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# Evaluation of Field Screening Kits

## Communication Manhole Water Study

By

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# Notice

# (Preliminary)

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# Foreword

# Acknowledgements

Many individuals helped carry out this project. Graduate student researchers at the University of Alabama at Birmingham who participated on this field screening kit evaluation project included: Jennifer Harper, Janice Lantrip, Christy Nix, and Olga Mirov. Dr. Keith Parmer was instrumental in helping establish test protocols and in offering overall project guidance. In addition, Nayela Khan and Erica Rodgers, summer interns in the NIH/NCRR program also assisted with the project. Thanks are also extended to Azur Environmental, GDS & Assoc., and IDE for donations and loans of equipment and supplies for evaluation.

# Abstract

The objective of this project task, described in this report, was to examine water field-screening methods that could be used to examine the quality of water found in communication manholes. The evaluating criteria established for water screening-kits was: field applicability, simple and safe to operate, inexpensive, accurate, reasonable storage life and storage conditions, minimal hazardous waste products generated, and being able to quickly examine the quality of water found in communication manholes. The evaluation procedure included numerous measures, stressing safety, ease of use, reliability, applicability, precision, and detection limits. The evaluations of most of the kits were made with four evaluation methods, using spiked samples, parallel analyses, replicate analyses and subjective evaluations of the ease of use and the health and safety features of each method. Several screening-kits were rejected because of obvious safety concerns or critical storage conditions, and many had unsuitable actual detection limits. Within a suitable range of concentrations, many of the screening-kits performed well. However, most were much less sensitive than anticipated, were more complex than desired, or required storage conditions that were not compatible with repair vehicles. Several of the most promising field procedures were also quite expensive.

Before a communication technician enters a manhole, industry practices and OSHA regulations require a combustible gas test and then an inspection of any existing water for possible abnormal conditions (e.g. surface oil sheen or obvious evidence of sewage contamination). If the water is found suitable for discharge, the technician will pump the water from the manhole, typically using a small submersible device. If the water is not suitable for discharge, a qualified waste vendor is used for removal and disposal in accordance with applicable environmental regulatory requirements. When these special handling procedures are needed, they significantly slow down the repair of telecommunications equipment, thus impacting the public's use of the communications network for emergencies and other essential services. These manhole entry procedures have been in effect for almost 50 years. However, with the increasing concern of the quality of water discharged to the environment, eight major communication companies (Ameritech, AT&T, Bell Atlantic, BellSouth, GTE, Pacific Bell, SNET and U S WEST) sponsored this project task through Telcordia Technologies (previously Bellcore, Inc.) to examine available field screening test kits to be able to more completely evaluate the quality of water found in communication manholes. The work performed under this project provides scientific research from the University of Alabama at Birmingham (UAB) on the characterization (reported in a companion document) and field testing of water found in communication manholes.

# Contents

# 1 Summary

## 1.1 Background

Communication cables are dispersed throughout the United States in above and below ground structures. Utility poles support aerial communication plant while manholes and conduits support the major underground components of the public communications network. Direct buried plant is generally representative of newly built residential area and is the last link in the network. Each part of a communication network is a critical component to providing quality service to customers. A communication network starts at a strategically located Central Office (CO) building from which multiple communications cables are generally dispersed through an underground pathway of conduits linked by manholes. A CO's function is to provide switching services to customers residing in its geographic area and to connect its customers incoming and outgoing calls.

Underground facilities are designed to provide non-intrusive pathways from COs to points along the network that distribute services to residential customers, to large business customer locations, to government offices and public institutions (including police, fire and other emergency services) and to adjacent COs. Manholes augment the placing and the maintenance of communication plant by providing technicians access to locations with key components along a cable route. Manholes and associated underground facilities also provide the communications infrastructure and network components protection from inclement weather, vandalism, motor vehicle impacts and other hazardous conditions. With the exception of a manhole cover, underground facilities are hidden from public view, and are therefore less disruptive to the public. Although an underground infrastructure of manholes and conduits is traditionally employed in urban environments, it is sometimes used in suburban and rural settings to facilitate the distribution of cables supporting the backbone of network architectures.

Manholes are not designed to eliminate all water from entering the space. The location and physical characteristics of these structures make it very difficult to prevent water intrusion. Surface water run-off and ground water hydrology conditions greatly influence the possibility of water entering a manhole. Industry practices require the proper sealing of underground cable plant to minimize water intrusion. Moisture entering the telephone plant (cable or splice cases) quickly leads to permanent physical damage and potential multiple service outages. If industry practices are correctly followed, the plant can withstand a submerged water environment.

Before a communication technician enters a manhole, industry practices and OSHA regulations require a combustible gas test and then an inspection of any existing water for possible abnormal conditions (e.g. surface oil sheen or obvious evidence of sewage contamination). If the water is found suitable for discharge, the technician will pump the water from the manhole, typically using a small submersible device. If the water is not suitable for discharge, a qualified waste vendor is used for removal and disposal in accordance with applicable environmental regulatory requirements. When these special handling procedures are needed, they significantly slow down the repair of telecommunications equipment, thus impacting the public's use of the communications network for emergencies and other essential services.

These manhole entry procedures have been in effect for almost 50 years. However, with the increasing concern of the quality of water discharged to the environment, eight major communication companies (Ameritech, AT&T, Bell Atlantic, BellSouth, GTE, Pacific Bell, SNET and U S WEST) sponsored this study through Telcordia Technologies (previously Bellcore, Inc.). The work performed under this project will provide scientific research from the University of Alabama at Birmingham (UAB) on the characterization of water found in communication manholes.

### *1.1.1 Objective*

The objective of this project task, described in this report, was to examine water field-screening methods that could be used to examine the quality of water found in communication manholes. The evaluating criteria established for water screening-kits was: field applicability, simple and safe to operate, inexpensive, accurate, reasonable storage life and storage conditions, minimal hazardous waste products generated, and being able to quickly examine the quality of water found in communication manholes.

### *1.1.2 Findings*

The evaluation procedure included numerous measures, stressing safety, ease of use, reliability, applicability, precision, and detection limits. Several screening-kits were rejected because of obvious safety concerns or critical storage conditions, and many had unsuitable actual detection limits. Within a suitable range of concentrations, many of the screening-kits performed well. However, most were more complex than desired, or required storage conditions that were not compatible with repair vehicles. Several of the most promising field procedures were also quite expensive.

# 2 Evaluation of Field-Screening Kits to Assess communication Manhole Water and Sediment Quality

Numerous tests were performed to evaluate field-screening kits for field evaluations of the quality of telecommunication manhole water and sediment. This report summarizes the test kit evaluation results, while complete evaluation information is included in Appendix A. This report also recommends the field equipment that may best fit the needs for these field evaluations. Selections were based on "fatal flaws" of the alternative equipment available for each parameter category. More than fifty screening-kits were subjected to preliminary evaluations and about half were subjected to more detailed tests. Safety hazards, cost, inappropriate sensitivity, and complexity of the screening-kits were all reasons for rejection. The "easiest" to conduct test and the "best" test in each category were then identified, after rejecting those kits that were much more expensive than alternatives in each category.

Of course, new test kits are continually being developed and marketed and older units become modified or discontinued. Therefore, these evaluations must be re-considered at the time of purchase to consider newer alternatives or changes in specifications. It is recommended that evaluations of new kits be made, at least by comparing the results with known standards and parallel analyses of samples being tested, before large-scale implementation. In addition, it must also be stressed that these are field screening test kits and most are not directly comparable to methods used by certified laboratories employing *Standard Methods.* The purpose of these screening methods is to correctly identify problem conditions that can be further evaluated or corrected. However, many of the screening test kits produced quite good results, if used within an acceptable range of concentrations. Most had useful detection limits much larger than advertised by the manufactures, possibly leading to false negative evaluations if these more stringent detection limits are not considered.

## 2.1 Methods

The comparison of field screening equipment is a combined objective/subjective process. Some parameters of interest are easily quantified; other features that should be evaluated require more subjective evaluation techniques. Therefore, we have tried to present our recommendations using both subjective and objective data. We have reported our finding for each test kit in Appendix A. The evaluations of most of the kits were made with four evaluation methods, using spiked samples, parallel analyses, replicate analyses and subjective evaluations of the ease of use and the health and safety features of each method. The general methods used to evaluate the methods are described in the following sections. Some methods were modified for more effective evaluations of certain parameters.

Some of the screening test kits (bacteria tests, the GDS Aqua Vats kit, detergents by fluorometry, and the electro-chemical metal analyzers, for example) were subjected to an abbreviated set of tests due to reduced funding, limited supplies, or late acquisition of the materials. Some of these methods were also quite expensive, making them unlikely to be used for all but the most unusual conditions. Specifically, these abbreviated tests were conducted to obtain practice using the methods for actual sample analyses (typically clean spring waters, ultra clean water, sanitary sewage dilutions, known standards, and previously analyzed water samples collected from manholes). This experience allowed us to make initial assessments of ease of use, safety issues, useful range, and accuracy of the method, but did not allow as much quantitative conclusions as were possible with some of the more intensely evaluated methods.

### *2.1.1 Spiked Samples*

The initial tests used spiked samples. The reported analytical ranges were used to define a gross range of suitable concentrations of all methods for each parameter. The gross range is bounded by the lowest reported detection limit and the highest upper limit reported by the manufacturers for all of the methods in a group. Two series of samples were prepared with known spikes, one using reverse osmosis water and another using runoff water as the solutes. Reverse osmosis water served as a control for detecting the optimal test procedure, while the runoff water was used to detect the presence of any major matrix interferences that may exist with a water type commonly found in communication manholes. The runoff water was collected from a UAB remote parking lot. The number of spiked samples prepared varied by parameter, depending on the magnitude of the gross range, but typically included from 3 to 5 different concentrations.

