "P" and the program number.

Note: Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.

Note: If samples cannot be analyzed immediately, see Sampling and Storage below.

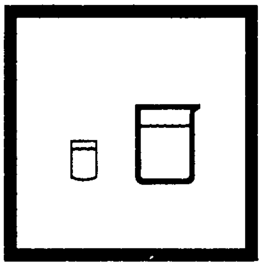


2. Rotate the wavelength dial until the small display shows:
450 nm



3. Press: **READ/ENTER**

The display will show:
mg/l SO$_4^{2-}$ AV



4. Fill a zeroing vial (the blank) with at least 10 mL of sample. Collect at least 40 mL of sample in a 50-mL beaker.

Note: Filter highly colored or turbid samples. Use labware listed under Optional Apparatus.

CALIBRATION

A new calibration may be performed for each lot of SulfaVer 4 Sulfate Reagent Powder Pillows as follows:

a) Prepare standards of 0, 10, 20, 30, 40, 50 and 60 mg/L sulfate by diluting 0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 mL of the contents of a Sulfate Voluette Ampule Standard, 2500 mg/L, to 25.0 mL with deionized water in mixing graduated cylinders. Use a TenSette pipet to measure the standard. Mix well. (Or, pipet 0, 1.0, 2.0, 3.0, 4.0, 5.0 and 6.0 mL of Sulfate Standard Solution into 1000-mL volumetric flasks. Dilute to volume. Mix well. Transfer 25 mL to each test cylinder.)

b) Store the calibration in the instrument memory using the procedure in the Operation section of the instrument manual. Follow the procedure described, choosing a wavelength of 450 nm, the decimal position as 0000, units as mg/L SO_4^{2-}, and a Timer 1 interval of 05:00. Note the program number assigned to the procedure.

c) Add the reagents to the deionized water (0 standard-reagent blank) and to the 10 mg/L standard as described in Steps 4 to 6 above, using the deionized water blank to perform the zero calibration. Enter the sulfate concentration of the first standard (10 mg/L) and measure the absorbance as directed by the instrument. React and measure the remaining standards.

d) Use this stored program number in the procedure above. Prepare a new calibration for each new lot of reagent, using the same stored program number.

SAMPLING AND STORAGE

Collect samples in clean glass or plastic bottles. Samples may be stored up to seven days by cooling to 4 °C (39 °F) or lower. Warm to room temperature before analysis.

ACCURACY CHECK

Standard Additions Method

a) Snap the neck off a Sulfate Voluette Ampule Standard Solution, 2500 mg/L.

b) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard to three 25-mL water samples. Mix each thoroughly. (For AccuVac ampuls, use 50-mL beakers.)

c) Analyze each sample as described above. The sulfate concentration should increase 10 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see Standard Additions (Section I) for more information.

Standard Solution Method

Check the accuracy of the test by using the Sulfate Standard Solution, 50 mg/L, listed under Optional Reagents. Or, prepare this solution by pipetting 1.0 mL of the contents of a Voluette Ampule Standard for Sulfate into a 50-mL volumetric flask. Dilute to volume with deionized water.

PRECISION

In a single laboratory using a standard solution of 50 mg/L sulfate and two repesentative lots of powder pillows with the DR/2000, a single operator obtained a standard deviation of ± 0.9 mg/L sulfate.

In a single laboratory using a standard solution of 50 mg/L sulfate and two representative lots of AccuVac ampuls with the DR/2000, a single operator obtained a standard deviation of ± 2.2 mg/L sulfate.

INTERFERENCES

Silica and calcium may interfere at levels above 500 mg/L and 20,000 mg/L as $CaCO_3$, respectively.

Chloride and magnesium do not interfere at levels up to at least 40,000 mg/L as Cl and 10,000 mg/L as $CaCO_3$, respectively.

SUMMARY OF METHOD

Sulfate ions in the sample react with barium in SulfaVer 4 Sulfate Reagent and form insoluble barium sulfate turbidity. The amount of turbidity formed is proportional to the sulfate concentration. See *Chemical Procedures Explained,* Appendix A, for more information.

REQUIRED REAGENTS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
SulfaVer 4 Sulfate Reagent Powder Pillows	1 pillow	50/pkg	12065-66

REQUIRED REAGENTS (Using AccuVac Ampuls)

Description	Quantity Required Per Test	Unit	Cat. No.
SulfaVer 4 Sulfate AccuVac Ampuls	1 ampul	25/pkg	25090-25

REQUIRED APPARATUS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
Clippers, for opening powder pillows	1	each	968-00

REQUIRED APPARATUS (Using AccuVac Ampuls)

Description	Quantity Required Per Test	Unit	Cat. No.
Adapter, AccuVac Vial	1	each	43784-00
Brush	1	each	690-00
Vial, zeroing	1	each	21228-00

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Sulfate Standard Solution, 50 mg/L	473 mL	2578-11
Sulfate Standard Solution, 1000 mg/L	473 mL	21757-11
Sulfate Standard Solution, Voluette ampule, 2500 mg/L, 10 mL	16/pkg	14252-10
Water, deionized	3.78 L	272-17

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Beaker, 50 mL	each	500-41
Filter Paper, folded, 12.5 cm	100/pkg	1894-57
Flask, volumetric, 50 mL	each	14574-41
Funnel, poly, 65 mm	each	1083-67
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, 1.0 mL	each	14515-35
Pipet Filler, safety bulb	each	14651-00

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224 toll-free for more information
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Sulfate, turbidimetric, barium sulfate, automated-discrete

Parameter and Code:
Sulfate, dissolved, I-2823-85 (mg/L as SO_4): 00945

1. Application

This method may be used to determine concentrations of sulfate in surface, domestic, and industrial water in the ranges of 0.2 to 1000 mg/L. Samples containing greater concentrations must first be diluted. Three working ranges are provided: from 0.2 to 10.0 mg/L, from 10 to 200 mg/L, and from 200 to 1000 mg/L.

2. Summary of method

Sulfate ion is reacted with barium chloride under acidic conditions to form barium sulfate. The absorbance of the resulting suspension is measured photometrically and is proportional to the sulfate concentration present in the original sample (Santiago and others, 1975).

3. Interferences

Suspended matter in large amounts will interfere. Natural color exceeding 50 platinum cobalt units may interfere. Silica, at concentrations less than 200 mg/L, does not interfere.

4. Apparatus

4.1 *Discrete analyzer system*, American Monitor IQAS or equivalent.

4.2 With this equipment the following operating conditions have been found satisfactory for the ranges: from 0.2 to 10.0 mg/L, from 10 to 200 mg/L, and from 200 to 1000 mg/L.

Wavelength	340 nm for 0.2 to 10.0 mg/L 410 nm for 10 to 200 mg/L 458 nm for 200 to 1000 mg/L
Absorption cell -----	1 cm square, temperature-controlled, flow-through quartz cuvette
Reaction temperature -	ambient
Sample volumes	0.450 mL with 0.050 mL of diluent for 0.2 to 10.0 mg/L 0.200 mL with 0.050 mL of diluent for 10 to 200 mg/L 0.140 mL with 0.075 mL of diluent for 200-1000 mg/L (NOTE 1)
Reagent volumes	0.25 mL $BaCl_2$-NaCl-HCl-gelatin solution and 0.25 mL sulfate standard solution IV for 0.2 to 10 mg/L 1.0 mL $BaCl_2$-NaCl-HCl-gelatin solution for 10 to 200 mg/L 2.0 mL $BaCl_2$-NaCl-HCl-gelatin solution for 200 to 1000 mg/L (NOTE 1)

NOTE 1. Sample-to-diluent ratio and reagent volumes must be optimized for each individual instrument according to manufacturer's specifications.

5. Reagents

5.1 *Barium chloride-sodium chloride-hydrochloric acid-gelatin solution.*

5.1.1. *Sulfate ranges 0.2 to 10.0 mg/L and 10 to 200 mg/L*: Dissolve 20 g $BaCl_2 \cdot 2H_2O$ in 500 mL demineralized water, and add 10 mL concentrated HCl (sp gr 1.19), 0.5 g gelatin (USP), and 20 g NaCl. Mix well, dilute to 1,000 mL with demineralized water, and filter. Prepare fresh weekly.

5.1.2. *Sulfate range, 200 to 1000 mg/L*: Dissolve 10 g $BaCl_2 \cdot 2H_2O$ in 500 mL demineralized water, and add 10 mL concentrated HCl (sp gr 1.19), 0.125 g gelatin (USP) and 20 g NaCl. Mix well, dilute to 1,000 mL with demineralized water, and filter. Prepare fresh weekly.

5.2 *Sulfate standard solution I*, 1.00 mL = 10.0 mg SO_4: Dissolve 14.787 g Na_2SO_4, dried for 2 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.3 *Sulfate standard solution II*, 1.00 mL = 1.00 mg SO_4: Dilute 100 mL standard solution I to 1,000 mL with demineralized water.

5.4 *Sulfate standard solution III*, 1.00 mL = 0.100 mg SO_4: Dilute 100 mL standard solution II to 1,000 mL with demineralized water.

5.5 *Sulfate standard solution IV*, 1.00 mL = 0.010 mg SO_4: Dilute 10.0 mL sulfate standard solution II to 1,000 mL with demineralized water.

5.6 *Sulfate working standards*: Prepare a blank and 1,000 mL each of a series of sulfate working standards by the appropriate dilution of sulfate standard solution I, II, or III as follows:

Standard solution I (mL)	Standard solution II (mL)	Standard solution III (mL)	Sulfate concentration (mg/L)
		5.0	0.5
		10.0	1.0
		50.0	5.0
		100.0	10.0
	20.0		20
	50.0		50
	125.0		125
20.0			200
30.0			300
50.0			500
80.0			800
100.0			1000

6. Procedure

6.1 Set up analyzer and computer-card assignments according to the manufacturer's instructions.

6.2 Place standards, beginning with the lowest concentration, in ascending order (computer-calibration curve) in the first five positions on the sample turntable. For the low range use 0.0, 0.5, 1.0, 5.0, and 10.0 mg/L SO_4; for the mid-range use 10, 20, 50, 125, and 200 mg/L; and for the high range, use 200, 300, 500, 800, and 1,000 mg/L. Place samples and quality-control reference samples in the remainder of the sample turntable.

6.3 Begin analysis (NOTE 2).

NOTE 2. The cathode-ray tube (CRT) will acknowledge parameter and concentration range selected, listing each sample-cup number and corresponding concentrations calculated from the working curve. During each run, the CRT display will provide a plot of standards, samples, and list blank and slope calculations. Retain copy of all information obtained from the printer.

7. Calculations

Determine the milligrams per liter of sulfate in each sample from either the CRT display or the computer printout.

8. Report

Report sulfate, dissolved (00945), concentrations as follows: 0.2 to 10.0 mg/L, one decimal, 10 mg/L and above, two significant figures.

9. Precision

Precision expressed in terms of the standard deviation the and percent relative standard deviation for replicates analysis by a single operator is as follows (NOTE 3):

Mean (mg/L)	Number of replicates	Standard deviation (mg/L)	Relative standard deviation (percent)
0.7	22	0.08	11.0
1.3	22	.14	7.6
2.7	22	.14	5.0
4.4	22	.12	2.7
6.2	22	.12	1.9
14.3	21	.11	.5
272	22	1.14	4.2
112	21	.68	3.2
387	10	5.5	1.4
612	10	5.0	.8

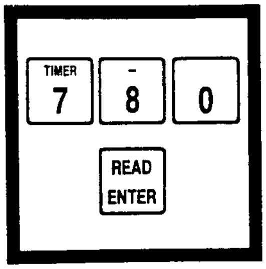
NOTE 3. Some imprecision has been observed in the range from 8 to 12 mg/L. More precise data can be obtained by diluting samples within this range and determining sulfate in the 0.2 to 10 mg/L range.

Method 8009

ZINC (0 to 2.00 mg/L)

For water and wastewater

Zincon Method*; EPA Approved†—Digestion is required; see Section I.



1. Enter the stored program number for zinc (Zn).

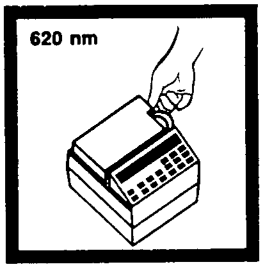
Press: **7 8 0 READ/ENTER**

The display will show:
DIAL nm TO 620

Note: DR/2000s with software versions 3.0 and greater will display "P" and the program number.

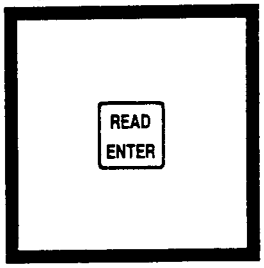
Note: Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.

Note: If samples cannot be analyzed immediately, see Sampling and Storage, following these steps. Adjust pH of stored samples before analysis.



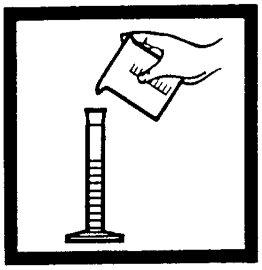
2. Rotate the wavelength dial until the small display shows:
620 nm

Note: Total zinc determination needs a prior digestion; use either the Digesdahl or mild digestion (Section I). Adjust the digested sample to a pH of 4–5; see Sampling and Storage following these steps.



3. Press: **READ/ENTER**

The display will show:
mg/l Zn



4. Fill a 50 mL mixing graduated cylinder to the 50-mL mark with sample.

Note: Use only glass stoppered cylinders in this procedure. Rinse with 1:1 hydrochloric acid and deionized water before use.

Note: For proof of accuracy, use a 0.5 mg/L zinc standard solution (preparation given in the Accuracy Check) in place of the sample.

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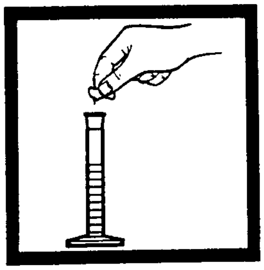
*Adapted from *Standard Methods for the Examination of Water and Wastewater*
†*Federal Register*, 45 (105) 36166 (May 29, 1980)



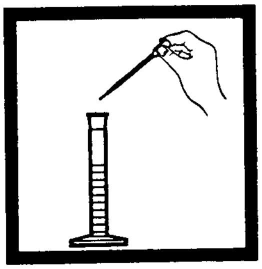
5. **CAUTION! This reagent contains cyanide and is very poisonous if taken internally or if the fumes are inhaled. Do not add to an acidic sample. Store away from water and acids.** Add the contents of one ZincoVer 5 Reagent Powder Pillow. Stopper. Invert several times to completely dissolve powder.

Note: Inconsistent readings may result for low zinc concentrations if all the particles are not dissolved.

Note: At this point the sample color should be orange. If the color is brown or blue, dilute the sample and repeat the test. Either the zinc concentration is too high, or an interfering metal is present.