For each parameter, the spiked standards were evaluated by all test methods. Due to the large number of methods to be evaluated, no replicate analyses were made during the preliminary tests. However, the measured results were plotted against the known concentration additions and the variations about the best-fit line were used to estimate the analytical precision and the detection limit. During these analyses, data were collected on "useful" range, capital costs, expendable costs, analysis time, health and safety considerations and "usability." These parameters are defined below:

- "useful" range: The range of concentrations that the instrument may measure with a specified certainty. The lower limit is defined by the detection limit (discussion to follow). The upper limit is defined by the highest measured concentration the method can measure without dilution of the sample. The upper limit values reported here were determined as the lowest spike concentration producing an "over range" error, or the lowest concentration that obviously deviated from the linear range of spike concentration to instrument response. If neither problem was identified, the manufacturer's reported upper limit was reported. The method for determining the upper limit for a particular method is described in Appendix A.

- capital costs: The initial costs associated with purchasing the capital equipment required to use the method. Most prices were obtained from the manufacturers or distributors during April 1996.

- expendable costs: The costs associated with buying replacement reagents for the method. The value reported is per sample. The costs do not include general glassware, tissues, gloves and other generic equipment required for many of the tests. These prices, for most of the methods examined, were also obtained from the manufacturers or distributors during April 1996. The costs reported are based on list price of the smallest quantity of reagent available, and therefore, the costs do not reflect bulk discounts which may be available.

- analysis time: The approximate time to analyze one sample with the instrument. In some cases, additional time must be allotted to prepare the instrumentation for measurement. The reported time for the analysis assumes that the instrument has been properly calibrated before the analysis begins.

- health and safety considerations: The health and safety considerations are a broad scope of factors that represent potential hazards to the user or the environment. The factors contributing to this consideration include the reagents used, the packaging of the reagents, disposal of wastes and waste glass, potential exposures of toxic and hazardous materials to the user, or any other concern associated with the kit requiring special attention.

- "usability": This ubiquitous term is a subjective evaluation of the expertise required to perform an acceptable analysis. Under this heading, we have attempted to describe any feature of the kit that may not represent a hazard, but could affect the quality of the test. Examples of factors

affecting usability include the number of steps, complexity of the procedure, additional equipment to make the procedure easier, or any special skill required to complete the analysis.

The spiked samples were analyzed for each method. For each matrix (reverse osmosis water and runoff water) a plot of instrument response to spike concentration was made. The plot is useful for estimating the range of linear response of the instrument. Spike responses showing a significant departure from a linear response indicate the limits for the useful range of the method. A regression analysis was performed on the data providing further information about the method. Ideally, the slope generated from these regression analyses should be 1. A slope significantly different from 1 indicates a bias in the method. Also, the slope of the regression in the reverse osmosis water matrix should be the same as the slope of the regression in the runoff sample matrix. The difference in the slopes between matrices indicates the magnitude of the matrix interference associated with the method. The standard error of the regression (the standard deviation of the residuals with n-2 degrees of freedom) may be used to estimate the detection limit of the method. The detection limit of a method may be estimated by the following equation:

$$D.L. = y_0 + s_y z_a$$

where:

D.L.=detection limit of the method
$y_0$=the intercept of the regression equation
$s_y$=standard error of the regression
$z_\alpha$=the area under the normal curve associated with a one-tail probability for a given confidence level (McCormick & Roach 1987).

In our evaluations, we have presented the standard error and calculated the detection limit for a 95% confidence level ($\alpha$=0.05).

Concentrations exceeding the detection limit only indicate the presence of the parameter. The equation may be modified to calculate the limit of quantification. Reported concentrations exceeding the limit of quantification may be used to quantify the results. The modified equation is presented below.

$$LOQ = y_0 + 2 s_y z_a$$

For example, if the D.L. is calculated to be 0.5 mg/L and the LOQ is calculated to be 1.0 mg/L, the following statements would be true:

1. A response of 0.25 mg/L does not positively indicate the presence of the pollutant with the desired 95% confidence.
2. A response of 0.75 mg/L does indicate the presence of the pollutant with the desired confidence, but the measured concentration does not have the desired level of confidence.
3. A response of 1.25 mg/L does indicate the presence of the pollutant and its measured concentration is within the desired level of 95% confidence.

The residuals of the regressions were used to further substantiate the presence of a bias. A plot of residuals versus predicted spike concentrations should produce a random band of points with an average value representing the concentration of the parameter of interest in the blank sample. Narrow error bands indicate a more precise method. A plot of residuals versus the order of analysis indicates if a bias is time dependent. For example, the calibration of a pH meter will drift over time. A plot of residuals versus the order of measurement may therefore show a linear trend if the meter is not regularly re-calibrated.

From these analyses, two subsets of equipment were identified for further study. The first set was defined by lowest detection limit with acceptable safety considerations (defined as the “best test”). The second set was chosen on the basis of shortest analysis time with acceptable safety considerations and good ease of use (identified as the “easiest

test"). In some cases, the same test kit received both designations for a parameter. Some additional tests were also selected for further evaluation based on their sensitivity.

### *2.1.2 Parallel Manhole Analysis*

The two sub-sets of methods, plus some additional tests, were then evaluated by parallel analysis of 25 to 30 samples of water obtained from manholes. The controls for this set of experiments were our standard laboratory procedures for measuring the parameters of interest.

### *2.1.3 Precision*

The precision of these selected methods were evaluated by evaluating five replicates of a composite sample. The composite was made from water collected from several randomly selected manholes to represent a wide variety of conditions. The average, standard deviation and relative standard deviation (RSD, also known as the coefficient of variation or COV) for the methods is presented for each test kit. The COV is simply the ratio of the standard deviation to the mean. The precision reported for each method is the COV of these replicate analyses.

## 2.2 Evaluation of Field Screening-kits

Table 3-1 summarizes the field screening-kits evaluated during this study, while Appendix A contains detailed test results. Table 3-2 presents ordering information. The appendix includes information for the following parameters of interest:

ammonia
bacteria
conductivity (surrogate for chloride)
copper
detergents
fluoride
hardness
hydrocarbons (including BTEX and PAH)
lead
nitrate
pH
potassium
toxicity
zinc

### *2.2.1 Recommended Simplest Field Screening Test Kit Package*

An adequate set of screening-kits can be recommended that will be sufficient to identify the most serious manhole water and sediment quality problems. This set would include analyses for the following parameters:

- detergents (most importantly), plus possibly fluoride, ammonia and potassium (which would indicate sewage contamination),

- conductivity to indicate elevated salinity levels (likely associated with snowmelt accumulation in northern areas or marine water intrusion in coastal areas),

- vapor analyses using personal safety monitor for methane and hydrogen sulfide (which would indicate gasoline and other fuels, plus sewage contamination), and

- visual inspections for the presence of sediment (especially dark and fine grained sediment) and sheens on the water surface, plus noting obvious odors.

If any of these tests confirm the presence of adverse quantities of sewage, fuels, or sediment, then water and/or sediment control would be initiated. If these tests were negative, but the manhole is still suspect (due to material use in the manhole, surrounding land use, placement of manhole in surface flow path, past problems, etc.), then additional tests would/could be conducted to confirm if a problem exists that would require treatment, or treatment could be conducted without further tests. Appropriate selections from the additional chemical tests would be made based on the specific conditions. The telecommunication manhole characterization study conducted as part of this research is very important for identifying which of the parameters should be selected under which conditions.

Additional parameters could be easily added to this field screening kit, including analyses for pH, nitrates and some heavy metals and hydrocarbons. Nitrate and pH analyses would be relatively simple and inexpensive (but not as useful as the other tests indicated above), while heavy metals and hydrocarbons would be very useful, but reasonable field screening methods (inexpensive, safe, relatively easy to use, and sensitive) for these parameters have not been identified. If cost was of lesser concern, the PetroSense (at $6,900) for hydrocarbons and the Metalyzer (at $4,200 for the instrument, plus $15 for each test) or the Palintest (at $2,400 for the instrument, plus $5.50 for each test) for copper and lead would be the best units for these analyses. It may be possible to consider having these units available at a regional Central Office for use to check known likely problematic manholes at time of needed maintenance, or for periodic checking of water in local manholes at times when emergency repairs are not needed.

GDS & Assoc. of Carson City, Nevada, has created a unique field screening test kit (AquaVats™) they designed and packaged for use in evaluating water found in utility manholes. The initial cost of this kit is about $800 and includes supplies for 10 analyses each of the following tests:

- pHTestr 2 pocket probe for pH measurements
- TDSTestr 3 pocket probe for conductivity measurements
- CHEMetrics C-3501 color comparator kit for copper
- CHEMetrics C-6350 color comparator kit for lead
- and a hydrocarbon test of their own packaging

A reagent re-fill kit costs about $600 for an additional 10 sets of samples for the copper, lead, and hydrocarbon analyses. These components were briefly evaluated as part of this project task and the results are included in the respective sections. An important aspect of this kit is the training and packaging. It is by far the best packaging of any test kit examined in that complete and useful instructions and documentation was provided for its use, especially for handling the hazardous chemicals used and the hazardous wastes generated. GDS provides and requires training of the kit users. A unique aspect of this kit is that the hazardous wastes from the lead and hydrocarbon tests are stored in the reagent shipping container and are shipped back to GDS for proper disposal. Unfortunately, these two analyses were not very useful during our evaluation (the lead provided spurious results and the hydrocarbon test had inadequate sensitivity) and we cannot recommend their use, especially as there are better methods available that do not pose the potential risks that this kit has. It is hoped that GDS could re-configure their kit to include the test parameters listed above (conductivity, detergents, fluoride, potassium, and ammonia) and retain their excellent documentation, packaging, and training.

### *2.2.2 Complete List of Recommended Screening-kits*

Table 2-1 summarizes the complete screening test kit costs, expertise required, and time required to conduct all of these tests. The major capital cost is for a HACH field spectrophotometer. Most of our initial evaluations used the older model DR 2000 spectrophotometer, while our newer evaluations have used the updated model DR 2010 which is recommended for these analyses. This unit currently costs about $1,500, but it can be used for 7 of the tests shown in

Table 2-1 Other major capital costs are associated with the Dtech Immunoassay analyses, requiring a color spot reader at $500. This is an optional device, but significantly improves the test sensitivity.