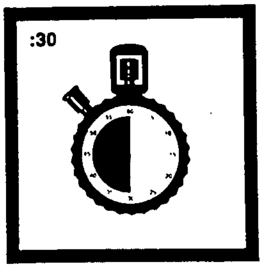
6. Measure 25 mL of the solution into a sample cell (the blank).

Note: The Pour-Thru Cell cannot be used with this procedure.



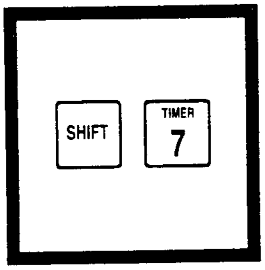
7. Add 1.0 mL of cyclohexanone to the remaining solution in the cylinder.

Note: Use a plastic dropper, as rubber bulbs may contaminate the cyclohexanone.



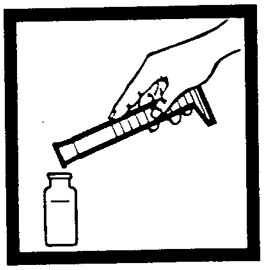
8. Stopper the cylinder (the prepared sample). Shake for 30 seconds.

Note: The sample color will be reddish-orange, brown or blue, depending on the zinc concentration.

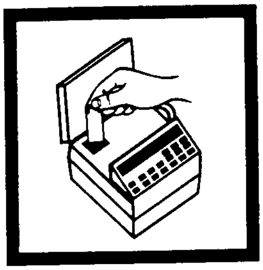


9. Press: **SHIFT TIMER**

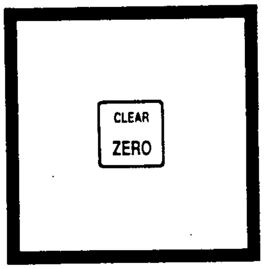
A three-minute reaction period will begin.



10. Pour the solution from the cylinder into a sample cell.



11. When the timer beeps, place the blank into the cell holder. Close the light shield.



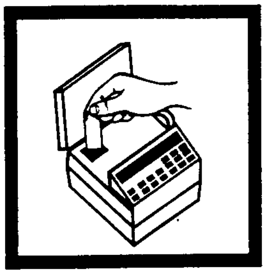
12. Press: **ZERO**

The display will show:

WAIT

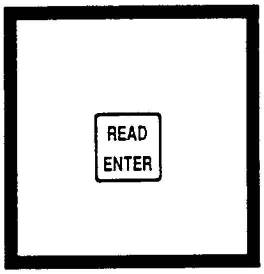
then:

0.00 mg/l Zn



13. Within ten minutes after the timer beeps, place the prepared sample into the cell holder. Close the light shield.

Note: If more than five minutes elapse after the timer beeps, ZERO SAMPLE may appear. Remove the prepared sample. Insert the blank. Press: ZERO. Insert the prepared sample.



14. Press: **READ/ENTER**

The display will show:

WAIT

then the result in mg/L zinc will be displayed.

Note: In the constant-on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.

Note: Determine a reagent blank for each lot of reagent by running the procedure on deionized water. Subtract this value from all following results obtained in Step 14.

SAMPLING AND STORAGE

Collect samples in acid-washed plastic bottles. For storage, adjust the pH to 2 or less with nitric acid (about 2 mL per liter). The preserved samples can be stored for up to six months at room temperature. Adjust the pH to 4 to 5 with 5.0 N sodium hydroxide before analysis. Do not exceed pH 5, as zinc may be lost as a precipitate. Correct the test result for volume additions; see Sampling and Storage, Volume Additions, (Section I) for more information. If only dissolved zinc is to be determined, filter the sample before acid addition.

ACCURACY CHECK

Standard Additions Method

a) Snap the neck off a Zinc Voluette Ampule Standard Solution, 25 mg/L.

b) Use the TenSette Pipet to add 0.2, 0.4, and 0.6 mL of standard to three 50-mL samples. Mix each thoroughly.

c) Analyze each sample as described above. The zinc concentration should increase 0.1 mg/L for each 0.2 mL of standard added.

d) If these increases do not occur, see Standard Additions (Section I) for more information.

Standard Solution Method

Prepare a 0.5 mg/L zinc standard solution by diluting 0.50 mL of zinc standard solution, 100 mg/L as Zn, to 100 mL with deionized water. Prepare this solution daily.

PRECISION

In a single laboratory using a standard solution of 1.00 mg/L zinc and two representative lots of reagent with the DR/2000, a single operator obtained a standard deviation of ± 0.008 mg/L zinc.

INTERFERENCES

The following may interfere when present in concentration exceeding those listed below:

Aluminum	6 mg/L
Cadmium	0.5 mg/L
Copper	5 mg/L
Iron (ferric)	7 mg/L
Manganese	5 mg/L
Nickel	5 mg/L

Large amounts of organic material may interfere. Perform the mild digestion (Section I), to eliminate this interference.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see Interferences, pH (Section I).

WASTE DISPOSAL

ZincoVer 5 Reagent contains cyanide. Dispose safely by:

a) Use good ventilation or a fume hood.

b) Add the waste while stirring to a beaker containing a strong solution of sodium hydroxide and calcium hypochlorite or sodium hypochlorite (household bleach).

c) Maintain a strong excess of hydroxide and hypochlorite. Let the solution stand for 24 hours.

d) Flush the solution down the drain with a large excess of water.

SUMMARY OF METHOD

Zinc and other metals in the sample are complexed with cyanide. The addition of cyclohexanone causes a selective release of zinc. The zinc then reacts with 2-carboxy-2'-hydroxy-5'-sulfoformazyl benzene (zincon) indicator. The zinc concentration is proportional to the resulting blue color. See *Chemical Procedures Explained*, Appendix A, for more information.

REQUIRED REAGENTS

	Cat. No.
Zinc Reagent Set (100 Tests[*])	22448-00
Includes: (1) 14033-37, (4) 14032-68	

Description	Quantity Required Per Test	Unit	Cat. No.
Cyclohexanone	1 mL	118 mL MDB	14033-37
ZincoVer 5 Reagent Powder Pillows	1 pillow	25/pkg	14032-68

REQUIRED APPARATUS

Clippers, for opening powder pillows	1	each	968-00
Cylinder, graduated, mixing, 50 mL	1	each	1896-41

OPTIONAL REAGENTS

Bleach, household	1 gal	obtain locally
Hydrochloric Acid, 6 N	500 mL	884-49
Nitric Acid, ACS	500 mL	152-49
Nitric Acid, 1:1	473 mL	2540-11
Sodium Hydroxide Standard Solution, 5.0 N	59 mL[†] SCDB	2450-26
Sodium Hydroxide, 50% w/w	473 mL	2180-11
Water, deionized	3.78 L	272-17
Zinc Standard Solution, 100 mg/L	118 mL	2378-14
Zinc Standard Solution, Voluette ampule, 25 mg/L as Zn, 10 mL	16/pkg	14246-10

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[*] Contact Hach for larger sizes.

[†] 100 Tests equals 100 samples and 100 blanks.

OPTIONAL APPARATUS

Aspirator, vacuum	each	2131-00
Beaker, glass, 1000 mL	each	500-53
Cylinder, graduated, 100 mL	each	508-42
Dropper, plastic, 0.5 & 1.0 mL	10/pkg	21247-10
Filter Discs, glass, 47 mm	100/pkg	2530-00
Filter Holder, 47 mm	each	2340-00
Flask, erlenmeyer, 250 mL	each	505-46
Flask, volumetric, Class A, 100 mL	each	14574-42
Hot Plate, micro	each	12067-01
pH Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, Hach One	each	43800-00
Pipet Filler, safety bulb	each	14651-00
Pipet, serological, 2 mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, 5 mL	each	515-37
Pipet, volumetric, Class A, 0.5 mL	each	14515-34

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224 toll-free for more information
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Appendix B: Results of Standard Solution Tests on Hach DR/2000 Spectrophotometer

Nitrate Nitrogen (NO_3^--N)

g Ca(NO3)2 /	g Ca(NO3)2 /	mol / L	g N / mol	g N / L	mg N / L
0.873	236.15	0.0036968	28	0.10351048	103.51

Source	aliquot vol (L)	dilution vol (L)	expected (mg/L)	measured (mg/L)	% difference
103.51	0.001	0.05	2.07020961	2	3.391%
103.51	0.0002	0.025	0.82808385	0.7	15.467%
103.51	0.0001	0.025	0.41404192	0.3	27.544%
103.51	0.0001	0.1	0.10351048	0	100.000%
103.51	0.001	0.025	4.14041923	3.9	5.807%

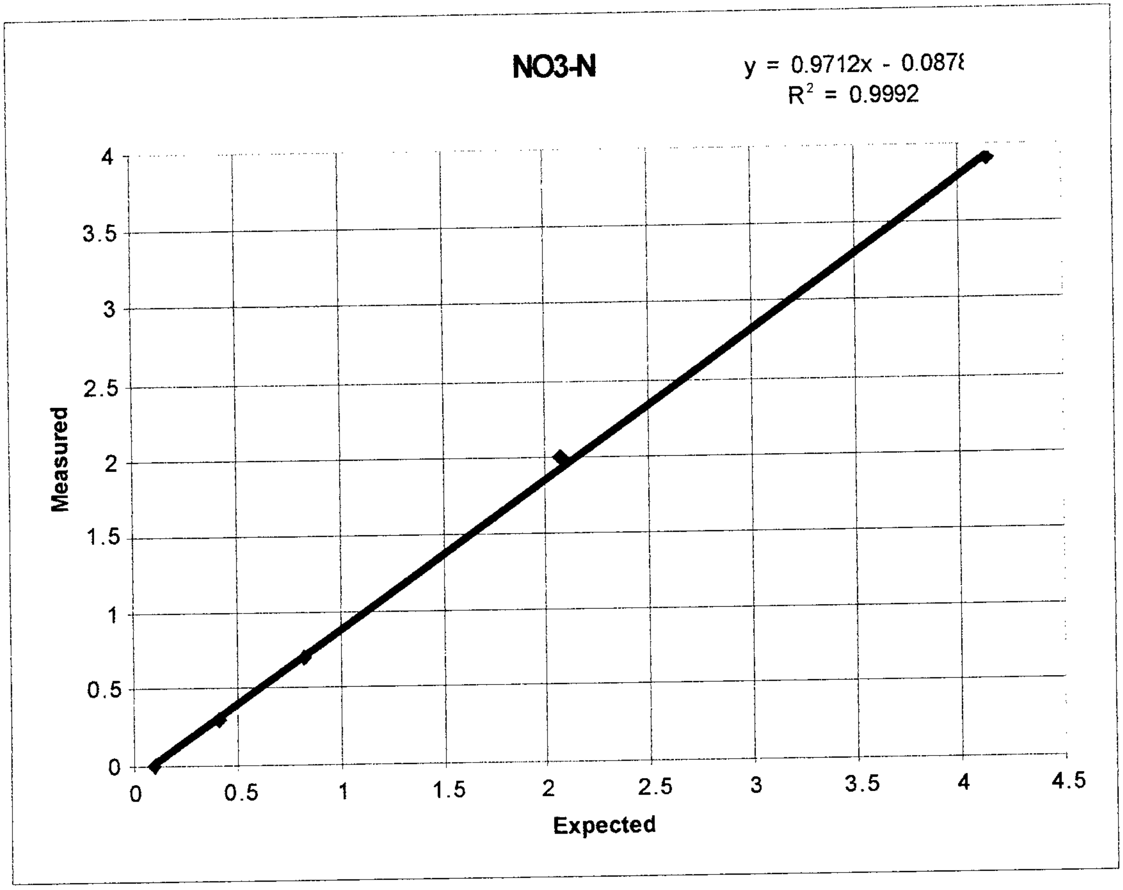

Figure 12: Nitrate Nitrogen Standard Solution Test Results

Nitrite-Nitrogen (NO_2^--N)

g NaNO2 / L	NaNO2 / mol	mol / L	g N / mol	g N / L	mg N / L
0.61	69	0.00884058	14	0.12376812	123.77

Source	aliquot vol (L)	dilution vol (L)	expected (mg/L)	measured (mg/L)	% difference
123.77	0.0001	0.1	0.12376812	0.167	-34.930%
123.77	0.0001	0.2	0.06188406	0.071	-14.731%
123.77	0.0001	0.5	0.02475362	0.038	-53.513%
123.77	0.0001	0.1	0.12376812	0.145	-17.155%

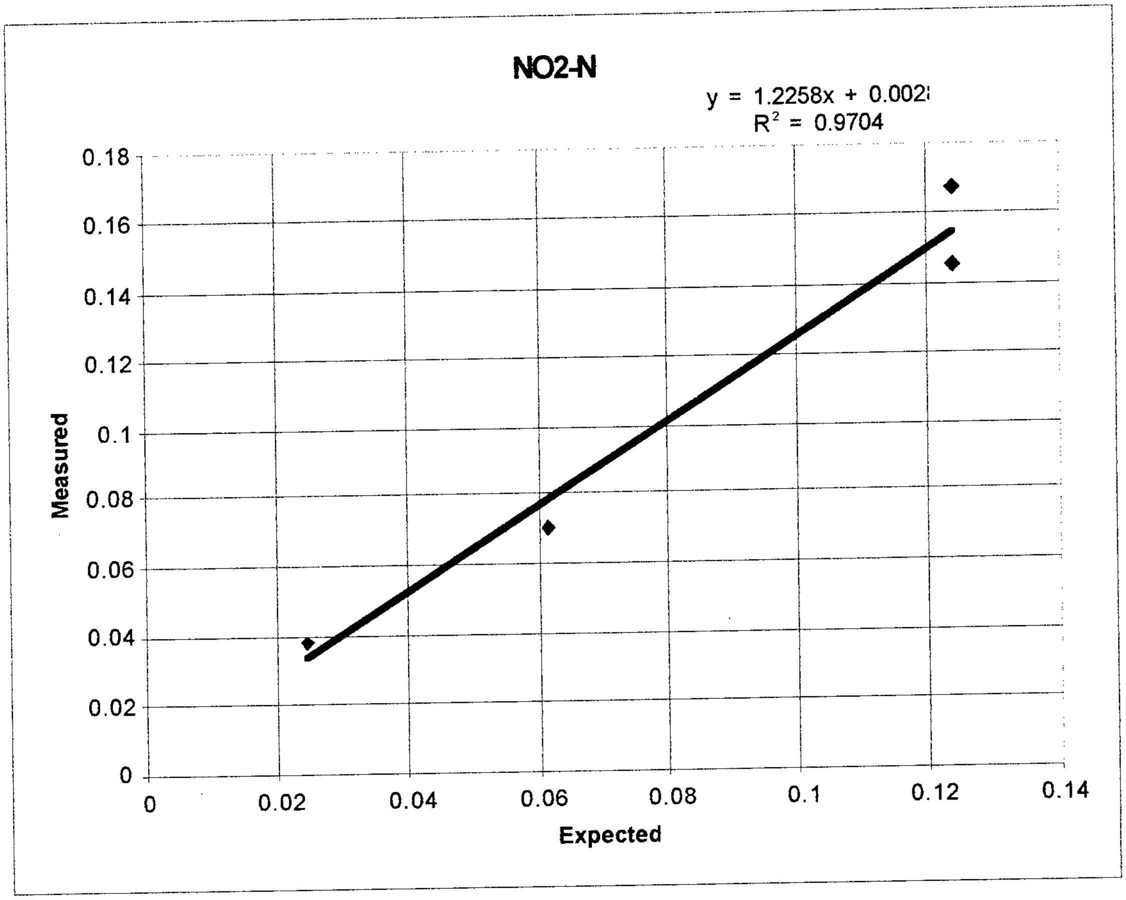

Figure 13: Nitrite Nitrogen Standard Solution Test Results

Sulfate (SO_4^{2-})

g Na2SO4 / L	g Na2SO4 / m	mol / L	g SO4 / mol	g SO4 / L	mg SO4 / L
0.302	142	0.00212676	96	0.20416901	204.17