The immunoassay tests are much more specific for BTEX and PAHs than the general hydrocarbon screening methods as demonstrated by the PetroSense instrument, for example. Unfortunately, they are very complex, have sensitive and short storage period requirements (making them impractical for use on a utility repair truck) time consuming, and have relatively expensive consumables ($25 per test for each parameter). If hydrocarbon screening is suitable, especially if a unit can be shared through the Central Office, the PetroSense hydrocarbon screening sensor (at $6,900) may be a more practical choice.

The Horiba Twin conductivity and temperature meter is $250, plus $60 for replacement sensors that are expected to last about 6 months.

The total capital costs are therefore about $1,750 (without the Dtech spot reader, the PetroSense, or the electro-chemical metal analyzers). For the simplest test kit, requiring only a few spectrophotometer determinations, alternative dedicated instruments are available for about $200 to $400 per test parameter (fluoride, ammonia and potassium, while the analysis method for detergents utilizes a color comparator) which would decrease the total kit costs somewhat. However, if a PetroSense and a Palintest unit were added for hydrocarbon screening plus copper and lead analyses, the equipment cost would increase by another $9,300, for a maximum kit equipment cost of about $11,050. Another expensive option is Azur's DeltaTox™ PS1 (we tested a beta version, and current cost is not available) which would add substantial information to the field screening activities, and could also be located at the Central Office for periodic use.

The total consumable costs per sample (for all analyses) total about $20. If immunoassay tests of BTEX and PAHs in water are desired, the per sample consumable cost would increase by another $50. If Palintest analyses were added for copper and lead, the costs would increase by another $5.50 per sample.

The major critical factors for these recommended screening tests are probably associated with the required time and expertise to conduct the analyses. Many of the analyses can be conducted simultaneously (especially those with extensive color development times, such as the immunoassays and the bacteria tests, plus the ammonia, copper, detergents, lead, and potassium tests). However, there will be a limit, as some of the tests are very complex (especially the immunoassays and the LeadTrak, which also require extensive expertise to obtain good results).

**Table 2-1 Summary of Recommended Screening-kits for all Parameters**

| parameter | screening test recommended | time required (min.) | expertise required | other potential concerns | useful range | capital cost | expendable cost ($/sample) |
|---|---|---|---|---|---|---|---|
| ammonia | HACH Salicylate | 20 | moderate | time consuming test | 0.10 – 0.7 mg/L | $1,595 for DR 2010 (used for other tests also) | $2.88 |
| bacteria | IME KoolKount | 30 min. to 13 hr | little | can require long time for results, non-selective test | na | none | $4.00 |
| BTEX | EM Science Dtech Immunoassay | 45 | extensive | time consuming, complex, critical and short allowable storage | very sensitive | $500 (optional) | $25 (water) to $50 (sediment) |
| chloride | use Horiba Twin, with ATC, conductivity | 1 | little | replacement probe cost ($60 every 6 months) | 75 to 50,000 µS/cm | $250 | none |
| copper | HACH Bicinchonate, AccuVac | 5 | little | sharps | 0.5 to 5.0 mg/L | also uses DR 2010 | $0.28 |
| copper (recommended alternative) | Palintest SA-1000 | 3 | little | expensive instrument | 70 – 300 µg/L | $2,300 (for lead also) | $5.50 (for both lead and copper) |
| detergents | CHEMetrics | 5 | moderate | chloroform extraction (but minimal exposure), sharps | 0.15 to 3.0 mg/L | none | $2.38 |
| fluoride | HACH SPADNS, AccuVac | 5 | little | sodium arsenite in waste, sharps | 0.1 to 2.0 mg/L | also uses DR 2010 | $1.17 |
| hardness | HACH field titrator | 5 | little | limited range tested, but other ranges available | 19 to 160 mg/L as $CaCO_3$ | $94 | <$1 |
| hydrocarbon screening (recommended alternative to immunoassay tests) | PetroSense | 5 | little | expensive instrument, general indicator | 0.1 to 10 mg/L | $6,900 | None |
| lead | HACH LeadTrak | 45 | extensive | time consuming and complex test | 5 to 150 µg/L | also uses DR 2010 | $4.61 |
| lead (recommended alternative) | Palintest SA-1000 | 3 | little | expensive instrument | 5 to 300 µg/L | $2,300 (for copper also) | $5.50 (for both lead and copper) |
| nitrate | HACH MR, AccuVac | 7 | little | cadmium waste | 2.8 to 16 mg/L | also uses DR 2010 | $0.56 |
| PAHs | EM Science Dtech Immunoassay | 45 | extensive | time consuming, complex, critical and short storage conditions. | very sensitive | same as for BTEX | $25 (water) to $50 (sediment) |
| pH | Horiba Twin pH meter | 1 | little | replacement probe cost ($70 every 6 months) | 0-12 pH units | $235 | none |
| potassium | LaMotte (can be used with HACH spectrophotometer or | 15 | moderate | time consuming test, best analyzed using | 3.3 to 10 mg/L | can use DR 2010 | $0.29 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | field turbidimeter) | | | turbidimeter and not spectro-photometer | | | |
| toxicity screening | Azur DeltaTox PS1 | 20 | moderate | expensive instrument and time consuming | na | beta version tested | beta version tested |
| Zinc | LaMotte (can be used with HACH spectrophotometer) | 5 | moderate | uses dilute cyanide solution and has short expiration date | 0.14 to 3 mg/L | can use DR 2010 | $0.59 |

# 3 Descriptions of Recommended Screening-Kits

## 3.1 Parameters

The following tests are our current recommendations as the best, easiest, quickest, and/or least expensive of the field screening-kits that have adequate performance for each of the parameters that we have tested. Of course, new tests are continually being developed and available tests are periodically discontinued or modified. Therefore, it is important that the user consider these possible changes.

### *3.1.1 Ammonia*

HACH, *Ammonia method using salicylate without distillation.* This is a colorimetric determination of ammonia using salicylate. The test requires a DR 2010 spectrophotometer at $1595 (which can also be used for several other parameters). The individual sample consumable cost is $2.88.

### *3.1.2 Bacteria*

Industrial Municipal Equipment, Inc. *IME Test KoolKount Assayer*. This is a visual colorimetric test that costs about $4.00 per test. It is a very unique test that requires from 30 min to 13 hr for a determination at "room temperature" incubation. Very high concentrations will be evident in the short period of time. This is not a selective test, but sensitive to a mixed microbial population. There are no currently available field tests for bacteria that do not require extended incubation. This is the only method known that doesn't require temperature controlled incubation and can produce some indication of bacterial contamination in a relatively short period of time. Unfortunately, it is easy to obtain false negative results, as problematic bacterial conditions may be present even when this test indicates an absence of bacteria. It is therefore recommended that other indicator methods be used to identify the potential presence of sanitary sewage (such as detergents, fluorides, potassium, and ammonia).

### *3.1.3 Conductivity*

The Horiba *Twin* is a very small meter that has performed very well in our tests. It costs about $250, but the sensor should be replaced about every 6 months at a cost of $60. The meter automatically compensates for temperature effects and is suited to very small samples (only requiring a few drops of water). The meter comes with a standard calibration solution. The procedure is to calibrate the meter using the provided standard solution and to select the conductivity mode. The user may immerse the probe in the sample, or cover the probe with 2-3 drops of sample and a cover paper.

### *3.1.4 Copper*

HACH *Bicinchonate Copper Method using AccuVac Ampoules.* This test also uses the DR 2010 spectrophotometer (at $1595) and the unit sample cost is $0.28. It uses AccuVac ampoules that are very easy to use and makes the test very repeatable. However, the glass ampoules do produce glass wastes and the sensitivity of the test is marginal.

The method uses the spectrophotometer to detect the presence of a copper bicinchonate complex in the sample solution. A sample blank is scanned by the DR2010. An AccuVac ampoule is immersed in approximately 50 mL of sample and broken. A specific volume is drawn into the ampoule. After a two minute reaction time, the ampoule is scanned to determine the copper complex concentration. This, and similar methods, is susceptible to interferences. The method depends on the formation of the copper bicinchonate complex. Any chemical agent

interfering with this reaction will skew the results. Potential interferences of this type include any chelating agent, such as EDTA, that will selectively bind any copper ions before complexation with the bicinchonate and will therefore lower the reported copper concentration from its true value. Other metal ions present in large concentrations may also compete with copper for bicinchonate ligands. This interference will most likely produce a reported concentration larger than the true value if the metal complex absorbs in the same range as the copper complex. The most important potential error associated with this method is it only indicates the presence of ionized copper. Any metallic or chelated copper will not be detected. This is important since small electrical potentials (ORP) or pH changes could release the copper at a later date.

The required materials include the HACH DR2010, AccuVac CuVer II reagent ampoules, a 100 mL beaker, and KimWipes. The procedure was tested using equipment in the lab , but a complete kit, excluding KimWipes is available. The HACH method produced the most promising results of the group of alternative tests. The improved performance is probably related to increased sample volume and superior quality of the HACH DR2010 spectrophotometer over the La Motte Smart Colorimeter and CheMetrics DCR Photometer.

A recommended alternative that is much more sensitive, but also is much more expensive, is the Palintest electro-chemical method. The instrument costs about $2,300 and each test costs an additional $5.50. The test also evaluated lead simultaneously. This test also only measures copper ions and not complexes or particulate forms of copper.

### *3.1.5 Detergents*

CHEMetrics *Detergents (Anionic Surfactants)*. This is really the only practical test for detergents, which is very important for identifying sewage and washwater contamination. The tests cost about $2.38 each and require about 5 minutes. The test uses a chloroform extraction, but the test is very well designed to minimize exposure to the operator and it uses a very small amount of chemical.

The CheMetrics procedure uses a visual comparator to determine the concentration of the detergents samples. A small volume of sample (5 mL) is required. An ampoule containing methylene blue and chloroform are mixed with the sample. Anionic detergents complex with the methylene blue and are extracted into the chloroform layer. Cationic detergents and sulfides interfere with the reaction and lead to diminished results.

The method is very quick and easy. However, the detection limit is higher than desired. The method also uses chloroform, a known carcinogen, which is not well stated in the test kit documentation. Users must therefore seek well-ventilated areas to perform this test. Furthermore, the waste must be disposed of properly. The kit is well designed to minimize the use and exposure of the chloroform. It was hoped that a fluorescence analysis could be used to indicate washwaters due to fabric brighteners. Unfortunately fluorometers are relatively expensive (about $10,000).

The kit also does not contain a few items required to complete the test. For example, a transfer pipette or medicine dropper is required to accurately measure 5 mL. A small cup should be used as a test tube holder for the reaction vessel. Finally, the reagent packs have a limited shelf life. The user must insure that the reagents are still fresh for testing.

### *3.1.6 Fluoride*

HACH *Fluoride SPADNS Reagent Using AccuVac Ampoules.* This is another AccuVac test that shares the DR 2010 spectrophotometer. The tests cost about $1.17 for each sample and requires about 5 minutes to conduct. The test does produce a small amount of glass waste and the expended reagent has enough sodium arsenite to be classified as a hazardous waste under Federal RCRA regulations. This test is important in identifying domestic water (including sanitary sewage) sources in manholes.

### *3.1.7 Hardness*

HACH *Total Hardness, with digital titrator*. This is a very well designed test kit from HACH that reduces reagent use and simplifies field titrations. This is based on a standard laboratory method and results in precise and sensitive determinations. The digital titrator kit costs about $94 and each test costs less than $1 and takes a few minutes.

### *3.1.8 Hydrocarbons, and Specific Tests for BTEX and PAH*

The PetroSense is a very useful field screening tool for hydrocarbons. It is reasonably sensitive to a broad range of petroleum hydrocarbons, is easy to use, and fast. Unfortunately, it is quite expensive (about $7,000). Petroleum hydrocarbon screening may be most effectively based on hazardous vapor analyses used before the manhole cover is opened (lower explosive limit or methane concentration), by smell, and by the presence of a visible oil sheen. If specific concentrations of BTEX or PAHs are needed, then the best procedures would probably be a test based on immunoassay procedures. Unfortunately, the reagents in these tests have short shelf lives and need to be carefully stored. In addition, each analysis is relatively expensive. The two units tested below were representative of the kits that were available during the period of the evaluations. New products using immunoassays are frequently being developed and simplifications in their use and more robust storage requirements are expected in the future.

Dtech (EM Science) *BTEX Test Kit*. This is an accurate and sensitive kit that can be used for both water and sediment BTEX analyses, but it is very complex and requires up to an hour for an analysis. The Dtech reader (at an initial cost of $500) can be used for both soil and water analyses and for both BTEX and PAH analyses. The per sample cost is about $25 for water samples and about $50 for sediment samples (which includes the cost for the required soil extraction kit).

The most specific test for PAH analyses is the EM Science *Dtech PAH Test Kit*, an immunoassay test that is quite complex, requires extensive training, and costs from $25 to $50 per sample. The Dtech reagent expires within about 1 to 2 months and needs refrigeration. However, the test results are quite accurate and the test has good sensitivity.

### *3.1.9 Lead*

HACH *LeadTrak system.* This is by far the most sensitive relatively inexpensive lead field test kit available that is suitable for detecting the small concentrations of lead that are likely present in water found in manholes (but still at important concentrations). Unfortunately, it is also quite complex and requires extensive experience to efficiently conduct. The test also is long, requiring about 45 minutes. The initial test kit costs about $395 and the per sample cost is about $4.61. More expensive adaptations of laboratory procedures (such as the anodic stripping voltammeter from Palintest would be much more suitable and easier to use, but the instrument costs about $2,300 and the per test cost is about $5 for both lead and copper).

The LeadTrak system determines lead concentrations through colorimetric determination of a lead complex extracted from the sample. The test procedure is quite complicated, requires a great deal of space compared to the other tests, and uses hazardous chemicals. However, it does produce good results. Like all of the field procedures for heavy metals, this test is only sensitive to the “soluble” fraction of the metals and does not detect metal forms bound to particulates. The test is very sensitive. It detected spike concentrations of 1 ppb. However, the procedure is quite complicated. As a result, mistakes are easy to make. Procedural errors produce colors that alert an experienced user that the test will be flawed. A single test will take at least 15 minutes for an experienced individual. The test requires at least 3 $ft^2$ of flat space. The test also uses several hazardous chemicals.

The LeadTrak procedure uses a 100 mL sample. The 100 mL sample is treated with an acid preservative, a nitric acid solution buffered with potassium nitrate. The solution is then treated with a solution of trishydroxymethylaminomethane, potassium nitrate, succinic acid, and imidazole. The prepared sample is then filtered through a solid phase extractor (basically a syringe with a cloth plug). The lead in solution is held by the filter in the extractor. The lead is then removed from the plug with the eluant solution, another nitric acid

solution. The eluant is allowed to pass over the plug until it stops flowing. The remaining eluant is forced through with the syringe plunger. This produces approximately 30 mL of extract containing the lead. The extract is neutralized with a solution of tris-hydroxyaminomethane, tartaric acid, and sodium hydroxide. One powder pillow, containing potassium chloride and meso-tetra(-4-N-methylpryidyl)-porphine tetratosylate is added to the elutant. Two 10 mL portions are taken. A decolorizing solution is added to one portion; this portion is now the blank.

### *3.1.10 Nitrate*

HACH *Nitrate, MR*. This test also shares the DR 2010 spectrophotometer and uses AccuVacs. The test is therefore very simple and quick, but produces glass debris. The expended test samples and blanks also contain cadmium metal (also present in most other field screening-kits for nitrate) in high enough concentrations to be regulated as a hazardous waste by Federal RCRA regulations. The test costs about $0.56 per sample and takes about 7 minutes.

### *3.1.11 pH*

Horida *pH Twin*. This is a very simple and relatively inexpensive instrument ($235) It requires a replacement sensor (at $70) every 6 months. None of the other small pocket pH meters which we have tried are nearly as reliable or maintenance free as this Horiba Twin meter. The Sentron pH meter is a fine and likely more rugged instrument, but it is more expensive at $595 and is substantially larger. pH paper was a disappointment, as we observed very little change with the papers for vastly different pH conditions measured by the laboratory meters.

### *3.1.12 Potassium*

*La Motte Potassium Reagent Set with the HACH DR 2010 Spectrophotometer*. This is an example of a hybrid test that we tested successfully by combining the very good La Motte reagents with the excellent (and needed for other tests) HACH DR 2010. The cost per test is about $0.29 and the test should take about 15 minutes. Potassium can be used as an indicator of sewage contamination in suspect water bodies, especially when used in combination with ammonia concentrations.

The HACH and La Motte kits both determine potassium concentrations using tetraphenylborate salts. These procedures add large doses of sodium tetraphenylborate to the sample. The potassium in the sample reacts with the sodium tetraphenylborate to form insoluble potassium tetraphenylborate. The insoluble potassium tetraphenylborate increases the turbidity of the sample solution. The presence of magnesium ($Mg^{2+}$), ammonium ($NH_4^+$) and calcium ($Ca^{2+}$) ions can interfere with the reaction by competing in the reaction with tetraphenylborate (HACH 1992). These salts will result in a reported potassium concentration larger than is actually present in the sample. Both methods measure this increase in turbidity using a spectrophotometer. This procedure can be improved by using a field turbidimeter to more accurately measure the resulting turbidity of the sample. Because these tests use a spectrophotometer, they include definite timing schemes that must be followed exactly in order to compare results from one sample with another.

After the blank scan, 4 drops of 1.0 M sodium hydroxide (NaOH) is added to mask interference. La Motte provides a spoon calibrated to deliver 0.05 g of sodium tetraphenylborate to the sample. The procedure indicates that the sample should be shaken until all tetraphenylborate has dissolved. There is a 5 minute reaction time after the dissolution. The La Motte procedure directs the user to re-suspend the particulates (increases turbidity) just before measurement.

The HACH potassium method is not pre-programmed into the DR 2010. However, this method can be programmed by the user. The key advantage to pre-programming a method is storage of the calibration curve. For this method, the calibration curve must be re-entered for each batch of potassium reagents.

### *3.1.13 Toxicity Screening*

A beta version of AZUR's DeltaTox PS 1 was successfully tested as a rapid screening method for water toxicity. This method is based on the Microtox procedure that uses a luminescent bacteria to indicate toxicity by a decreased light output when exposed to a test sample. The DeltaTox is unique in that it can be operated in the field with much less temperature control than is required by the Microtox method. The test requires approximately 20 minutes, but is very simple to conduct.

### *3.1.14 Zinc*

Zinc: La Motte *Zinc*. This is the only acceptable zinc method investigated, as it uses a dilute solution containing cyanide, whereas the alternative tests use full strength granular cyanide. The test costs about $0.59 each and requires about 5 minutes.