Source	aliquot vol (L)	dilution vol (L)	expected (mg/L)	measured (mg/L)	% difference
204.17	0.001	0.05	4.08338028	0	100.000%
204.17	0.002	0.05	8.16676056	9	-10.203%
204.17	0.005	0.05	20.4169014	18	11.838%

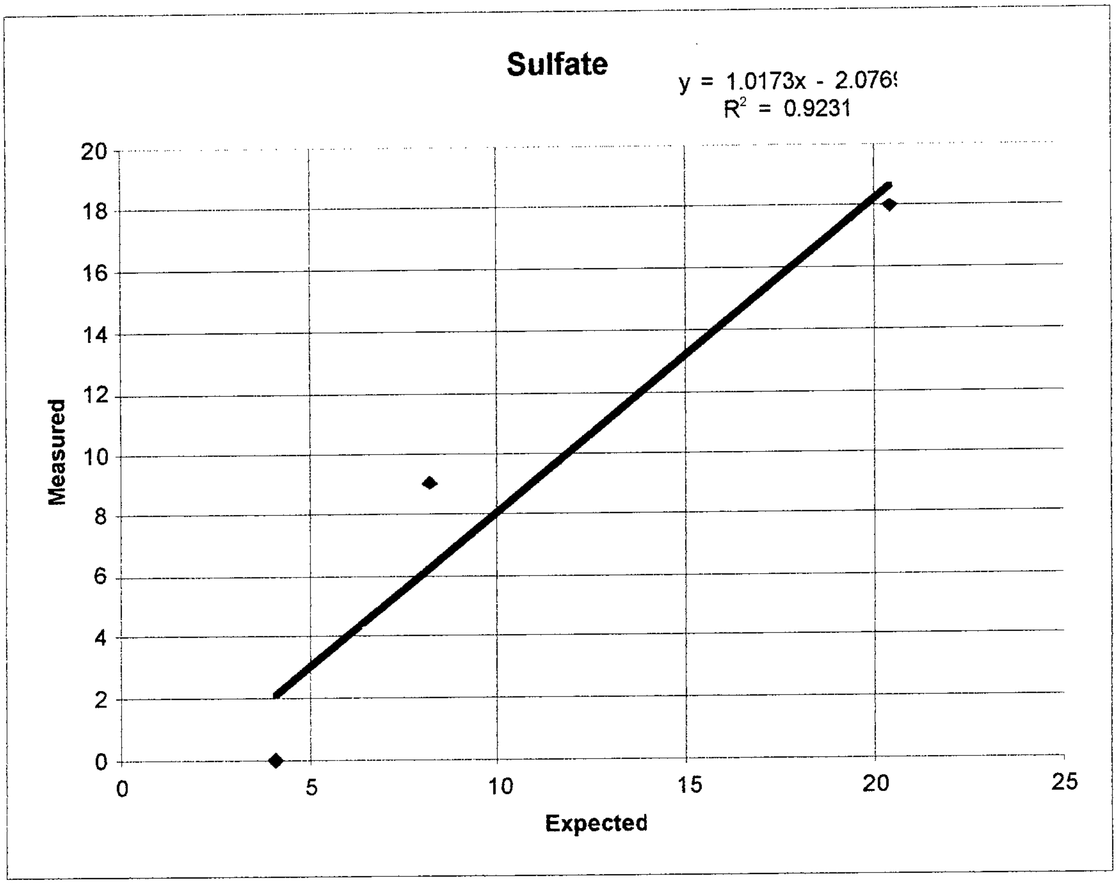

Figure 14: Sulfate Standard Solution Test Results

Phosphorus (P)

g Na2HPO4 /	g Na2HPO4 /	mol / L	g P / mol	g P / L	mg P / L
0.11133333	141.96	0.00078426	30.97376	0.02429143	24.2914338

Source	aliquot vol (L)	dilution vol (L)	expected (mg/L)	measured (mg/L)	% difference
24.2914338	0.001	0.05	0.48582868	0.1	79.417%
24.2914338	0.0005	0.05	0.24291434	0.15	38.250%
24.2914338	0.0001	0.05	0.04858287	0.02	58.833%
24.2914338	0.0001	0.1	0.02429143	0.02	17.666%
24.2914338	0.001	0.05	0.48582868	0.05	89.708%

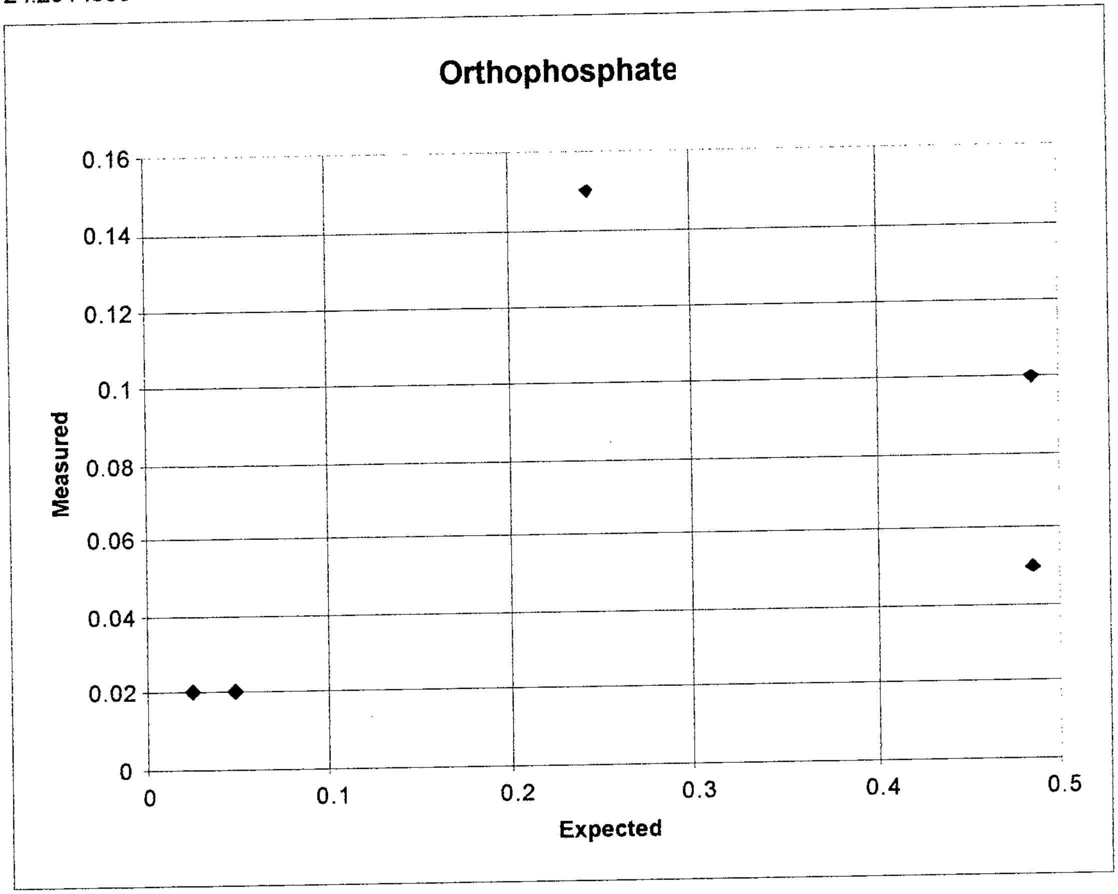

Figure 15: Phosphorus Standard Solution Test Results

Iron (Fe)

g FAS / L	g FAS / mol	mol / L	g Fe / mol	g Fe / L	mg Fe / L
0.0716	392.15	0.00018258	55.847	0.01019672	10.20

Source	aliquot vol (L)	dilution vol (L)	expected (mg/L)	measured (mg/L)	% difference
10.20	0.001	0.025	0.40786895	0.45	-10.330%
10.20	0.001	0.05	0.20393447	0.19	6.833%
10.20	0.004	0.05	0.8157379	0.66	19.092%
10.20	0.0005	0.05	0.10196724	0.1	1.929%
10.20	0.001	0.05	0.20393447	0.18	11.736%

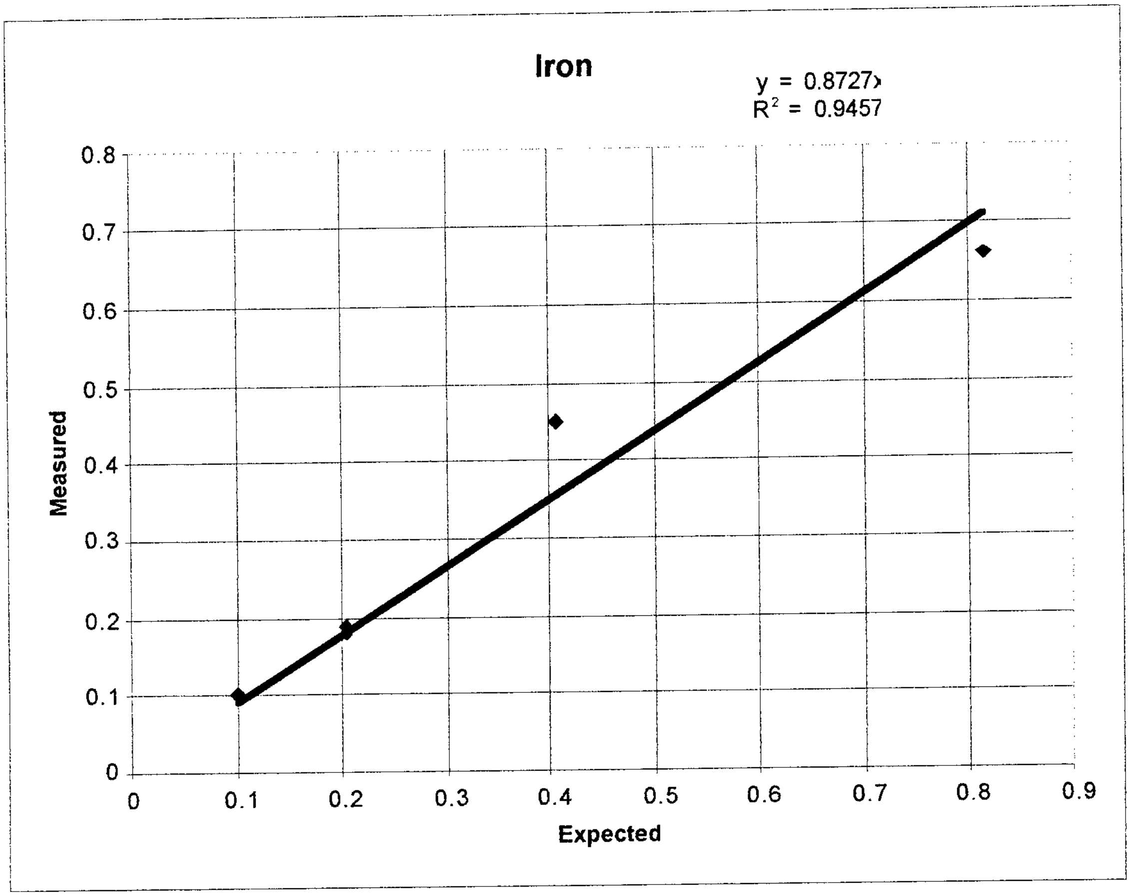

Figure 16: Iron Standard Solution Test Results

Zinc (Zn)

g ZnCl2 / L	g ZnCl2 / mol	mol / L	g Zn / mol	g Zn / L	mg Zn / L
0.057	136.28	0.00041826	65.38	0.02734561	27.35

Source	aliquot vol (L)	dilution vol (L)	expected (mg/L)	measured (mg/L)	% difference
27.35	0.001	0.05	0.54691224	0.5	8.578%
27.35	0.002	0.05	1.09382448	0.98	10.406%
27.35	0.0035	0.05	1.91419284	1.71	10.667%
27.35	0.0001	0.05	0.05469122	0.06	-9.707%
27.35	0.0001	0.05	0.05469122	0.07	-27.991%

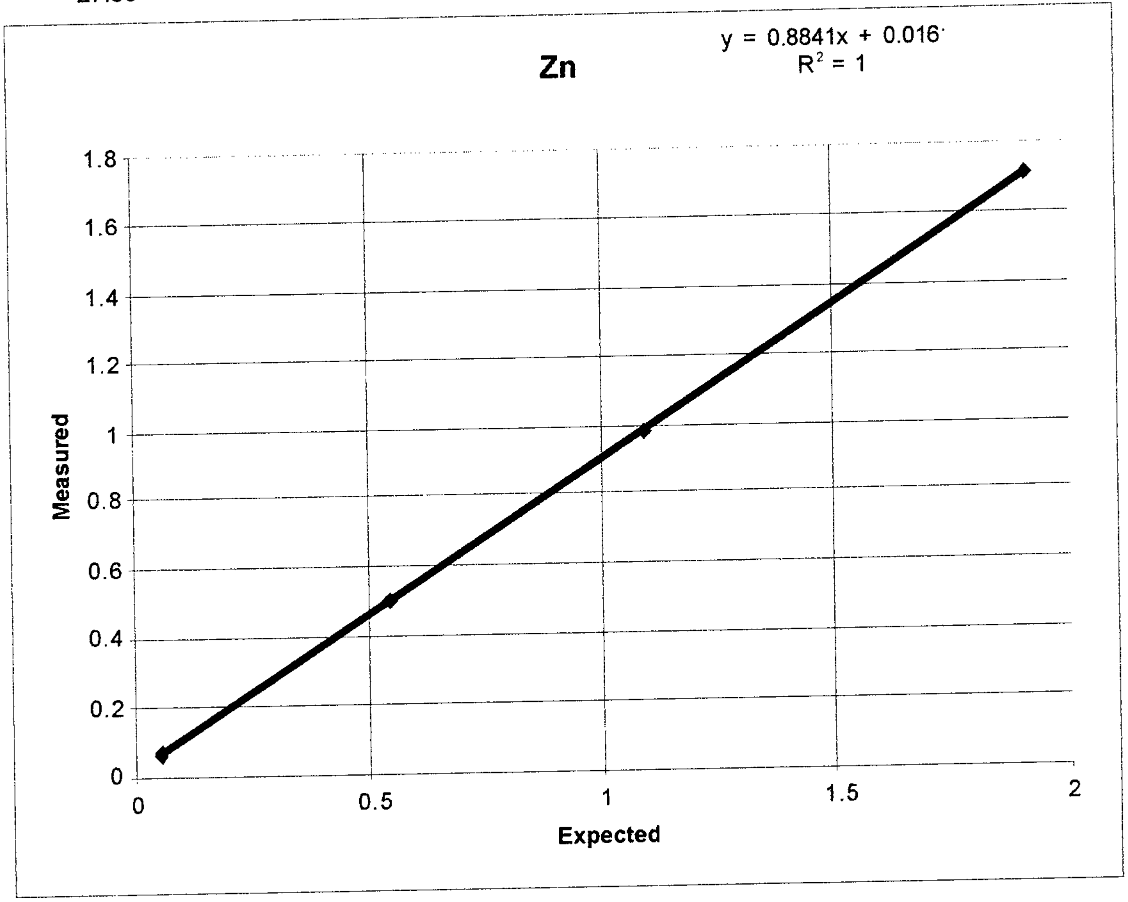

Figure 17: Zinc Standard Solution Test Results

Chloride (Cl)

g NaCl / L	g NaCl / mol	mol / L	g Cl / mol	g Cl / L	mg Cl / L
0.166	58.45	0.00284003	35.5	0.10082121	100.82

Source	aliquot vol (L)	dilution vol (L)	expected (mg/L)	measured (mg/L)	% difference
100.82	0.001	0.025	4.03284859	4	0.815%
100.82	0.0005	0.025	2.01642429	1.9	5.774%
100.82	0.0001	0.025	0.40328486	0.4	0.815%
100.82	0.0001	0.1	0.10082121	0.3	-197.556%
100.82	0.0005	0.025	2.01642429	1.8	10.733%

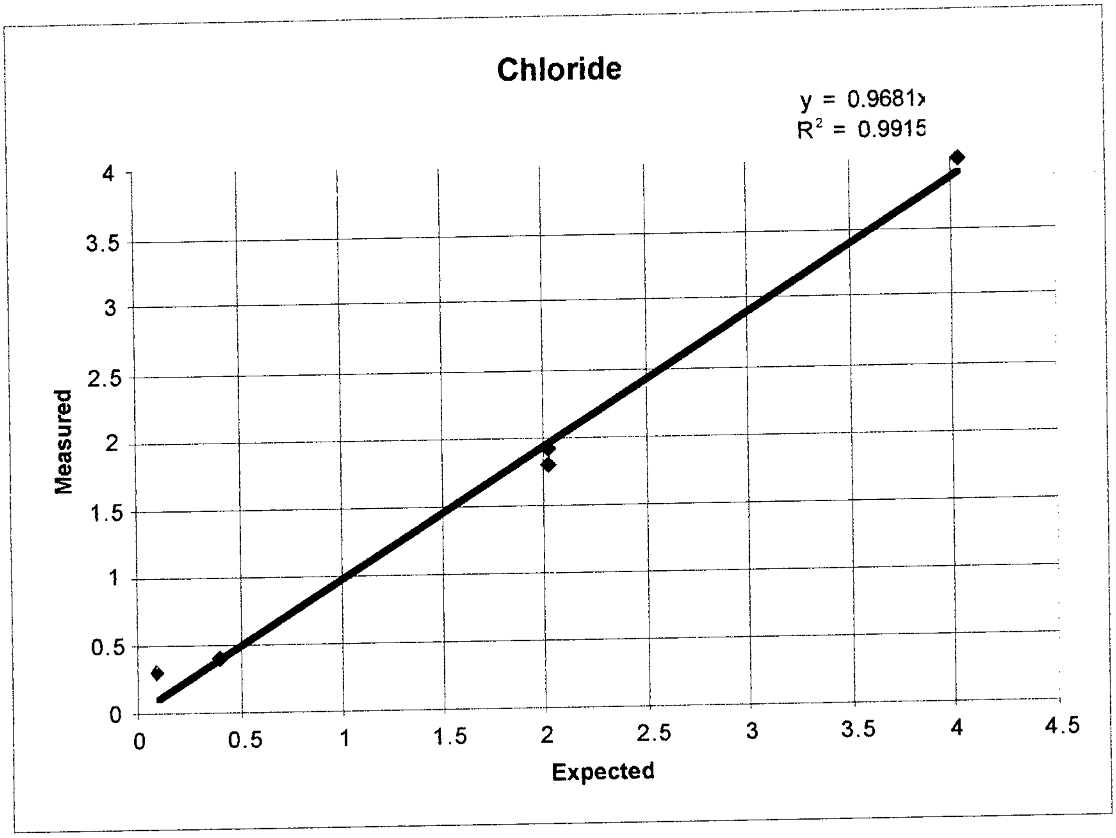

Figure 18: Chloride Standard Solution Test Results

Ammonia Nitrogen (NH_3-N)

g NH4Cl / L	g NH4Cl / mo	mol / L	g N / mol	g N / L	mg N / L
0.372	53.49	0.00695457	14	0.09736399	97.36

Source	aliquot vol (L)	dilution vol (L)	expected (mg/L)	measured (mg/L)	% difference
97.36	0.0005	0.025	1.94727987	1.69	13.212%
97.36	0.0001	0.025	0.38945597	0.56	-43.790%
97.36	0.00005	0.025	0.19472799	0.34	-74.603%
97.36	0.0001	0.1	0.09736399	0.1	-2.707%
97.36	0.0005	0.025	1.94727987	2.35	-20.681%

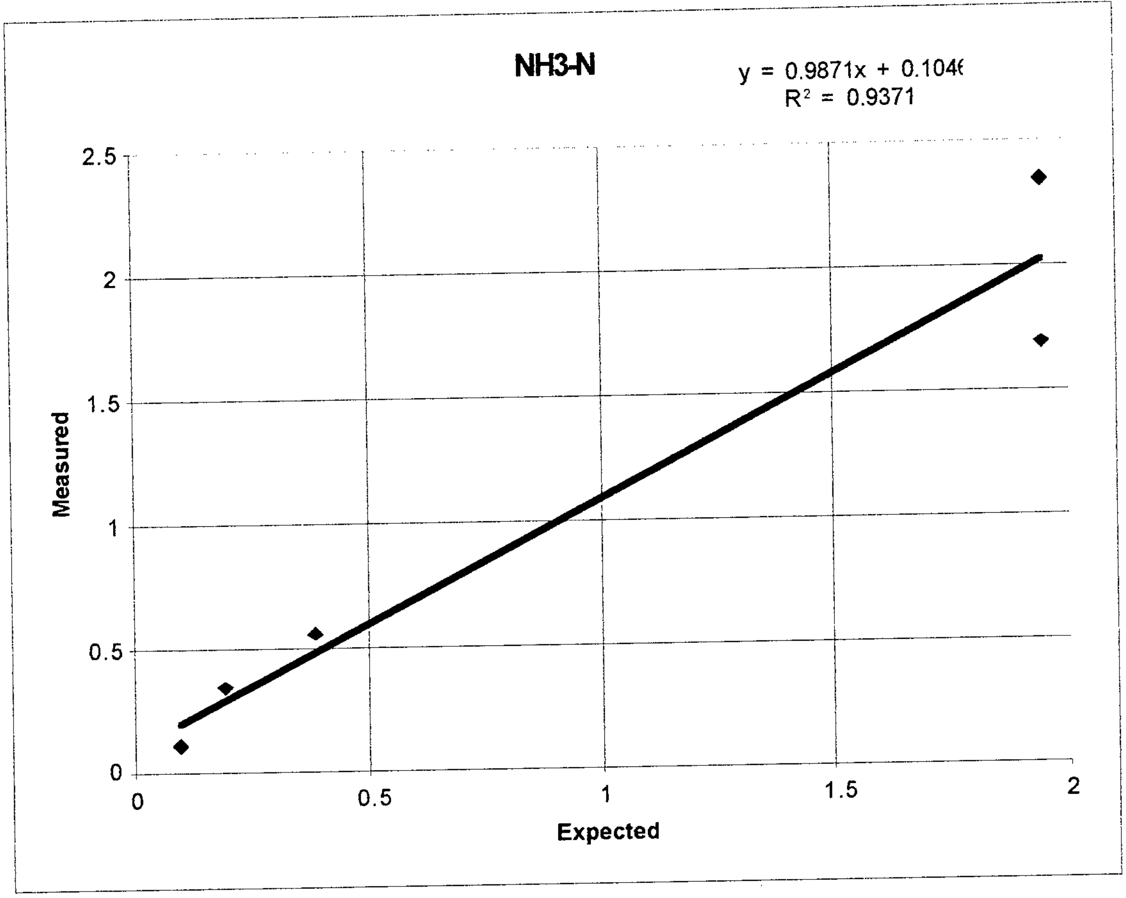

Figure 19: Ammonia Nitrogen Standard Solution Test Results

Nickel (Ni)

mg Ni / L
300.00

Source	aliquot vol (L)	dilution vol (L)	expected (mg/L)	measured (mg/L)	% difference
300.00	0.0001	0.3	0.1	0.04	60.000%
300.00	0.0002	0.3	0.2	0.09	55.000%
300.00	0.0003	0.3	0.3	0.26	13.333%
300.00	0.0001	0.3	0.1	0.09	10.000%