**Table 3-1 Summary of All Field Screening-kits Evaluated**

| Method | Manufacturer and Kit Name | Capital Cost | Expend-able Cost (per sample) | Time Reqd. (min) | Useful Range | Precision (COV) | Recovery (RO/runoff) | Problems with Test (safety hazards, expertise required, etc.) |
|---|---|---|---|---|---|---|---|---|
| **AMMONIA** | | | | | | | | |
| Colorimetric determination of ammonia using Nessler's Reaction | CHEMetrics *Ammonia 1 DCR Photometer* **EASIEST TEST** | $435 for kit | $0.63 | 5 | 0.03-2.5 mg/L | 0.15 | 0.85/1.27 | 6 month shelf life, with refrigeration; sharps and mercury in waste. |
| Colorimetric determination of ammonia using salicylate. | HACH *Nitrogen, Ammonia: Salicylate Method without Distillation* **BEST TEST** | $1595 for DR 2010 | $2.88 | 20 | 0.10-0.7 | 0.17 | 1.15/1.10 | |
| Colorimetric determination of ammonia using Nessler's Reaction | La Motte *Ammonia Nitrogen, High Range* | $895 for Smart Color. | $0.33 | 10 | 0.38-3 | na | 1.22/1.21 | Waste contains a mercury compound; high detection limit (0.4 mg/L). |
| Colorimetric determination of ammonia using salicylate. | La Motte *Ammonia Nitrogen, Low Range* | $895 for Smart Color. | $0.76 | 20 | 0.17-1.5 | na | 1.04/0.96 | Would require the Smart Colorimeter (most of the selected tests are using the HACH DR 2010 instead). |

**Table 3-1 Summary of Field Screening-kits Evaluated** (Cont.)

| Method | Manufacturer and Kit Name | Capital Cost | Exp. Cost | Time (min) | Useful Range | Precision (COV) | Recovery (RO/runoff) | Problems with Test |
|---|---|---|---|---|---|---|---|---|
| **BACTERIA** | | | | | | | | |
| Colorimetric | IDEXX *Colilert* **BEST TEST** | $3,000 for sealer tray needed for quantitative work | $4.00 | 24 hr | na | na | na | 24 hour test period required. |
| Colorimetric | Industrial Municipal Equipment, Inc. *IME Test KoolKount Assayer* **EASIEST TEST** | $0.00 | $4.00 | 30 min to 13 hr | na | na | na | Not a selective test, but sensitive to a mixed microbial population. |
| **BTEX and PAH (including general Hydrocarbon screening methods)** | | | | | | | | |
| Solvent extraction | Dexsil *PetroFlag* | $695 | $10 | 10 | na | na | na | Poor detection limits (100 ppm in soil). |
| Immunoassay | Dtech (EM Science) *BTEX Test Kit* **BEST TEST SPECIFIC TO BTEX** | $500 | $25 | 30-60 | na | na | na | Reagents expire in 1 to 2 months and require refrigeration; requires 30-60 minutes to conduct test; requires extensive expertise; $25 per test. |
| Absorption onto fiber optic | PetroSense **EASIEST TEST** | $6,900 | 0 | 5 | 0.1 - 10 | 0.56 | na | Expensive instrument ($6,900). |

**Table 3-1 Summary of Field Screening-kits Evaluated** (Cont.)

| Method | Manufacturer and Kit Name | Capital Cost | Exp. Cost | Time (min) | Useful Range | Precision (COV) | Recovery (RO/runoff) | Problems with Test |
|---|---|---|---|---|---|---|---|---|
| **BTEX and PAH, continued** | | | | | | | | |
| Fluorometry | Turner Designs *10-AU field fluorometer* **MOST SENSITIVE TEST** | $10,500 | 0 | 1 | 0.01 - ? | 0.072 | na | Expensive instrument ($10,500) |
| Infrared | Wilkes *Infracal Oil in Water Analyzer* | $4,850 | $10 | 5 | na | na | na | Expensive instrument ($4,850). |
| Stain free oil | Forestry Supply *Oil in Water Test Kit* | $60 | $3.00 | 5 | na | na | na | Low sensitivity (3 ppm in water, 10 ppm in soil). |
| Immunoassay | EM Science *Dtech PAH Test Kit* **BEST TEST SPECIFIC TO PAHs** | $500 | $25 | 30-60 | na | na | na | Reagents expire in 1 to 2 months and require refrigeration; requires 30-60 minutes to conduct test; requires extensive expertise; $25 per test. |

**Table 3-1 Summary of Field Screening-kits Evaluated** (Cont.)

| Method | Manufacturer and Kit Name | Capital Cost | Exp. Cost | Time (min) | Useful Range | Precision (COV) | Recovery (RO/runoff) | Problems with Test |
|---|---|---|---|---|---|---|---|---|
| **CHLORIDES** | | | | | | | | |
| silver nitrate titration | HACH *silver nitrate titration* **USE CONDUCT-IVITY** | $94 for digital titrator | $0.66 | not evalu-ated | na | na | na | Unclear titration endpoint, no useful data obtainable. |
| **CONDUCTIVITY** | | | | | | | | |
| electronic probe | YSI *Model 33 SCT* | $600 for kit | $0.00 | 1 | 98-? µS/cm | na | 0.90/0.93 | |
| electronic probe | Horiba *Twin* **BEST AND EASIEST TEST** | $250 for kit | $0.00 | 1 | 75-50,000 | 0.04 | 1.08/1.02 | Replace sensor every 6 months for $60. |
| Electronic probe | Horiba *U-10 (Cond., temp., DO, turbidity, pH)* | $2800 for kit | $0.00 | 1 | 87-? | na | 0.95/0.96 | Expensive instrument. |

**Table 3-1 Summary of Field Screening-kits Evaluated** (Cont.)

| Method | Manufacturer and Kit Name | Capital Cost | Exp. Cost | Time (min) | Useful Range | Precision (COV) | Recovery (RO/runoff) | Problems with Test |
|---|---|---|---|---|---|---|---|---|
| **COPPER** | | | | | | | | |
| colorimeter | CHEMetrics *Copper 1 DCR Photometer Kit* | $435 for kit | $0.63 | 15 | 0.3-3.5 mg/L | na | 0.64/0.52 | Sharps and poor recovery. Not very repeatable. |
| Colorimeter | La Motte *Copper (Diethyldithio-carbamate)* **EASIEST TEST** | $895 for Smart Color. | $0.41 | 10 | 0.1-3.5 | na | 1.11/0.93 | Would require the Smart Colorimeter (most of the selected tests are using the HACH DR 2010 instead). |
| Anodic stripping voltometer | Palintest *SA-1000 Scanning Analyzer* **MOST SENSITIVE TEST** | $2,295 | $5.50 (for both Cu and Pb) | 3 | 70 - 300 µg/L | na | na/na | Expensive instrument ($2,300) |
| Potentiometric stripping analyzer | Environmental Technologies Group *Metalyzer 3000* **MOST SENSITIVE TEST** | $4,200 | $15 (for both Cu and Pb) | 3 | 70 - 300 µg/L | na | na/na | Expensive instrument ($4,200) |

**Table 3-1 Summary of Field Screening-kits Evaluated** (Cont.)

| Method | Manufacturer and Kit Name | Capital Cost | Exp. Cost | Time (min) | Useful Range | Precision (COV) | Recovery (RO/runoff) | Problems with Test |
|---|---|---|---|---|---|---|---|---|
| **COPPER, continued** | | | | | | | | |
| colorimeter | La Motte *Copper (Bicinchoninic Acid)* | $895 for Smart Color. | $0.23 | 20 | 0.6-3.5 | na | 0.94/0.93 | Extra time required to dissolve reagent. Not very repeatable. |
| Colorimeter | HACH *Bicinchonate Copper Method using AccuVac Ampoules* **BEST TEST** | $1595 for DR 2010 | $0.28 | 5 | 0.5-5.0 | na | 0.97/0.96 | Sharps. |
| **DETERGENTS** | | | | | | | | |
| Colorimetric | CHEMetrics *Detergents (Anionic Surfactants)* **BEST AND EASIEST TEST** | $60 for 1st 30 tests and standards | $2.38 | 10 | 0.15-3 mg/L | na | 1.66/1.82 | Sharps; chloroform extraction (very small volume and well contained). |
| Colorimetric | HACH *Surfactants, Anionic, Crystal Violet Method* | $1595 for DR 2010 | $1.10 | 30 | na | na | na | Large amounts of benzene required; require laboratory hood; waste disposal problem. |

**Table 3-1 Summary of Field Screening-kits Evaluated** (Cont.)

| Method | Manufacturer and Kit Name | Capital Cost | Exp. Cost | Time (min) | Useful Range | Precision (COV) | Recovery (RO/runoff) | Problems with Test |
|---|---|---|---|---|---|---|---|---|
| **FLUORIDE** | | | | | | | | |
| Ion Selective Electrode | Cole-Parmer *Fluoride Tester* | $600 for electrode, meter and calib. Kit | $0.25 | 5-10 | 0.1-20 mg/L | 0.22 | 0.97/0.96 | Requires frequent and time consuming calibration; too fragile for field use. |
| Spectrophotometric determination of bleaching by fluoride | HACH *Fluoride SPADNS Reagent* | $1595 for DR 2010 | $0.37 | 10 | 0.3-2 | na | 1.10/1.07 | Should use automatic pipettes, hard to use in field. Sodium arsenite in wastes. |
| Spectrophotometric determination of bleaching by fluoride | HACH *Fluoride SPADNS Reagent Using AccuVac Ampoules* **BEST AND EASIEST** | $1595 for DR 2010 | $1.17 | 5 | 0.1-2 | 0.05 | 0.97/0.94 | Sharps and sodium arsenite in wastes. |

**Table 3-1 Summary of Field Screening-kits Evaluated** (Cont.)

| Method | Manufacturer and Kit Name | Capital Cost | Exp. Cost | Time (min) | Useful Range | Precision (COV) | Recovery (RO/runoff) | Problems with Test |
|---|---|---|---|---|---|---|---|---|
| **HARDNESS** | | | | | | | | |
| EDTA titration | CHEMetrics *Hardness, Total 20-200 ppm* **EASIEST TEST** | $0.00 | $2.25 | 5-10 | na | 0.01 | na | Sharps. |
| EDTA titration | HACH *Total Hardness Using Digital Titrator* **BEST TEST** | $94 for digital titrator | varies with sample strength | varies with sample strength | na | na | na | |
| **LEAD** | | | | | | | | |
| chloroform extraction, visual comparator | La Mott *Lead in Water Kit* | $74.85 for kit | $1.57 | 20 | 0.3-1.5 mg/L | na | 0.96/1.02 | Discontinued. |
| Solid phase extraction, colorimeter | HACH *LeadTrak system* **BEST TEST** | $395 for DR/100 kit or $1595 for DR 2010 | $4.61 | 45 | 0.005-0.15 | na | 0.84/0.87 | Requires extensive expertise; complex kit; time consuming (45 minutes). |