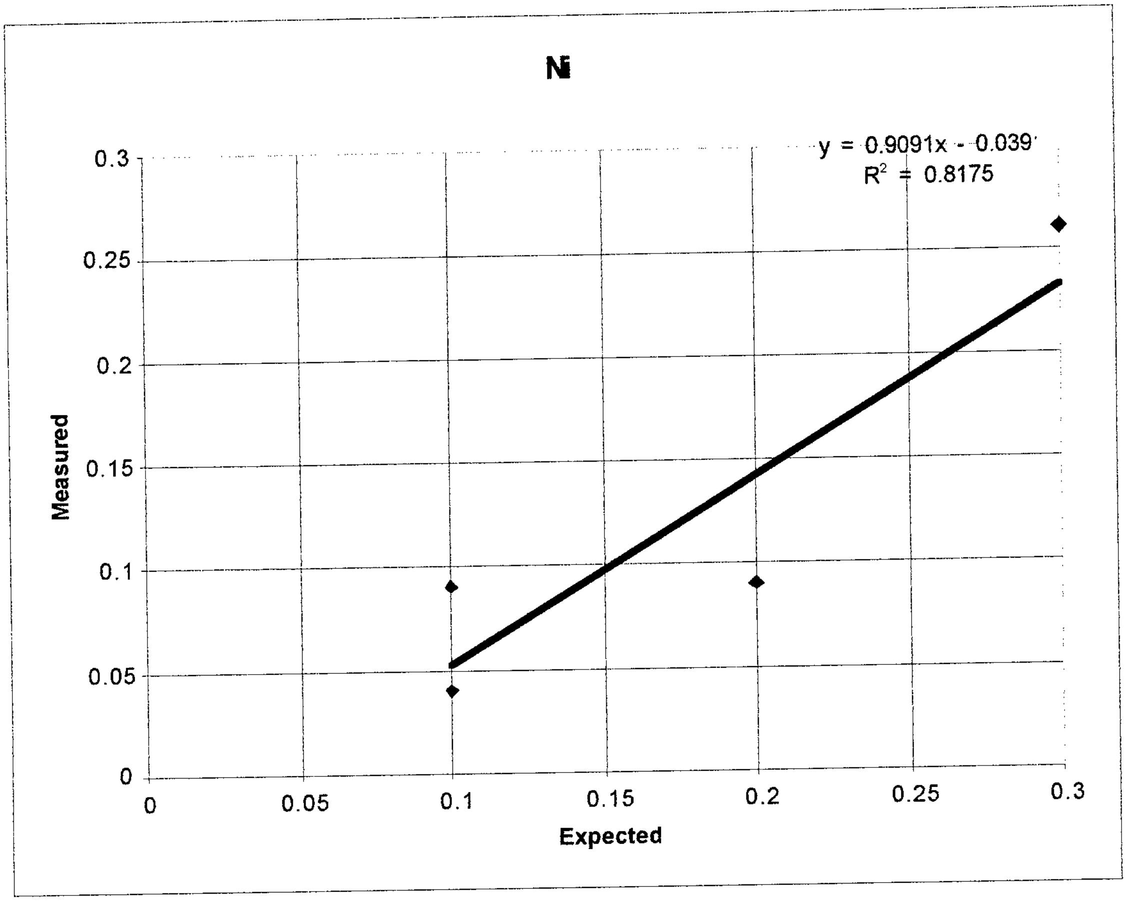

Figure 20: Nickel Standard Solution Test Results

Appendix C: Sample Water Quality Data

Table 14: Sample Water Quality Data

Sample Number	Collection Date	Site	Type	Temp (C)	pH	TDS (g/L)	Cond (mS/cm)	SS	Turb (FTU)	NO_3^--N	NO_2^--N	SO_4^{2-}	P	Fe	Zn	Cl^-	NH_3-N	Ni
1	4/10/96	PM-1	Ambient		7.46	0.90	1.79	0	0	0.1	0.006		0.17	0.04				
2	4/10/96	PM-2	Ambient	21.6	8.03	14.14		1	7	0.2	0.013		0.14	0.10				
3	4/10/96	PM-3	Ambient	21.8	8.50	14.14		9	15	0.2	0.003		0.15	0.05				
4	4/10/96	PM-4	Ambient	21.9	8.45	14.80		14	19	0.3	0.003		0.16	0.03				
5	4/10/96	PM-5	Ambient	21.8	8.24	14.87		16	19	0.4	0.004		0.13	0.05				
6	4/22/96	PM-1	Ambient	22.3	7.55	8.87	4.43	14	16	0.2	0.005		0.10	0.06				
7	4/22/96	PM-2	Ambient	23.1	7.99	15.38		7	13	0.4	0.009	2050	0.08	0.05				
8	4/22/96	PM-3	Ambient	23.6	8.18	15.76		14	16	0.4	0.005	1650	0.13	0.05				
9	4/22/96	PM-4	Ambient	23.8	8.45	12.71		16	22	0.4	0.003	2100	0.12	0.07				
10	4/22/96	PM-5	Ambient	23.7	8.52	15.57		15	22	0.2	0.006	1650	0.05	0.04				
11	4/22/96	DI Blank	Ambient					0	0	0.0	0.011	0	0.01	0.01				
12	4/29/96	PM-1	Storm Influenced	20.0	9.15	0.21	0.43	21	24	0.4	0.013	22	0.11	0.22				
13	4/29/96	PM-2	Storm Influenced	19.6	8.27	0.39	0.80	12	45	0.8	0.005	90	0.13	0.04				
14	4/29/96	PM-3	Storm Influenced	22.2	8.12	13.07		21	28	0.4	0.004	1350	0.20	0.09				
15	4/29/96	PM-4	Storm Influenced	22.3	8.54	10.26		30	44	0.6	0.004	1250	0.13	0.09				
16	4/29/96	PM-5	Storm Influenced	22.4	8.78	15.94		58	64	0.7	0.022	700	0.32	0.13				
17	4/29/96	DI Blank	Storm Influenced					0	0	0.0	0.004	0	0.02	0.01				
18	5/15/96	PM-1	Ambient	23.5	7.59	0.47	0.96	38	10	0.4	0.013	56	0.07	0.03	0.06	67	0.15	
19	5/15/96	PM-2	Ambient	26.8	7.69	10.17		43	54	0.7	0.015	950	0.22	0.58	0.01	7500	2.03	
20	5/15/96	PM-3	Ambient	27.6	8.39	11.70		70	56	0.6	0.000	950	0.12	0.22	0.00	7800	2.74	
21	5/15/96	PM-4	Ambient	27.1	8.57	11.01		55	52	0.6	0.004	1100	0.13	0.09	0.00	5600	2.59	
22	5/15/96	PM-5	Ambient	27.4	8.53	11.53		58	66	1.0	0.000	1100	0.13	0.19	0.01	6700	1.26	
23	5/15/96	DI Blank	Ambient					6	0	0.0	0.002	0	0.14	0.01	0.04	0.1	0.00	
24	5/21/96	PM-1	Ambient	24.1	7.13	0.66	1.32	6	5	0.3	0.004	56	0.13	0.03	0.02	94	0.05	
25	5/21/96	PM-2	Ambient	27.9	7.85	12.73		20	20	0.5	0.017	1200	0.13	0.08	0.00	6100	1.94	
26	5/21/96	PM-3	Ambient	29.7	8.15	13.71		36	35	0.4	0.005	1200	0.22	0.08	0.00	6900	1.16	
27	5/21/96	PM-4	Ambient	29.3	8.53	11.72		37	45	0.5	0.001	1050	0.22	0.09	0.00	6400	1.28	
28	5/21/96	PM-5	Ambient	29.4	8.31	13.24		55	64	0.8	0.001	1450	0.31	0.12	0.00	6600	0.62	
29	5/21/96	DI Blank	Ambient	21.9	9.04	0.02	0.03	1	0	0.0	0.009	0	0.04	0.02	0.02	2.4	0.02	

Table 14 Continued

Sample Number	Collection Date	Site	Type	Temp (C)	pH	TDS (g/L)	Cond (mS/cm)	SS	Turb (FTU)	NO_3^--N	NO_2^--N	SO_4^{2-}	P	Fe	Zn	Cl	NH_3-N	Ni
30	6/4/96	PM-1	Ambient	24.8	7.27	0.70	1.41	3	4	2.0	0.005	82	0.04	0.03	0.08	110	0.08	0.01
31	6/4/96	PM-2	Ambient															
32	6/4/96	PM-3	Ambient	30.1	8.70	13.97		38	40	0.6	0.004	1400	0.22	0.06	0.02	4100	1.38	0.11
33	6/4/96	PM-4	Ambient	29.6	8.90	15.16		70	52	0.5	0.004	1450	0.21	0.00	0.00	8100	1.42	0.15
34	6/4/96	PM-5	Ambient	29.5	8.67	14.00		60	47	0.6	0.002	1750	0.24	0.11	0.00	7100	1.22	0.07
35	6/4/96	DI Blank	Ambient					2	1	0.0	0.004	0	0.01	0.01	0.02	1	0.01	0.01
36	6/18/96	PM-1	Ambient	25.4	8.00	0.75	1.50	5	5	0.1	0.005	71	0.04	0.03		4	0.07	0.01
37	6/18/96	PM-2	Ambient															
38	6/18/96	PM-3	Ambient	31.7	8.85	14.44		90	55	0.6	0.005	1350	0.23	0.00	0.05	5500	1.6	0.09
39	6/18/96	PM-4	Ambient	31.2	9.21	18.90		46	45	0.6	0.003	950	0.18	0.07	0.01	8000	1.2	0.16
40	6/18/96	PM-5	Ambient	31.3	9.61	14.20		61	64	0.7	0.002	1250	0.28	0.05	0.00	5500	0.7	0.14
41	6/18/96	DI Blank	Ambient	16.7	10.62	0.01		7	1	0.0	0.005	0	0.03	0.00	0.01	0.7	0	0.00
42	6/25/96 10:30	PM-1 Up	Storm Influenced	18.3	7.28	0.04	0.09	360	194	0.3	0.000	0.00	0.10	0.47	0.05	15.3	1.42	0.09
43	6/25/96 11:00	PM-1 Up	Storm Influenced	21	7.5	0.04	0.09	204	149	0.3	0.000	0.00	0.07	0.41	0.04	15.6	0.88	0.05
44	6/25/96 11:15	PM-1 Up	Storm Influenced	20.9	8.2	0.04	0.1	140	105	0.3	0.008	0.00	0.11	0.32	0.06	13.2	0.82	0.04
45	6/25/96 11:30	PM-1 Up	Storm Influenced	21.6	8.43	0.04	0.1	140	106	0.2	0.018	0.00	0.11	0.25	0.01	13.2	0.73	0.03
46	6/25/96 11:45	PM-1 Up	Storm Influenced	21.2	8.54	0.04	0.09	185	99	0.4	0.011	4.00	0.00	0.27	0.04	12.2	0.87	0.08
47	6/25/96 12:00	PM-1 Up	Storm Influenced	20.2	8.03	0.04	0.09	260	133	0.3	0.007	0.00	0.07	0.45	0.05	16.5	0.79	0.1
48	6/25/96 10:30	PM-1	Storm Influenced	20.9	7.84	0.05	0.12	310	186	0.3	0.004	0.00	0.08	0.49	0.05	15.3	1.29	0.1
49	6/25/96 11:00	PM-1	Storm Influenced	21.2	8.13	0.04	0.08	220	138	0.3	0.000	0.00	0.08	0.46	0.04	15.3	0.90	0.09
50	6/25/96 11:15	PM-1	Storm Influenced	21.2	8.38	0.05	0.11	214	83	0.3	0.003	0.00	0.10	0.38	0.01	14.0	0.84	0.05
51	6/25/96 11:30	PM-1	Storm Influenced	21.3	8.63	0.05	0.12	160	98	0.3	0.010	0.00	0.06	0.22	0.02	13.8	0.70	0.04
52	6/25/96 11:45	PM-1	Storm Influenced	21.9	8.56	0.04	0.09	204	104	0.2	0.008	3.00	0.01	0.27	0.01	10.9	0.95	0.08
53	6/25/96 12:00	PM-1	Storm Influenced	21.7	8.44	0.04	0.08	310	176	0.2	0.006	0.00	0.03	0.40	0.00	16.7	0.86	0.15

Table 14 Continued

Sample Number	Collection Date	Site	Type	Temp (C)	pH	TDS (g/L)	Cond (mS/cm)	SS	Turb (FTU)	NO_3^--N	NO_2^--N	SO_4^{2-}	P	Fe	Zn	Cl^-	NH_3-N	Ni
54	6/25/96 10:30	TSC 1 Up	Storm Influenced	21.8	9.01	0.08	0.16	440	263	0.7	0.051	0.00	0.00	0.30	0.10	17.2	1.92	0.14
55	6/25/96 11:00	TSC 1 Up	Storm Influenced	22.1	9.57	0.12	0.25	310	198	0.7	0.074	0.00	0.01	0.15	0.04	20.7	1.80	0.02
56	6/25/96 11:15	TSC 1 Up	Storm Influenced	21.4	9.86	0.15	0.31	366	205	0.8	0.096		0.04	0.05	0.09	23.9	2.27	0.15
57	6/25/96 11:30	TSC 1 Up	Storm Influenced	21.1	9.71	0.13	0.27	430	184	0.7	0.093		0.10	0.08	0.08	22.1	1.52	0.13
58	6/25/96 11:45	TSC 1 Up	Storm Influenced	20.2	8.89	0.04	0.1	1320	450	0.4	0.003		0.10	0.60	0.06	16.6	4.46	0.3
59	6/25/96 12:00	TSC 1 Up	Storm Influenced	20.1	9.83	0.12	0.25	380	168	0.4	0.045		0.00	0.06	0.04	8.2	1.81	0.09
60	6/25/96 10:30	TSC 1 Dn	Storm Influenced	19.4	9.01	0.08	0.16	400	203	0.6	0.050	0.00	0.00	0.08	0.20	23.0	1.73	0.02
61	6/25/96 11:00	TSC 1 Dn	Storm Influenced	19.4	9.66	0.11	0.22	283	174	0.8	0.078	0.00	0.19	0.16	0.01	19.3	1.84	0.13
62	6/25/96 11:15	TSC 1 Dn	Storm Influenced	20	9.75	0.12	0.25	270	155	0.7	0.091		0.00	0.08	0.05	15.4	1.78	0.11
63	6/25/96 11:30	TSC 1 Dn	Storm Influenced	20.2	9.72	0.13	0.26	225	137	0.7	0.085		0.08	0.00	0.01	14.6	1.83	0.12
64	6/25/96 11:45	TSC 1 Dn	Storm Influenced	21.1	9.58	0.12	0.25		154	0.8	0.081		0.11	0.03	0.08	19.1	1.75	0.13
65	6/25/96 12:00	TSC 1 Dn	Storm Influenced	21	9.76	0.13	0.27	280	144	0.6	0.065		0.12	0.05	0.05	10.8	1.50	0.12
66	6/25/96	PM-3 Up	Storm Influenced	23.5	8.06	0.14	0.3	27	23	0.4	0.008	0	0.06	0.02		7	0.37	
67	6/25/96	PM-3	Storm Influenced	23.3	7.26	5.9	11.82	35	42	0.3	0.007	750	0.11	0.07		o/r	0.66	
68	6/25/96	PM-4 Up	Storm Influenced	23.8	7.15	0.31	0.63	12	18	0.2	0.006	200	0.12	0.03		80	0.23	
69	6/25/96	PM-4	Storm Influenced	24.2	6.98	2.76	5.53	35	34	0.2	0.021	700	0.09	0.1		1600	0.6	
70	6/25/96	PM-5	Storm Influenced	24.2	6.91	1.03	2.07	78	78	0.6	0.055	58	0.09	0.31		542.5	1.08	
71	7/9/96	PM-1	Ambient	27	6.80	0.66	1.32	35	28	0.1	0.003	50	0.12	0.24	0.00	160	0.21	0.00
72	7/9/96	PM-2	Ambient															
73	7/9/96	PM-3	Ambient	33.4	8.21	6.35	12.68	31	37	0.4	0.006	1200	0.12	0.08	0.01	5000	1.42	0.11
74	7/9/96	PM-4	Ambient	33.1	8.45	9.43	18.86	35	39	0.3	0.007	900	0.10	0.08	0.01	5500	0.58	0.16
75	7/9/96	PM-5	Ambient	33	8.89	9.76	19.54	42	48	0.4	0.006	850	0.11	0.07	0.00	3300	0.84	0.18
76	7/9/96	DI Blank	Ambient	22	3.07	0.02	0.05	0	0	0.0	0.006	0	0.12	0.02	0.08	0.1	0.02	
77	7/23/96	PM-1	Ambient	28.5	6.10	0.49	0.98	8	11	0.1	0.002	45	0.10	0.64	0.00	140	0.3	0.02
78	7/23/96	PM-2	Ambient															
79	7/23/96	PM-3	Ambient	31.6	7.11	11.84		115	90	0.5	0.013	1950	0.06	0.20	0.00	9300	0.92	0.02
80	7/23/96	PM-4	Ambient	32.1	7.70	8.25	16.50	56	55	0.5	0.005	1100	0.09	0.11	0.01	6600	0.62	0.10
81	7/23/96	PM-5	Ambient	31.7	8.17	8.94	17.89	77	77	0.8	0.005	700	0.10	0.08	0.00	4500	0.76	0.11
82	7/23/96	DI Blank	Ambient	22.1	8.80	0.49	0.0086	2	1	0.0	0.006	0	0.01	0.01	0.06	0.1	0.01	0.02

Table 14 Continued

Sample Number	Collection Date	Site	Type	Temp (C)	pH	TDS (g/L)	Cond (mS/cm)	SS	Turb (FTU)	NO_3^--N	NO_2^--N	SO_4^{2-}	P	Fe	Zn	Cl^-	NH_3-N	Ni
83	8/5/96	PM-1	Ambient	28	7.01	2.85	5.72	27	28	0.2	0.005	550	0.12	0.28	0.00	2000	0.37	0.09
84	8/5/96	PM-2	Ambient															
85	8/5/96	PM-3	Ambient	31.4	7.70	11.18		33	40	0.4	0.007	1200	0.11	0.16	0.01	9700	0.66	0.16
86	8/5/96	PM-4	Ambient	29.8	8.28	7.23	14.50	60	50	0.3	0.010	1050	0.06	0.12	0.03	10700	0.84	0.27
87	8/5/96	PM-5	Ambient	31.4	8.34	12.40		38	43	0.4	0.005	1950	0.07	0.08	0.01	10200	0.72	0.26
88	8/5/96	DI Blank	Ambient	21.5	8.90	0.09	0.19	3	2	0.0	0.005	0	0.12	0.05	0.01	1.8	0.01	0.00
89	8/9/96	TSC 1 Up	Storm Influenced	22.2	6.82	0.03	0.07	36	25	0.6	0.017	0	0.10	0.06	0.06	1.5	0.28	0.11
90	8/9/96	TSC 1 Dn	Storm Influenced	22.3	6.36	0.03	0.06	30	23	0.3	0.014	0	0.10	0.04	0.04	1.6	0.23	0.03
91	8/9/96	TSC 2 Up	Storm Influenced	22.3	8.91	0.08	0.08	685	366	1.6	0.066	13	0.00	0.60	0.01		2.5	0.08
92	8/9/96	TSC 2 Dn	Storm Influenced	22.3		0.09	0.20	960		2.4	0.026	23	0.00	0.70	0.01		1.68	0.12
93	8/9/96	PM-1 Up	Storm Influenced	22.3		0.10	0.21	70	60	0.8	0.071	0	0.06	0.02	0.04	9.1	0.63	0.06
94	8/9/96	PM-1	Storm Influenced	22.3		0.11	0.23			0.8	0.067	0	0.04	0.04	0.01	11	0.63	0.05
95	8/9/96	PM-3 Up	Storm Influenced	22.3		2.59	5.18		52	0.7	0.090		0.00	0.05	0.03	1070	0.62	0.03
96	8/9/96	PM-3	Storm Influenced	22.3		9.50	19.04		34	0.3	0.012	1350	0.10	0.05	0.01	5900	1.4	0.03
97	8/9/96	PM-4 Up	Storm Influenced	22.3		3.42	6.85		23	0.3	0.010	750	0.02	0.02	0.02	3100	0.36	0.04
98	8/9/96	PM-4	Storm Influenced	22.3		10.23			29	0.3	0.005	1450	0.12	0.02	0.02	6100	1.55	0.05
99	8/9/96	PM-5	Storm Influenced	22.3		9.93	19.91				0.007	1500	0.03	0.03	0.00	400	1.53	0.07
100	8/20/96	PM-1	Ambient	27.2	6.43	0.39	0.79	5	9	0.1	0.004	24	0.08	0.51	0.00	90	0.13	0.02
101	8/20/96	PM-2	Ambient															
102	8/20/96	PM-3	Ambient	30.2	7.70	6.57	13.12	24	30	0.2	0.006	1250	0.24	0.06	0.01	8500	0.5	0.50
103	8/20/96	PM-4	Ambient	31.3	7.94	6.45	12.93	36	39	0.4	0.005	1250	0.23	0.07	0.00	6800	0.46	0.24
104	8/20/96	PM-5	Ambient	30.7	8.37	7.68	15.34	29	41	0.3	0.005	900	0.23	0.03	0.00	4800	0.56	0.18
105	8/20/96	DI Blank	Ambient	22.7	8.53	0.00	0.00	3	11	0.0	0.004	0	0.00	0.29	0.05	0	0.01	0.00

Table 14 Continued

Sample Number	Collection Date	Site	Type	Temp (C)	pH	TDS (g/L)	Cond (mS/cm)	SS	Turb (FTU)	NO_3^--N	NO_2^--N	SO_4^{2}	P	Fe	Zn	Cl^-	NH_3-N	Ni
106	8/22/96	TSC 1 Up	Storm Influenced	24.2		0.08	0.18	55	47	0.6	0.122	0	0.00	0.01	0.04	23.1	0.37	0.05
107	8/22/96	TSC 1 Dn	Storm Influenced	24.3		0.06	0.12	99	43	0.5	0.108	0	0.00	0.01	0.02	5.4	0.28	0.05
108	8/22/96	TSC 2 Up	Storm Influenced	24.6		0.16	0.33	396	264	4.1	0.261	25	0.00	0.37	0.01	30	1.72	0.04
109	8/22/96	TSC 2 Dn	Storm Influenced	24.7		0.16	0.33	334	232	4.3	0.283	43	0.00	0.26	0.01	40	1.50	0.05
110	8/22/96	TSC 3 Up	Storm Influenced	24.7		0.09	0.19	396	305	1.2	0.050	0	0.00	0.55	0.02	50	1.85	0.04
111	8/22/96	TSC 3 Dn	Storm Influenced	24.6		0.10	0.20	394	303	1	0.043	0	0.00	0.50	0.00	30	1.71	0.00
112	8/22/96	TSC 4 Up	Storm Influenced	24.7		0.11	0.22	328	205	0.8	0.170	13	0.04	0.28	0.04	40	1.66	0.00
113	8/22/96	TSC 4 Dn	Storm Influenced	24.5		0.10	0.21	371	235	0.8	0.071	0	0.00	0.44	0.01	50	1.69	0.01
114	8/22/96	TSC 5 Up	Storm Influenced	24.5		0.13	0.26	286	201	0.7	0.122	16	0.00	0.34	0.02	50	1.38	0.02
115	8/22/96	TSC 5 Dn	Storm Influenced	24.5		0.11	0.22	329	199	0.7	0.183	20	0.00	0.27	0.09	50	1.50	0.02
116	8/22/96	PM-1 Up	Storm Influenced	24.6		0.09	0.17	17	24	0.2	0.037	4	0.02	0.05	0.03	8	0.27	0.03
117	8/22/96	PM-1	Storm Influenced	24.7		0.30	0.60	29	23	0.2	0.032	36	0.01	0.03	0.04	150	0.28	0.07
118	8/22/96	PM-3 Up	Storm Influenced	25		6.49	13.00	306	148	0.4	0.033	600	0.01	0.29	0.02	9100	0.54	0.10
119	8/22/96	PM-3	Storm Influenced	25.4		10.02		96	48	0.3	0.018	850	0.22	0.16	0.01	15100	1.66	0.07
120	8/22/96	PM-4 Up	Storm Influenced	25.3		6.27	12.55	27	20	0.2	0.009	650	0.14	0.02	0.02	9300	0.35	0.08
121	8/22/96	PM-4	Storm Influenced	25.9		10.03		24	22	0.1	0.011	900	0.13	0.05	0.04	17100	1.76	0.08
122	8/22/96	PM-5	Storm Influenced	25.6		10.41		24	23	0.2	0.008	950	0.23	0.04	0.02	18900	1.72	0.00
123	8/22/96	DI Blank	Storm Influenced	23.4		0.01	0.03	1	0	0	0.006	0	0.00			0.6	0.00	
124	9/3/96	PM-1	Ambient	24.6	6.70	0.28	0.51	5	30	0.6	0.002	0	0.03	0.34	0.01	10	0.53	0.00
126	9/3/96	PM-3	Ambient	27	7.06	2.78	4.18	44	72	0.6	0.033	200	0.02	0.27	0.04	1200	0.86	0.01
127	9/3/96	PM-4	Ambient	28	6.94	4.29	6.48	42	63	0.5	0.039	220	0.21	0.24	0.04	1900	0.88	0.07
128	9/3/96	PM-5	Ambient	27.7	7.10	3.25	4.60	40	61	0.5	0.044	150	0.01	0.20	0.03	1000	0.74	0.00
129	9/3/96	DI Blank	Ambient	21.6	8.86	0.00	0.00	0	0	0.0	0.007	0	0.01	0.01	0.02	0.4	0.02	0.00
130	9/16/96	PM-1	Ambient	25	7.16	0.47	0.94	12	14	0.2	0.004	37	0.02	0.51	0.00	120	0.24	0.00
132	9/16/96	PM-3	Ambient	27	8.08	7.58	15.15	41	40	0.3	0.009	1050	0.08	0.08	0.01	2300	0.99	0.07
133	9/16/96	PM-4	Ambient	28	8.16	7.15	14.28	27	42	0.4	0.005	1200	0.17	0.07	0.01	2800	1.12	0.05
134	9/16/96	PM-5	Ambient	28	8.23	6.97	13.93	32	40	0.3	0.005	950	0.08	0.10	0.01	2400	0.86	0.03
135	9/16/96	DI Blank	Ambient	21.5	6.48	0.00	0.00	0	0	0.0	0.005	1	0.01	0.10	0.01	0	0	0.00
136	10/2/96	PM-1	Ambient	23.1	7.08	1.09	2.19	11	17	0.2	0.003	20	0.08	0.28	0.00	480	0.28	0.07
138	10/2/96	PM-3	Ambient	23.8	8.45	5.55	11.09	32	40	0.3	0.003	1000	0.23	0.07	0.01	2600	0.45	0.18
139	10/2/96	PM-4	Ambient	24.2	8.32	7.21	14.41	32	40	0.3	0.001	850	0.02	0.07	0.00	6100	0.61	0.11
140	10/2/96	PM-5	Ambient	24.1	8.45	5.69	11.38	27	41	0.2	0.002	850	0.00	0.07	0.00	3300	0.46	0.18
141	10/2/96	DI Blank	Ambient	21.7	6.03	0.00	0.00	1	0	0.0	0.002	0	0.00	0.01	0.01	0.7	0.01	0.01

Appendix D: t-Test Analysis of Laboratory Results

Table 15: t-Test at PM-1: Ambient (Var. 1) vs. Storm Influenced (Var. 2)

PM 1 Turb

	Variable 1	*Variable 2*
Mean	13.615385	104
Variance	97.25641	3786
Observations	13	8
Hypothesized Mean Difference	0	
df	7	
t Stat	-4.122	
P(T<=t) one-tail	0.0022233	
t Critical one-tail	1.8945775	
P(T<=t) two-tail	0.0044465	
t Critical two-tail	2.3646226	

Two-tail t stat <-t crit< t crit
REJECT

PM1 SO4

	Variable 1	*Variable 2*
Mean	90.090909	6.7777778
Variance	23812.691	171.94444
Observations	11	9
Hypothesized Mean Difference	0	
df	10	
t Stat	1.783	
P(T<=t) one-tail	0.052476	
t Critical one-tail	1.8124615	
P(T<=t) two-tail	0.104952	
t Critical two-tail	2.2281392	

Two-tail -t crit< t stat <t crit
ACCEPT

PM1 Cl

	Variable 1	*Variable 2*
Mean	297.72727	30.875
Variance	334858.42	2321.0279
Observations	11	8
Hypothesized Mean Difference	0	
df	10	
t Stat	1.522	
P(T<=t) one-tail	0.0794642	
t Critical one-tail	1.8124615	
P(T<=t) two-tail	0.1589283	
t Critical two-tail	2.2281392	

Two-tail -t crit< t stat <t crit
ACCEPT

PM1 SS

	Variable 1	*Variable 2*
Mean	13	183.5
Variance	153.83333	12216.571
Observations	13	8
Hypothesized Mean Difference	0	
df	7	
t Stat	-4.346	
P(T<=t) one-tail	0.001685	
t Critical one-tail	1.8945775	
P(T<=t) two-tail	0.0033701	
t Critical two-tail	2.3646226	

Two-tail t stat <-t crit< t crit
REJECT

PM1 Phosphorus

	Variable 1	*Variable 2*
Mean	0.0846154	0.0577778
Variance	0.0019769	0.0013944
Observations	13	9
Hypothesized Mean Difference	0	
df	19	
t Stat	1.532	
P(T<=t) one-tail	0.0710413	
t Critical one-tail	1.7291313	
P(T<=t) two-tail	0.1420827	
t Critical two-tail	2.0930247	

Two-tail -t crit< t stat <t crit
ACCEPT

PM 1 NH3

	Variable 1	*Variable 2*
Mean	0.2190909	0.80625
Variance	0.0213091	0.0838268
Observations	11	8
Hypothesized Mean Difference	0	
df	10	
t Stat	-5.270	
P(T<=t) one-tail	0.0001815	
t Critical one-tail	1.8124615	
P(T<=t) two-tail	0.000363	
t Critical two-tail	2.2281392	

Two-tail t stat <-t crit< t crit
REJECT

Table 15 Continued

PM1 NO3-N

	Variable 1	*Variable 2*
Mean	0.3538462	0.3333333
Variance	0.2660256	0.035
Observations	13	9
Hypothesized Mean Difference	0	
df	16	
t Stat	0.131	
P(T<=t) one-tail	0.4485297	
t Critical one-tail	1.7458842	
P(T<=t) two-tail	0.8970595	
t Critical two-tail	2.1199048	

Two-tail -t crit< t stat <t crit
ACCEPT

PM 1 NO2-N

	Variable 1	*Variable 2*
Mean	0.0046923	0.0158889
Variance	7.731E-06	0.0004544
Observations	13	9
Hypothesized Mean Difference	0	
df	8	
t Stat	-1.567	
P(T<=t) one-tail	0.0779191	
t Critical one-tail	1.8595483	
P(T<=t) two-tail	0.1558382	
t Critical two-tail	2.3060056	

Two-tail -t crit< t stat <t crit
ACCEPT

PM 1 Iron

	Variable 1	*Variable 2*
Mean	0.2323077	0.2788889
Variance	0.0472526	0.0285361
Observations	13	9
Hypothesized Mean Difference	0	
df	20	
t Stat	-0.565	
P(T<=t) one-tail	0.2892946	
t Critical one-tail	1.724718	
P(T<=t) two-tail	0.5785892	
t Critical two-tail	2.0859625	

Two-tail -t crit< t stat <t crit
ACCEPT

PM 1 Zn

	Variable 1	*Variable 2*
Mean	0.017	0.0225
Variance	0.0008456	0.0003357
Observations	10	8
Hypothesized Mean Difference	0	
df	15	
t Stat	-0.489	
P(T<=t) one-tail	0.3159671	
t Critical one-tail	1.753051	
P(T<=t) two-tail	0.6319343	
t Critical two-tail	2.1314509	

Two-tail -t crit< t stat <t crit
ACCEPT

PM 1 Ni

	Variable 1	*Variable 2*
Mean	0.0244444	0.07875
Variance	0.0010778	0.0012696
Observations	9	8
Hypothesized Mean Difference	0	
df	14	
t Stat	-3.254	
P(T<=t) one-tail	0.0028813	
t Critical one-tail	1.7613092	
P(T<=t) two-tail	0.0057626	
t Critical two-tail	2.1447886	

Two-tail t stat <-t crit< t crit
REJECT

Table 16: t-Test at PM-3: Ambient (Var. 1) vs. Storm Influenced (Var. 2)

Turbidity

	Variable 1	*Variable 2*
Mean	43.538462	38
Variance	431.4359	77.333333
Observations	13	4
Hypothesized Mean Difference	0	
df	13	
t Stat	0.764	
P(T<=t) one-tail	0.2291891	
t Critical one-tail	1.7709317	
P(T<=t) two-tail	0.4583781	
t Critical two-tail	2.1603682	

Two-tail -t crit< t stat <t crit
ACCEPT

S

	Variable 1	*Variable 2*
Mean	1200	1075
Variance	177727.27	102500
Observations	12	4
Hypothesized Mean Difference	0	
df	7	
t Stat	0.622	
P(T<=t) one-tail	0.2769431	
t Critical one-tail	1.8945775	
P(T<=t) two-tail	0.5538861	
t Critical two-tail	2.3646226	

Two-tail -t crit< t stat <t crit
ACCEPT

Cl

	Variable 1	*Variable 2*
Mean	5718.1818	10500
Variance	8715636.4	42320000
Observations	11	2
Hypothesized Mean Difference	0	
df	1	
t Stat	-1.021	
P(T<=t) one-tail	0.246756	
t Critical one-tail	6.3137486	
P(T<=t) two-tail	0.493512	
t Critical two-tail	12.70615	

Two-tail -t crit< t stat <t crit
ACCEPT

SS

	Variable 1	*Variable 2*
Mean	44.384615	50.666667
Variance	908.25641	1590.3333
Observations	13	3
Hypothesized Mean Difference	0	
df	3	
t Stat	-0.256	
P(T<=t) one-tail	0.4070855	
t Critical one-tail	2.353363	
P(T<=t) two-tail	0.8141711	
t Critical two-tail	3.1824493	