**Table 3-1 Summary of Field Screening-kits Evaluated** (Cont.)

| Method | Manufacturer and Kit Name | Capital Cost | Exp. Cost | Time (min) | Useful Range | Precision (COV) | Recovery (RO/runoff) | Problems with Test |
|---|---|---|---|---|---|---|---|---|
| **LEAD, continued** | | | | | | | | |
| Anodic stripping voltometer | Palintest *SA-1000 Scanning Analyzer* **MOST SENSITIVE TEST** | $2,295 | $5.50 (for both Cu and Pb) | 3 | 5 - 300 µg/L | na | na/na | Expensive instrument ($2,300) |
| Potentiometric stripping analyzer | Environmental Technologies Group *Metalyzer 3000* **MOST SENSITIVE TEST** | $4,200 | $15 (for both Cu and Pb) | 3 | 5 - 300 µg/L | na | na/na | Expensive instrument ($4,200) |
| Sulfide Staining | Innovative Synthesis Corporation *The Lead Detective* | | $3.00 | 5 | na | na | na | Poor sensitivity. |
| Colorimetric | HybriVet Systems *Lead Check Swabs* | | $3.00 | 5 | na | na | na | Poor sensitivity. |
| Colorimetric | Carolina Environment Company *KnowLead* | | $3.00 | 5 | na | na | na | Poor sensitivity. |
| Test strips | EM Science *Lead* | $500 for Reflecto-Quant Meter | $1.11 | 10 | na | na | na | Not sensitive enough. |

**Table 3-1 Summary of Field Screening-kits Evaluated** (Cont.)

| Method | Manufacturer and Kit Name | Capital Cost | Exp. Cost | Time (min) | Useful Range | Precision (COV) | Recovery (RO/runoff) | Problems with Test |
|---|---|---|---|---|---|---|---|---|
| **NITRATE** | | | | | | | | |
| colorimeter | La Motte *Nitrate* | $895 for Smart Color. | $1.22 | 20 | 0.8-3 mg/L | na | 0.81/1.06 | Would require the Smart Colorimeter (most of the selected tests are using the HACH DR 2010 instead). |
| ISE | Horiba *CARDY* **EASIEST TEST** | $235 for kit | $60.00/ sensor (per 6 months) | N/A | 4.9-? | 0.97 | 0.90/0.70 | Designed for high concentrations; poor recoveries and precision at lower concentrations. |
| Test strips | EM Science *Nitrate Quant Test Strips* | $500 for Reflecto-Quant Meter | $0.49 | 2 | 1.7-500 | na | 1.00/1.61 | Reagents must be refrigerated. More scatter than most other tests. |
| Spectrophotometric | HACH *Nitrate, LR* | $1595 for DR 2010 | | | na | na | na | Sharps; too sensitive of a test and cadmium metal in wastes. |
| Spectrophotometric | HACH *Nitrate, MR* **BEST TEST** | $1595 for DR 2010 | $0.56 | 7 | 2.8-16 | na | 0.93/1.06 | Sharps and cadmium metal in wastes. |
| Colorimeter | CHEMetrics *Nitrate (Nitrogen)* | $48 for 1st 30 tests and standards | $0.73 | 30 | 0.5-22 | na | 1.06/1.02 | Sharps. |

**Table 3-1 Summary of Field Screening-kits Evaluated** (Cont.)

| Method | Manufacturer and Kit Name | Capital Cost | Exp. Cost | Time (min) | Useful Range | Precision (COV) | Recovery (RO/runoff) | Problems with Test |
|---|---|---|---|---|---|---|---|---|
| **pH** | | | | | | | | |
| electrode | Cole-Parmer *pH Wand* | $155 for kit | $92/ electro. | 5 | 0-14 | 0.01 | na | Daily calibration; fragile meter. |
| Electrode | Horiba *Twin pH* **EASIEST TEST** | $235 for kit | $70 for sensor. $25 for stand. | 1 | 0-12 | <0.01 | na | . |
| Electrode | Sentron *pH Probe* **BEST TEST** | $595 for meter and electrode | none | 1 | 0-14 | <0.01 | na | Expensive instrument ($595). |
| Test paper | EM Science *ReflectoQuant pH* | $500 for Reflecto-Quant Meter | $0.89 | 2 | 4-9 | 0.08 | na | Optics of expensive instrument ($500) are difficult to keep clean. |

**Table 3-1 Summary of Field Screening-kits Evaluated** (Cont.)

| Method | Manufacturer and Kit Name | Capital Cost | Exp. Cost | Time (min) | Useful Range | Precision (COV) | Recovery (RO/runoff) | Problems with Test |
|---|---|---|---|---|---|---|---|---|
| **pH (Continued)** | | | | | | | | |
| Spectrophotometric | La Motte *pH* | $895 for Smart Color. | $0.22 | 5 | 5-9.5 | na | na | Would require the Smart Colorimeter (most of the selected tests are using the HACH DR 2010 instead). |
| Test paper | Fisher Scientific *Alkacid Test Strips* | $0.00 | | 1 | 0-12 | 0.07 | na | Only readable to within +/- 1 pH unit, poorly correlated to pH meters during laboratory tests |
| **POTASSIUM** | | | | | | | | |
| Spectrophotometric | HACH *Potassium Tetraphenylborate* | $1595 for DR 2010 | $2.99 | 30 | 0.5-7 mg/L | na | 0.81/0.90 | |
| ISE | Horiba *CARDY* | $235 for kit | $60/ sensor (per 6 months) | 5 | 2.0-? | 0.04 | 0.53/0.46 | Method designed for much higher concentrations. More scatter than other tests. |
| Colorimeter | La Motte *Potassium* **BEST TEST** | $895 for Smart Color. | $0.29 | 15 | 3.3-10 | na | 1.35/1.05 | Would require the Smart Colorimeter (most of the selected tests are using the HACH DR 2010 instead). |

**Table 3-1 Summary of Field Screening-kits Evaluated** (Concluded**)**

| Method | Manufacturer and Kit Name | Capital Cost | Exp. Cost | Time (min) | Useful Range | Precision (COV) | Recovery (RO/runoff) | Problems with Test |
|---|---|---|---|---|---|---|---|---|
| **POTASSIUM, continued** | | | | | | | | |
| Spectrophotometric | La Motte and HACH *La Motte Potassium Reagent Set, HACH DR 2010 Spectro-photometer* **EASIEST TEST** | $1595 for DR 2010 | $0.29 | 15 | 1.3-7 | 0.06 | ?/0.90 | |
| **ZINC** | | | | | | | | |
| Spectrophotometric | La Motte *Zinc* **BEST TEST** | $895 for Smart Color. | $0.59 | 5 | 0.14-3 mg/L | na | 0.88/0.85 | Dilute indicator expires in a month. Uses dilute cyanide. |
| Spectrophotometric | HACH *Zinc, Zincon Method* | $1595 for DR 2010 | $0.37 | 10 | na | na | na | Used granular cyanide and is unacceptable for field use. |
| Test strips | EM Science *ReflectoQuant Zinc* **EASIEST TEST** | $500 for Reflecto-Quant Meter | $0.56 | 5 | na | na | na | Reflectoquant requires frequent cleaning and test has high detection limit. |

**Table 3-2 Manufacturer's and Distributor's Information**

| Manufacturer | Kit Name | Catalog Number | Supplier | Address | City | ST | Zip | Phone |
|---|---|---|---|---|---|---|---|---|
| CHEMetrics | Ammonia 1 DCR Photometer | I-3001 | CHEMetrics, Inc. | Route 28 | Calverton | VA | 20138 | (800) 356-3072 |
| HACH | Nitrogen, Ammonia: Salicylate Method without Distillation | 261480-00 for reagent set 44800-00 for DR 2010 | HACH Company | PO BOX 389 | Loveland | CO | 80539 | (800) 227-4224 |
| La Motte | Ammonia Nitrogen, High Range | 3642-SC for reagent set 1911 for Smart Colorimeter | La Motte Company | PO Box 329 | Chesterfield | MD | 21620 | (800) 344-3100 |
| La Motte | Ammonia Nitrogen, Low Range | 3659-SC for reagent set 1911 for Smart Colorimeter | La Motte Company | PO Box 329 | Chesterfield | MD | 21620 | (800) 344-3100 |
| IDEXX | Colilert | WP600 | IDEXX | 1 IDEXX Drive | Westbrook | MN | 04092 | (800) 248-2483 |
| Industrial Municipal Equipment, Inc. | Ime.Test KoolKount Assayer | IM 95077 | Industrial Municipal Equipment | PO Box 335 | Bohemia | NY | 11716 | (800) 858-4857 |

**Table 3-2 Manufacturer's and Distributor's Information** (Continued)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Dtech (EM Science | Dtech BTEX Test Kit | TK-1003-1(test kit) TK-1003S-1 (soil extraction kit) | DTECH Environmental Detection Systems | 480 Democrat Road | Gibbstown | NJ | 08027 | (800) 222-0342 |
| Forestry Supply | Oil in Water Test Kit | 77649 | Forestry Supply | 205 W Rankin Street | Jackson | MS | 39201 | (800) 547-5368 |
| FCI Environmental Inc. | PetroSense | PHA-100Plus | FCI Environmenta Inc. | 1181 Grier Drive, Building B | Las Vegas | NV | 89119 | (800) 510-3627 |
| Wilks Enterprise, Inc. | Infracal Oil in Water Analyzer | Infracal Cuvette Holder, Model CVH | Wilks Enterprise, Inc. | 140 Water Street | Norwalk | CT | 06856 | (203) 855-9136 |
| Turner Designs | 10-AU Fluorometer | | Tuner Designs | 845 W. Maude Avenue | Sunnyvale | CA | 94086 | (408) 749-0994 |
| Dexsil | PetroFlag | | Dexsil | 1 Hamden Park Drive | Hamden | CT | | (800) 4-DEXSIL |
| HACH | Chloride, silver nitrate titration | 22880-00 for reagent set 16900-01 for digital titrator | HACH Company | PO BOX 389 | Loveland | CO | 80539 | (800) 227-4224 |
| YSI | YSI SCT | | | | | | | |

**Table 2. Manufacturer's and Distributor's Information** (Continued)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Horiba | Horiba Twin Cond | | Spectrum Technologies | 12010 South Aero Drive | Plainfield | IL | 60544 | (800) 248-8873 |
| Horiba | Horiba U-10 | | Spectrum Technologies | 12010 South Aero Drive | Plainfield | IL | 60544 | (800) 248-8873 |
| CHEMetrics | Copper 1 DCR Photometer Kit | I-3006 | CHEMetrics, Inc. | Route 28 | Calverton | VA | 20138 | (800) 356-3072 |
| La Motte | Copper (Diethyldithiocarbamate) | 3646-SC for reagent set 1911 for Smart Colorimeter | La Motte Company | PO Box 329 | Chesterfield | MD | 21620 | (800) 344-3100 |
| La Motte | Copper (Bicinchoninic Acid) | 3640-SC for reagent set 1911 for Smart Colorimeter | La Motte Company | PO Box 329 | Chesterfield | MD | 21620 | (800) 344-3100 |
| HACH | Copper, Bicinchonate Method using AccuVac Ampoules | 25040-25 | HACH Company | PO BOX 389 | Loveland | CO | 80539 | (800) 227-4224 |
| Palintest | SA-1000 Scanning Analyzer | PT 425 for Sensor Pack. PT 420 for Analyzer | Palintest USA | 21 Kenton Lands Road PO Box 18733 | Erlanger | KY | 41018 | (800) 835-9629 |

**Table 3-2 Manufacturer's and Distributor's Information** (Continued)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Environmental Technologies Group | Metalyzer 3000 | M-3000 | Environmental Technologies Group | 1400 Taylor Avenue | Baltimore | MD | 21284 | (800) 635-4598 |
| CHEMetrics | Detergents (Anionic Surfactants) | K-9400 | CHEMetrics, Inc. | Route 28 | Calverton | VA | 20138 | (800) 356-3072 |
| HACH | Surfactants, Anionic, Crystal Violet Method | 24468-00 for reagent set 44800-00 for DR 2010 | HACH Company | PO BOX 389 | Loveland | CO | 80539 | (800) 227-4224 |
| Cole-Parmer | Fluoride Tester | H-59001-10 for meter H-59001-12 for calibration kit | Cole-Parmer | 7425 North Oak Park Avenue | Niles | IL | 60714 | (800) 323-4340 |
| HACH | Fluoride SPADNS Reagent | 444-11 for reagent 44800-00 for DR 2010 | HACH Company | PO BOX 389 | Loveland | CO | 80539 | (800) 227-4224 |
| HACH | Fluoride SPADNS Reagent Using AccuVac Ampoules | 25060-25 for reagent 44800-00 for DR 2010 | HACH Company | PO BOX 389 | Loveland | CO | 80539 | (800) 227-4224 |
| CHEMetrics | Hardness, Total 20-200 ppm | K-4250 | CHEMetrics, Inc. | Route 28 | Calverton | VA | 20138 | (800) 356-3072 |

**Table 3-2 Manufacturer's and Distributor's Information** (Continued)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| HACH | Total Hardness Using Digital Titrator | 24480-00 for reagent 16900-01 for digital titrator | HACH Company | PO BOX 389 | Loveland | CO | 80539 | (800) 227-4224 |
| La Motte | Lead in Water Kit | 7439 | La Motte Company | PO Box 329 | Chesterfield | MD | 21620 | (800) 635-4598 |
| HACH | LeadTrak system | 41100-48 for kit 44800-00 for DR 2010 (optional) | HACH Company | PO BOX 389 | Loveland | CO | 80539 | (800) 227-4224 |
| Innovative Synthesis Corporation | The Lead Detective | | Innovative Synthesis Corporation | 2143 Commonwealth Avenue | Newton | MA | 02166 | (617) 965-5653 |
| HybriVet Systems | Lead Check Swabs | PB-2M48 | HybriVet Systems | | Natick | MA | 07160 | (800) 262-5323 |
| Carolina Environment Company | KnowLead | | Carolina Environment Company | PO Box 26661 | Charlotte | NC | 28221 | (800) 448-LEAD |
| EM Science | Lead | 16999-1for test strips 16950-1 for RQFlex Meter (optional) | EM Science | 480 S Democrat Road | Gibbstown | NJ | 08027 | (800) 222-0342 |

**Table 3-2 Manufacturer's Information** (Continued)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| La Motte | La Motte Nitrate | 3649-SC for reagent set 1911 for Smart Colorimeter | La Motte Company | PO Box 329 | Chesterfield | MD | 21620 | (800) 635-4598 |
| Horiba | Horiba CARDY Nitrate | | Spectrum Technologies | 12010 South Aero Drive | Plainfield | IL | 60544 | (800) 248-8873 |
| EM Science | Nitrate Quant Test Strips | 16995-1 for test strips 16950-1 for RQFlex Meter (optional) | EM Science | 480 S Democrat Road | Gibbstown | NJ | 08027 | (800) 222-0342 |
| HACH | Nitrate, LR | 14065-66 and 14119-66 for reagents 44800-00 for DR 2010 | HACH Company | PO BOX 389 | Loveland | CO | 80539 | (800) 227-4224 |
| HACH | Nitrate, MR | 25110-25 for reagents 44800-00 for DR 2010 (optional) | HACH Company | PO BOX 389 | Loveland | CO | 80539 | (800) 227-4224 |
| CHEMetrics | Nitrate (Nitrogen) | K-6902A | CHEMetrics, Inc. | Route 28 | Calverton | VA | 20138 | (800) 356-3072 |
| Dtech (EM Science | Dtech PAH Test Kit | TK-1006-1(test kit) TK-1006S-1 (soil extraction kit) | DTECH Environmental Detection Systems | 480 Democra Road | Gibbstown | NJ | 08027 | (800) 222-0342 |

**Table 3-2 Manufacturer's and Distributor's Information** (Continued)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Cole-Parmer | pH Wand | H-59000-10 | Cole-Parmer | 7425 North Oak Park Avenue | Niles | IL | 60714 | (800) 323-4340 |
| Horiba | Horiba Twin pH | | Spectrum Technologies | 12010 South Aero Drive | Plainfield | IL | 60544 | (800) 248-8873 |
| Sentron | Sentron pH Probe | | Sentron Integrated Sensor Technology | 33320 1st Way S | Federal Way | WA | 98003 | (206) 838-7933 |
| EM Science | ReflectoQuant pH | 16996-1 for test strips 16950-1 for RQFlex Meter (optional) | EM Science | 480 S Democrat Road | Gibbstown | NJ | 08027 | (800) 222-0342 |
| La Motte | pH | 3700-SC for reagent set 1911 for Smart Colorimeter | La Motte Company | PO Box 329 | Chesterfield | MD | 21620 | (800) 635-4598 |
| Fisher Scientific | Alkacid Test Strips | A980 | Fisher Scientific | PO Box 4829 | Norcross | GA | 30091 | (800) 766-7000 |
| HACH | Potassium Tetraphenylborate | 14321-98, 14322-98, & 14323-96 for reagents 44800-00 for DR 2010 (optional) | HACH Company | PO BOX 389 | Loveland | CO | 80539 | (800) 227-4224 |

**Table 3-2 Manufacturer's and Distributor's Information** (Continued)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Horiba | Horiba CARDY | | Spectrum Technologies | 12010 South Aero Drive | Plainfield | IL | 60544 | (800) 248-8873 |
| La Motte | Potassium | 3639-SC for reagent set 1911 for Smart Colorimeter | La Motte Company | PO Box 329 | Chesterfield | MD | 21620 | (800) 635-4598 |
| La Motte and HACH | La Motte Potassium Reagent Set, HACH DR 2010 Spectrophotometer | see above | see above | see above | see above | see above | see above | |
| La Motte | Zinc | 3667-SC for reagent set 1911 for Smart Colorimeter | La Motte Company | PO Box 329 | Chesterfield | MD | 21620 | (800) 635-4598 |
| HACH | Zinc, Zincon Method | 22792-00 for reagent 16900-01 for digital titrator | HACH Company | PO BOX 389 | Loveland | CO | 80539 | (800) 227-4224 |
| EM Science | ReflectoQuant Zinc | 10038-1 for test strips 16950-1 for RQFlex Meter (optional) | EM Science | 480 S Democrat Road | Gibbstown | NJ | 08027 | (800) 222-0342 |

Contacts for two additional field screening kits that were evaluated are:

GDS & Associates, Inc. (Aqua Vats)
3107 N. Deer Run Rd., Suite 12
Carson City, NV 89701
(775) 884-4353
www.gdsassociate.com

Azur Environmental (DeltaTox PS1)
2232 Rutherford Road
Carlsbad, CA 92008-8883
www.azurenv.com
(760) 438-8282

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# Appendix A: Screening-Kit Performance Evaluations

Ammonia
Bacteria
Conductivity
Copper
Detergents
Fluoride
Hardness
Hydrocarbons
Lead
Nitrates
pH
Potassium
Zinc

# Ammonia Summary

# 4 Ammonia

Four methods for the measurement of ammonia were evaluated: CHEMetrics Ammonia DCR, HACH Salicylate Method, La Motte High Range Ammonia and La Motte Low Range Ammonia. The CHEMetrics and La Motte High Range methods both take advantage of the Nessler Reaction to determine the concentration of ammonia. The HACH Salicylate and La Motte Low Range Ammonia methods both use a modified phenate method to determine the ammonia concentration. General information about all methods is presented below.