Two-tail -t crit< t stat <t crit
ACCEPT

P

	Variable 1	*Variable 2*
Mean	0.1484615	0.1575
Variance	0.0053641	0.0037583
Observations	13	4
Hypothesized Mean Difference	0	
df	6	
t Stat	-0.246	
P(T<=t) one-tail	0.4070165	
t Critical one-tail	1.9431809	
P(T<=t) two-tail	0.814033	
t Critical two-tail	2.4469136	

Two-tail -t crit< t stat <t crit
ACCEPT

NH3-N

	Variable 1	*Variable 2*
Mean	1.1527273	1.24
Variance	0.4171618	0.2692
Observations	11	3
Hypothesized Mean Difference	0	
df	4	
t Stat	-0.244	
P(T<=t) one-tail	0.4095227	
t Critical one-tail	2.1318465	
P(T<=t) two-tail	0.8190455	
t Critical two-tail	2.7764509	

Two-tail -t crit< t stat <t crit
ACCEPT

Table 16 Continued

NO3-N

	Variable 1	*Variable 2*
Mean	0.4230769	0.325
Variance	0.0219231	0.0025
Observations	13	4
Hypothesized Mean Difference	0	
df	15	
t Stat	2.040	
P(T<=t) one-tail	0.0296825	
t Critical one-tail	1.753051	
P(T<=t) two-tail	0.059365	
t Critical two-tail	2.1314509	

Two-tail -t crit< t stat <t crit
ACCEPT

NO2-N

	Variable 1	*Variable 2*
Mean	0.0076154	0.01025
Variance	6.792E-05	3.758E-05
Observations	13	4
Hypothesized Mean Difference	0	
df	7	
t Stat	-0.689	
P(T<=t) one-tail	0.2564962	
t Critical one-tail	1.8945775	
P(T<=t) two-tail	0.5129924	
t Critical two-tail	2.3646226	

Two-tail -t crit< t stat <t crit
ACCEPT

Fe

	Variable 1	*Variable 2*
Mean	0.1061538	0.0925
Variance	0.0063923	0.0022917
Observations	13	4
Hypothesized Mean Difference	0	
df	9	
t Stat	0.418	
P(T<=t) one-tail	0.3427094	
t Critical one-tail	1.8331139	
P(T<=t) two-tail	0.6854188	
t Critical two-tail	2.2621589	

Two-tail -t crit< t stat <t crit
ACCEPT

Zn

	Variable 1	*Variable 2*
Mean	0.0145455	0.01
Variance	0.0002673	0
Observations	11	2
Hypothesized Mean Difference	0	
df	10	
t Stat	0.922	
P(T<=t) one-tail	0.1890837	
t Critical one-tail	1.8124615	
P(T<=t) two-tail	0.3781673	
t Critical two-tail	2.2281392	

Two-tail -t crit< t stat <t crit
ACCEPT

Ni

	Variable 1	*Variable 2*
Mean	0.1388889	0.05
Variance	0.0215111	0.0008
Observations	9	2
Hypothesized Mean Difference	0	
df	9	
t Stat	1.683	
P(T<=t) one-tail	0.0633516	
t Critical one-tail	1.8331139	
P(T<=t) two-tail	0.1267031	
t Critical two-tail	2.2621589	

Two-tail -t crit< t stat <t crit
ACCEPT

Table 17: t-Test at PM-4: Ambient (Var. 1) vs. Storm Influenced (Var. 2)

SS

	Variable 1	*Variable 2*
Mean	40.461538	29.666667
Variance	279.4359	30.333333
Observations	13	3
Hypothesized Mean Difference	0	
df	11	
t Stat	1.920	
P(T<=t) one-tail	0.0405672	
t Critical one-tail	1.7958837	
P(T<=t) two-tail	0.0811343	
t Critical two-tail	2.2009863	

Two-tail -t crit< t stat <t crit
ACCEPT

Turb

	Variable 1	*Variable 2*
Mean	43.307692	32.25
Variance	151.73077	85.583333
Observations	13	4
Hypothesized Mean Difference	0	
df	7	
t Stat	1.923	
P(T<=t) one-tail	0.0479574	
t Critical one-tail	1.8945775	
P(T<=t) two-tail	0.0959148	
t Critical two-tail	2.3646226	

Two-tail -t crit< t stat <t crit
ACCEPT

S

	Variable 1	*Variable 2*
Mean	1101.6667	1075
Variance	187215.15	114166.67
Observations	12	4
Hypothesized Mean Difference	0	
df	7	
t Stat	0.127	
P(T<=t) one-tail	0.4512854	
t Critical one-tail	1.8945775	
P(T<=t) two-tail	0.9025708	
t Critical two-tail	2.3646226	

Two-tail -t crit< t stat <t crit
ACCEPT

P

	Variable 1	*Variable 2*
Mean	0.1461538	0.1175
Variance	0.0043423	0.0003583
Observations	13	4
Hypothesized Mean Difference	0	
df	15	
t Stat	1.392	
P(T<=t) one-tail	0.0920798	
t Critical one-tail	1.753051	
P(T<=t) two-tail	0.1841597	
t Critical two-tail	2.1314509	

Two-tail -t crit< t stat <t crit
ACCEPT

Cl

	Variable 1	*Variable 2*
Mean	6227.2727	8266.6667
Variance	5856181.8	63583333
Observations	11	3
Hypothesized Mean Difference	0	
df	2	
t Stat	-0.438	
P(T<=t) one-tail	0.3522221	
t Critical one-tail	2.9199873	
P(T<=t) two-tail	0.7044443	
t Critical two-tail	4.3026557	

Two-tail -t crit< t stat <t crit
ACCEPT

NH3-N

	Variable 1	*Variable 2*
Mean	1.0545455	1.3033333
Variance	0.3609073	0.3820333
Observations	11	3
Hypothesized Mean Difference	0	
df	3	
t Stat	-0.622	
P(T<=t) one-tail	0.2891003	
t Critical one-tail	2.353363	
P(T<=t) two-tail	0.5782007	
t Critical two-tail	3.1824493	

Two-tail -t crit< t stat <t crit
ACCEPT

Table 17 Continued

NO3-N

	Variable 1	*Variable 2*
Mean	0.4307692	0.3
Variance	0.0123077	0.0466667
Observations	13	4
Hypothesized Mean Difference	0	
df	4	
t Stat	1.164	
P(T<=t) one-tail	0.1544937	
t Critical one-tail	2.1318465	
P(T<=t) two-tail	0.3089873	
t Critical two-tail	2.7764509	

Two-tail -t crit< t stat <t crit
ACCEPT

NO2-N

	Variable 1	*Variable 2*
Mean	0.0069231	0.01025
Variance	9.858E-05	6.092E-05
Observations	13	4
Hypothesized Mean Difference	0	
df	6	
t Stat	-0.697	
P(T<=t) one-tail	0.2560721	
t Critical one-tail	1.9431809	
P(T<=t) two-tail	0.5121442	
t Critical two-tail	2.4469136	

Two-tail -t crit< t stat <t crit
ACCEPT

Fe

	Variable 1	*Variable 2*
Mean	0.0853846	0.065
Variance	0.0031103	0.0013667
Observations	13	4
Hypothesized Mean Difference	0	
df	8	
t Stat	0.846	
P(T<=t) one-tail	0.2111313	
t Critical one-tail	1.8595483	
P(T<=t) two-tail	0.4222626	
t Critical two-tail	2.3060056	

Two-tail -t crit< t stat <t crit
ACCEPT

Zn

	Variable 1	*Variable 2*
Mean	0.01	0.03
Variance	0.00018	0.0002
Observations	11	2
Hypothesized Mean Difference	0	
df	1	
t Stat	-1.854	
P(T<=t) one-tail	0.157448	
t Critical one-tail	6.3137486	
P(T<=t) two-tail	0.314896	
t Critical two-tail	12.70615	

Two-tail -t crit< t stat <t crit
ACCEPT

Ni

	Variable 1	*Variable 2*
Mean	0.1455556	0.065
Variance	0.0053778	0.00045
Observations	9	2
Hypothesized Mean Difference	0	
df	7	
t Stat	2.809	
P(T<=t) one-tail	0.0130957	
t Critical one-tail	1.8945775	
P(T<=t) two-tail	0.0261914	
t Critical two-tail	2.3646226	

Two-tail -t crit< t crit <t stat
REJECT

Table 18: t-Test at PM-5: Ambient (Var. 1) vs. Storm Influenced (Var. 2)

SS

	Variable 1	*Variable 2*
Mean	42.307692	53.333333
Variance	354.39744	745.33333
Observations	13	3
Hypothesized Mean Difference	0	
df	2	
t Stat	-0.664	
P(T<=t) one-tail	0.2874926	
t Critical one-tail	2.9199873	
P(T<=t) two-tail	0.5749853	
t Critical two-tail	4.3026557	

Two-tail -t crit< t stat <t crit
ACCEPT

Turb

	Variable 1	*Variable 2*
Mean	48.692308	55
Variance	295.39744	817
Observations	13	3
Hypothesized Mean Difference	0	
df	2	
t Stat	-0.367	
P(T<=t) one-tail	0.3743377	
t Critical one-tail	2.9199873	
P(T<=t) two-tail	0.7486755	
t Critical two-tail	4.3026557	

Two-tail -t crit< t stat <t crit
ACCEPT

S

	Variable 1	*Variable 2*
Mean	1129.1667	802
Variance	257481.06	357682.67
Observations	12	4
Hypothesized Mean Difference	0	
df	5	
t Stat	0.983	
P(T<=t) one-tail	0.1854793	
t Critical one-tail	2.0150492	
P(T<=t) two-tail	0.3709586	
t Critical two-tail	2.5705776	

Two-tail -t crit< t stat <t crit
ACCEPT

P

	Variable 1	*Variable 2*
Mean	0.1338462	0.1675
Variance	0.010159	0.0173583
Observations	13	4
Hypothesized Mean Difference	0	
df	4	
t Stat	-0.470	
P(T<=t) one-tail	0.3313257	
t Critical one-tail	2.1318465	
P(T<=t) two-tail	0.6626514	
t Critical two-tail	2.7764509	

Two-tail -t crit< t stat <t crit
ACCEPT

Cl

	Variable 1	*Variable 2*
Mean	5036.3636	6614.1667
Variance	6596545.5	113211352
Observations	11	3
Hypothesized Mean Difference	0	
df	2	
t Stat	-0.255	
P(T<=t) one-tail	0.4113331	
t Critical one-tail	2.9199873	
P(T<=t) two-tail	0.8226662	
t Critical two-tail	4.3026557	

Two-tail -t crit< t stat <t crit
ACCEPT

NH3-N

	Variable 1	*Variable 2*
Mean	0.7945455	1.4433333
Variance	0.0620073	0.1080333
Observations	11	3
Hypothesized Mean Difference	0	
df	3	
t Stat	-3.179	
P(T<=t) one-tail	0.0250642	
t Critical one-tail	2.353363	
P(T<=t) two-tail	0.0501285	
t Critical two-tail	3.1824493	

Two-tail -t crit< t stat <t crit
ACCEPT (but barely)

Table 18 Continued

NO3-N

	Variable 1	*Variable 2*
Mean	0.5076923	0.5
Variance	0.0641026	0.07
Observations	13	3
Hypothesized Mean Difference	0	
df	3	
t Stat	0.046	
P(T<=t) one-tail	0.4831905	
t Critical one-tail	2.353363	
P(T<=t) two-tail	0.966381	
t Critical two-tail	3.1824493	

Two-tail -t crit< t stat <t crit
ACCEPT

NO2-N

	Variable 1	*Variable 2*
Mean	0.0066923	0.023
Variance	0.0001296	0.000502
Observations	13	4
Hypothesized Mean Difference	0	
df	3	
t Stat	-1.401	
P(T<=t) one-tail	0.1278526	
t Critical one-tail	2.353363	
P(T<=t) two-tail	0.2557052	
t Critical two-tail	3.1824493	

Two-tail -t crit< t stat <t crit
ACCEPT

Fe

	Variable 1	*Variable 2*
Mean	0.0915385	0.1275
Variance	0.0028141	0.016825
Observations	13	4
Hypothesized Mean Difference	0	
df	3	
t Stat	-0.541	
P(T<=t) one-tail	0.3131252	
t Critical one-tail	2.353363	
P(T<=t) two-tail	0.6262505	
t Critical two-tail	3.1824493	

Two-tail -t crit< t stat <t crit
ACCEPT

Zn

	Variable 1	*Variable 2*
Mean	0.0054545	0.01
Variance	8.727E-05	0.0002
Observations	11	2
Hypothesized Mean Difference	0	
df	1	
t Stat	-0.438	
P(T<=t) one-tail	0.3687202	
t Critical one-tail	6.3137486	
P(T<=t) two-tail	0.7374404	
t Critical two-tail	12.70615	

Two-tail -t crit< t stat <t crit
ACCEPT

Ni

	Variable 1	*Variable 2*
Mean	0.1277778	0.035
Variance	0.0069194	0.00245
Observations	9	2
Hypothesized Mean Difference	0	
df	3	
t Stat	2.078	
P(T<=t) one-tail	0.0646381	
t Critical one-tail	2.353363	
P(T<=t) two-tail	0.1292762	
t Critical two-tail	3.1824493	

Two-tail -t crit< t stat <t crit
ACCEPT

Table 19: t-Test at PM-1: Storm Influenced Downstream (Var. 1) vs. Upstream (Var. 2)

SS

	Variable 1	*Variable 2*
Mean	183.5	172
Variance	12216.5714	11536.8571
Observations	8	8
Pearson Correlation	#N/A	
Hypothesized Mean Difference	0	
df	7	
t Stat	0.19268922	
P(T<=t) one-tail	0.4263368	
t Critical one-tail	1.89457751	
P(T<=t) two-tail	0.8526736	
t Critical two-tail	2.36462256	

Two-tail -t crit< t stat <t crit
Accept

S

	Variable 1	*Variable 2*
Mean	4.875	1
Variance	159.267857	3.42857143
Observations	8	8
Pearson Correlation	0.71526529	
Hypothesized Mean Difference	0	
df	7	
t Stat	0.96398755	
P(T<=t) one-tail	0.18358219	
t Critical one-tail	1.89457751	
P(T<=t) two-tail	0.36716437	
t Critical two-tail	2.36462256	

Two-tail -t crit< t stat <t crit
Accept

Cl

	Variable 1	*Variable 2*
Mean	30.875	12.8875
Variance	2321.02786	9.30410714
Observations	8	8
Pearson Correlation	-0.6171593	
Hypothesized Mean Difference	0	
df	7	
t Stat	1.01515025	
P(T<=t) one-tail	0.17191517	
t Critical one-tail	1.89457751	
P(T<=t) two-tail	0.34383033	
t Critical two-tail	2.36462256	

Two-tail -t crit< t stat <t crit
Accept

Turb

	Variable 1	*Variable 2*
Mean	104	108.75
Variance	3786	2735.92857
Observations	8	8
Pearson Correlation	#N/A	
Hypothesized Mean Difference	0	
df	7	
t Stat	-0.1637696	
P(T<=t) one-tail	0.43727035	
t Critical one-tail	1.89457751	
P(T<=t) two-tail	0.8745407	
t Critical two-tail	2.36462256	

Two-tail -t crit< t stat <t crit
Accept

P

	Variable 1	*Variable 2*
Mean	0.05125	0.0675
Variance	0.00115536	0.00165
Observations	8	8
Pearson Correlation	0.85101608	
Hypothesized Mean Difference	0	
df	7	
t Stat	-2.1538839	
P(T<=t) one-tail	0.03411063	
t Critical one-tail	1.89457751	
P(T<=t) two-tail	0.06822126	
t Critical two-tail	2.36462256	

Two-tail -t crit< t stat <t crit
Accept

NH3-N

	Variable 1	*Variable 2*
Mean	0.80625	0.80125
Variance	0.08382679	0.10155536
Observations	8	8
Pearson Correlation	0.98153452	
Hypothesized Mean Difference	0	
df	7	
t Stat	0.21674839	
P(T<=t) one-tail	0.417293	
t Critical one-tail	1.89457751	
P(T<=t) two-tail	0.834586	
t Critical two-tail	2.36462256	

Two-tail -t crit< t stat <t crit
Accept

Table 19 Continued

NO3-N

	Variable 1	*Variable 2*
Mean	0.325	0.35
Variance	0.03928571	0.03714286
Observations	8	8
Pearson Correlation	0.89754911	
Hypothesized Mean Difference	0	
df	7	
t Stat	-0.797724	
P(T<=t) one-tail	0.22561944	
t Critical one-tail	1.89457751	
P(T<=t) two-tail	0.45123887	
t Critical two-tail	2.36462256	

Two-tail -t crit< t stat <t crit
Accept

NO2-N

	Variable 1	*Variable 2*
Mean	0.01625	0.019
Variance	0.00051793	0.00058286
Observations	8	8
Pearson Correlation	0.98932874	
Hypothesized Mean Difference	0	
df	7	
t Stat	-2.1058383	
P(T<=t) one-tail	0.03661855	
t Critical one-tail	1.89457751	
P(T<=t) two-tail	0.0732371	
t Critical two-tail	2.36462256	

Two-tail -t crit< t stat <t crit
Accept

Fe

	Variable 1	*Variable 2*
Mean	0.28625	0.28
Variance	0.03205536	0.02928571
Observations	8	8
Pearson Correlation	0.97680476	
Hypothesized Mean Difference	0	
df	7	
t Stat	0.45890048	
P(T<=t) one-tail	0.33010739	
t Critical one-tail	1.89457751	
P(T<=t) two-tail	0.66021479	
t Critical two-tail	2.36462256	

Two-tail -t crit< t stat <t crit
Accept

Zn

	Variable 1	*Variable 2*
Mean	0.0225	0.04
Variance	0.00033571	0.00022857
Observations	8	8
Pearson Correlation	-0.1547132	
Hypothesized Mean Difference	0	
df	7	
t Stat	-1.9414507	
P(T<=t) one-tail	0.0466677	
t Critical one-tail	1.89457751	
P(T<=t) two-tail	0.09333541	
t Critical two-tail	2.36462256	

Two-tail -t crit< t stat <t crit
Accept

Ni

	Variable 1	*Variable 2*
Mean	0.07875	0.06
Variance	0.00126964	0.00074286
Observations	8	8
Pearson Correlation	0.79433241	
Hypothesized Mean Difference	0	
df	7	
t Stat	2.44716022	
P(T<=t) one-tail	0.02214567	
t Critical one-tail	1.89457751	
P(T<=t) two-tail	0.04429133	
t Critical two-tail	2.36462256	

Two-tail -t crit <t crit < t stat
Reject

Table 20: t-Test at PM-3: Storm Influenced Downstream (Var 1) vs. Upstream (Var 2)

SS

	Variable 1	*Variable 2*
Mean	65.5	166.5
Variance	1860.5	38920.5
Observations	2	2
Pearson Correlation	1	
Hypothesized Mean Difference	0	
df	1	
t Stat	-0.9266055	
P(T<=t) one-tail	0.26212023	
t Critical one-tail	6.3137486	
P(T<=t) two-tail	0.52424046	
t Critical two-tail	12.7061503	

Two-tail -t crit< t stat <t crit
Accept

Turb

	Variable 1	*Variable 2*
Mean	41.3333333	74.3333333
Variance	49.3333333	4280.33333
Observations	3	3
Pearson Correlation	0.67533522	
Hypothesized Mean Difference	0	
df	2	
t Stat	-0.9385257	
P(T<=t) one-tail	0.22352408	
t Critical one-tail	2.91998731	
P(T<=t) two-tail	0.44704816	
t Critical two-tail	4.30265573	

Two-tail -t crit< t stat <t crit
Accept

S

	Variable 1	*Variable 2*
Mean	983.333333	266.666667
Variance	103333.333	93333.3333
Observations	3	3
Pearson Correlation	-0.0339422	
Hypothesized Mean Difference	0	
df	2	
t Stat	2.75279292	
P(T<=t) one-tail	0.05525702	
t Critical one-tail	2.91998731	
P(T<=t) two-tail	0.11051404	
t Critical two-tail	4.30265573	

Two-tail -t crit< t stat <t crit
Accept

P

	Variable 1	*Variable 2*
Mean	0.14333333	0.02333333
Variance	0.00443333	0.00103333
Observations	3	3
Pearson Correlation	-0.2881145	
Hypothesized Mean Difference	0	
df	2	
t Stat	2.53924422	
P(T<=t) one-tail	0.06317885	
t Critical one-tail	2.91998731	
P(T<=t) two-tail	0.12635769	
t Critical two-tail	4.30265573	

Two-tail -t crit< t stat <t crit
Accept

Cl-

	Variable 1	*Variable 2*
Mean	10500	5085
Variance	42320000	32240450
Observations	2	2
Pearson Correlation	1	
Hypothesized Mean Difference	0	
df	1	
t Stat	9.25641026	
P(T<=t) one-tail	0.03425519	
t Critical one-tail	6.3137486	
P(T<=t) two-tail	0.06851039	
t Critical two-tail	12.7061503	

Two-tail -t crit< t stat <t crit
Accept

NH3-N

	Variable 1	*Variable 2*
Mean	1.24	0.51
Variance	0.2692	0.0163
Observations	3	3
Pearson Correlation	0.84086033	
Hypothesized Mean Difference	0	
df	2	
t Stat	3.03028937	
P(T<=t) one-tail	0.04691293	
t Critical one-tail	2.91998731	
P(T<=t) two-tail	0.09382586	
t Critical two-tail	4.30265573	

Two-tail -t crit< t stat <t crit
Accept

Table 20 Continued

NO3-N

	Variable 1	*Variable 2*
Mean	0.3	0.5
Variance	2.7756E-17	0.03
Observations	3	3
Pearson Correlation	0	
Hypothesized Mean Difference	0	
df	2	
t Stat	-2	
P(T<=t) one-tail	0.09175171	
t Critical one-tail	2.91998731	
P(T<=t) two-tail	0.18350342	
t Critical two-tail	4.30265573	

Two-tail -t crit< t stat <t crit
Accept

Fe

	Variable 1	*Variable 2*
Mean	0.09333333	0.12
Variance	0.00343333	0.0219
Observations	3	3
Pearson Correlation	0.96295598	
Hypothesized Mean Difference	0	
df	2	
t Stat	-0.4970958	
P(T<=t) one-tail	0.33419467	
t Critical one-tail	2.91998731	
P(T<=t) two-tail	0.66838933	
t Critical two-tail	4.30265573	

Two-tail -t crit< t stat <t crit
Accept

Ni

	Variable 1	*Variable 2*
Mean	0.05	0.065
Variance	0.0008	0.00245
Observations	2	2
Pearson Correlation	1	
Hypothesized Mean Difference	0	
df	1	
t Stat	-1	
P(T<=t) one-tail	0.25	
t Critical one-tail	6.3137486	
P(T<=t) two-tail	0.5	
t Critical two-tail	12.7061503	

Two-tail -t crit< t stat <t crit
Accept

NO2-N

	Variable 1	*Variable 2*
Mean	0.01233333	0.04366667
Variance	3.0333E-05	0.00176633
Observations	3	3
Pearson Correlation	0.24697129	
Hypothesized Mean Difference	0	
df	2	
t Stat	-1.3231565	
P(T<=t) one-tail	0.15839631	
t Critical one-tail	2.91998731	
P(T<=t) two-tail	0.31679262	
t Critical two-tail	4.30265573	

Two-tail -t crit< t stat <t crit
Accept

Zn

	Variable 1	*Variable 2*
Mean	0.01	0.025
Variance	0	5E-05
Observations	2	2
Pearson Correlation	#DIV/0!	
Hypothesized Mean Difference	0	
df	1	
t Stat	-3	
P(T<=t) one-tail	0.10241638	
t Critical one-tail	6.3137486	
P(T<=t) two-tail	0.20483276	
t Critical two-tail	12.7061503	

Two-tail -t crit< t stat <t crit
Accept

Table 21: t-Test at PM-4: Storm Influenced Downstream (Var. 1) vs. Upstream (Var. 2)

SS

	Variable 1	*Variable 2*
Mean	29.5	19.5
Variance	60.5	112.5
Observations	2	2
Pearson Correlation	-1	
Hypothesized Mean Difference	0	
df	1	
t Stat	0.76923077	
P(T<=t) one-tail	0.2912856	
t Critical one-tail	6.3137486	
P(T<=t) two-tail	0.5825712	
t Critical two-tail	12.7061503	

Two-tail -t crit< t stat <t crit
Accept

Turb

	Variable 1	*Variable 2*
Mean	28.3333333	20.3333333
Variance	36.3333333	6.33333333
Observations	3	3
Pearson Correlation	-0.3076366	
Hypothesized Mean Difference	0	
df	2	
t Stat	1.92153785	
P(T<=t) one-tail	0.09730637	
t Critical one-tail	2.91998731	
P(T<=t) two-tail	0.19461273	
t Critical two-tail	4.30265573	

Two-tail -t crit< t stat <t crit
Accept

S

	Variable 1	*Variable 2*
Mean	1016.66667	533.333333
Variance	150833.333	85833.3333
Observations	3	3
Pearson Correlation	0.81661428	
Hypothesized Mean Difference	0	
df	2	
t Stat	3.71306952	
P(T<=t) one-tail	0.03274403	
t Critical one-tail	2.91998731	
P(T<=t) two-tail	0.06548806	
t Critical two-tail	4.30265573	

Two-tail -t crit< t stat <t crit
Accept

P

	Variable 1	*Variable 2*
Mean	0.11333333	0.09333333
Variance	0.00043333	0.00413333
Observations	3	3
Pearson Correlation	-0.1245339	
Hypothesized Mean Difference	0	
df	2	
t Stat	0.49487166	
P(T<=t) one-tail	0.33485544	
t Critical one-tail	2.91998731	
P(T<=t) two-tail	0.66971087	
t Critical two-tail	4.30265573	

Two-tail -t crit< t stat <t crit
Accept

Cl

	Variable 1	*Variable 2*
Mean	8266.66667	4160
Variance	63583333.3	22094800
Observations	3	3
Pearson Correlation	0.99916023	
Hypothesized Mean Difference	0	
df	2	
t Stat	2.16659783	
P(T<=t) one-tail	0.08130217	
t Critical one-tail	2.91998731	
P(T<=t) two-tail	0.16260433	
t Critical two-tail	4.30265573	

Two-tail -t crit< t stat <t crit
Accept

NH3-N

	Variable 1	*Variable 2*
Mean	1.30333333	0.31333333
Variance	0.38203333	0.00523333
Observations	3	3
Pearson Correlation	0.97136697	
Hypothesized Mean Difference	0	
df	2	
t Stat	3.12856987	
P(T<=t) one-tail	0.04438635	
t Critical one-tail	2.91998731	
P(T<=t) two-tail	0.08877269	
t Critical two-tail	4.30265573	

Two-tail -t crit< t stat <t crit
Accept

Table 21 Continued

NO3-N

	Variable 1	*Variable 2*
Mean	0.2	0.23333333
Variance	0.01	0.00333333
Observations	3	3
Pearson Correlation	0.8660254	
Hypothesized Mean Difference	0	
df	2	
t Stat	-1	
P(T<=t) one-tail	0.21132487	
t Critical one-tail	2.91998731	
P(T<=t) two-tail	0.42264973	
t Critical two-tail	4.30265573	

Two-tail -t crit< t stat <t crit
Accept

NO2-N

	Variable 1	*Variable 2*
Mean	0.01233333	0.00833333
Variance	6.5333E-05	4.3333E-06
Observations	3	3
Pearson Correlation	-0.9905361	
Hypothesized Mean Difference	0	
df	2	
t Stat	0.68265615	
P(T<=t) one-tail	0.28264293	
t Critical one-tail	2.91998731	
P(T<=t) two-tail	0.56528587	
t Critical two-tail	4.30265573	

Two-tail -t crit< t stat <t crit
Accept

Fe

	Variable 1	*Variable 2*
Mean	0.05666667	0.02333333
Variance	0.00163333	3.3333E-05
Observations	3	3
Pearson Correlation	0.92857143	
Hypothesized Mean Difference	0	
df	2	
t Stat	1.64398987	
P(T<=t) one-tail	0.12095098	
t Critical one-tail	2.91998731	
P(T<=t) two-tail	0.24190196	
t Critical two-tail	4.30265573	

Two-tail -t crit< t stat <t crit
Accept

Zn

	Variable 1	*Variable 2*
Mean	0.03	0.02
Variance	0.0002	0
Observations	2	2
Pearson Correlation	#DIV/0!	
Hypothesized Mean Difference	0	
df	1	
t Stat	1	
P(T<=t) one-tail	0.25	
t Critical one-tail	6.3137486	
P(T<=t) two-tail	0.5	
t Critical two-tail	12.7061503	

Two-tail -t crit< t stat <t crit
Accept

Ni

	Variable 1	*Variable 2*
Mean	0.065	0.06
Variance	0.00045	0.0008
Observations	2	2
Pearson Correlation	1	
Hypothesized Mean Difference	0	
df	1	
t Stat	1	
P(T<=t) one-tail	0.25	
t Critical one-tail	6.3137486	
P(T<=t) two-tail	0.5	
t Critical two-tail	12.7061503	

Two-tail -t crit< t stat <t crit
Accept