*Table 3: Methods, Costs and Requirements for Ammonia Kits*

| Kit Name | Method | Capital cost | Expendable Cost (per sample) | Time Required (min) | Sample Vol. (ml) | Expertise Required |
|---|---|---|---|---|---|---|
| CHEMetrics Ammonia 1 DCR Photometer | Colorimetric determination of Ammonia using Nessler's Reaction | $435 for kit | $0.63 | 5 | 25 | little |
| HACH Nitrogen, Ammonia: Salicylate Method without Distillation | Colorimetric determination of ammonia using salicylate. | $1495 for DR 2000 | $2.88 | 20 | 25 | some |
| La Motte Ammonia Nitrogen, High Range | Colorimetric determination of Ammonia using Nessler's Reaction | $895 for Smart Colorimeter | $0.33 | 10 | 10 | some |
| La Motte Ammonia Nitrogen, Low Range | Colorimetric determination of ammonia using salicylate. | $895 for Smart Colorimeter | $0.76 | 20 | 10 | some |

*Table 4: Precision, Shelf Life, Maintenance, Safety and Upper Limits for Ammonia Kits*

| Kit Name | Precision | Shelf Life | Regular Maintenance | Safety Hazards | Upper Limit of Useful Range (mg/L) |
|---|---|---|---|---|---|
| CHEMetrics Ammonia 1 DCR Photometer | 0.15000 | 6 months refrigerated | Calibrate and re-zero about every 6 months or battery change. | Sharps. Waste ampoule contain a mercury compound. | <2.5 |
| HACH Nitrogen, Ammonia: Salicylate Method without Distillation | 0.17000 | not indicated | Recharge batteries. | | <0.7 |
| La Motte Ammonia Nitrogen, High Range | not tested | not indicated | Recharge batteries. | Wastes contain a mercury compound. Recharge batteries. | 3* |
| La Motte Ammonia Nitrogen, Low | not tested | not indicated | Recharge batteries. | | <1.5 |

* reported by manufacturer

## 4.1

## 4.2 Spiked Samples

The following figures depict the relative performance of all methods with spiked samples. The CHEMetrics kit shows evidence of some interference. In reverse osmosis water, the CHEMetrics kit consistently under-estimates the spike concentration. However, in the runoff samples the kit consistently over-estimates the same spike concentration. The regression summaries are presented in tables 3 and 4.

*Table 5 Reverse Osmosis Measurements*

| Kit Name | Adjusted $R^2$ | Standard Error | Intercept | p-Value | Slope | p-Value | Detection Limit ($\alpha$=0.05) (mg/L) | Limit of Quantification ($\alpha$=0.05) (mg/L) |
|---|---|---|---|---|---|---|---|---|
| CHEMetrics Ammonia 1 DCR Photometer | 0.9973 | 0.0267 | -0.0191 | 0.3250 | 0.8455 | 3.9662E-05 | 0.0259 | 0.0709 |
| HACH Nitrogen, Ammonia: Salicylate Method without Distillation | 0.9730 | 0.0520 | 0.0112 | 0.7909 | 1.1456 | 9.0308E-03 | 0.0988 | 0.1863 |
| La Motte Ammonia Nitrogen, High Range | 0.9789 | 0.1742 | 0.0863 | 0.4251 | 1.2174 | 1.0737E-04 | 0.3796 | 0.6728 |
| La Motte Ammonia Nitrogen, Low Range | 0.9519 | 0.0616 | 0.0699 | 0.2645 | 1.0443 | 1.6166E-02 | 0.1736 | 0.2773 |

*Table 6 Runoff Measurements*

| Kit Name | Adjusted $R^2$ | Standard Error | Intercept | p-Value | Slope | p-Value | Detection Limit ($\alpha$=0.05) (mg/L) | Limit of Quantification ($\alpha$=0.05) (mg/L) |
|---|---|---|---|---|---|---|---|---|
| CHEMetrics Ammonia 1 DCR Photometer | 0.9890 | 0.0807 | 0.1407 | 0.0646 | 1.2695 | 3.1947E-04 | 0.2766 | 0.4125 |
| HACH Nitrogen, Ammonia: Salicylate Method without Distillation | 0.9941 | 0.0222 | 0.0569 | 0.0744 | 1.0964 | 1.9551E-03 | 0.0943 | 0.1318 |
| La Motte Ammonia Nitrogen, High Range | 0.9847 | 0.1472 | 0.0918 | 0.3267 | 1.2108 | 5.6415E-05 | 0.3396 | 0.5875 |
| La Motte Ammonia | 0.8897 | 0.0868 | -0.0229 | 0.7618 | 0.9517 | 3.7468E-02 | 0.1233 | 0.2695 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Nitrogen, Low Range | | | | | | | | |

## Ammonia Measurements in Reverse Osmosis Water

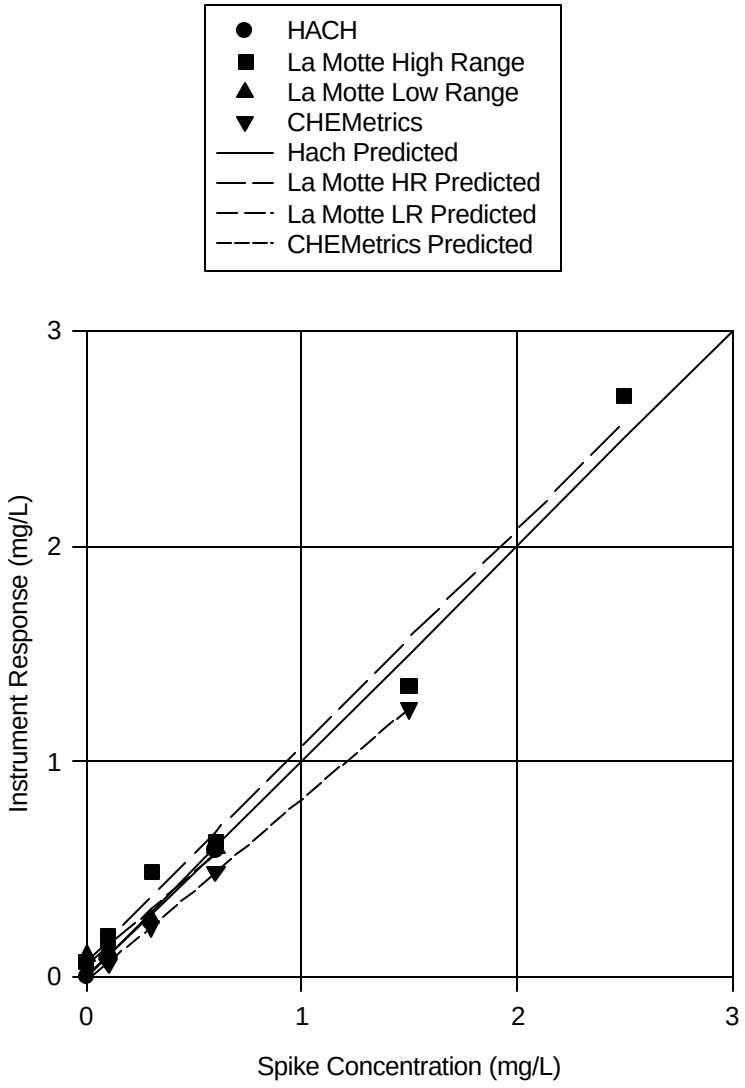



*Figure 1*

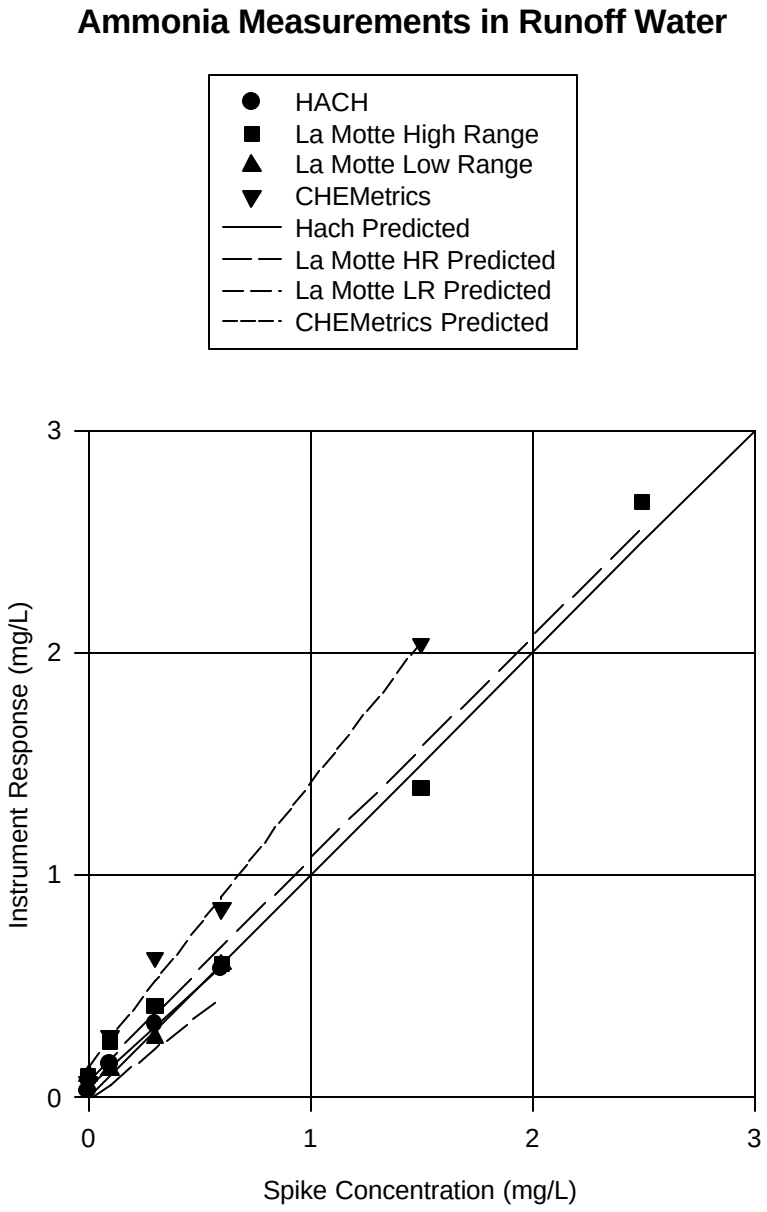



*Figure 2*

## 4.3 Parallel Analyses

Only one data point exists above the detection limits of both kits while several samples were over range for both methods. Therefore, statistical analysis is not suitable. The random nature of the data values below the limit of quantification is normal.

*Table 7*

| CHEMetrics | | | HACH | | |
|---|---|---|---|---|---|
| Sample ID | Response | Order | Sample ID | Response | Order |
| 2464 | 0.09 | 7 | 2464 | 0.00 | 7 |
| 2473 | OVER RANGE | 14 | 2473 | OVER RANGE | 14 |
| 2491 | 0.10 | 33 | 2491 | 0.10 | 33 |
| 2501 | 0.25 | 1 | 2501 | 0.00 | 1 |
| 2511 | 0.17 | 18 | 2511 | 0.00 | 18 |
| 2521 | 0.02 | 12 | 2521 | 0.00 | 12 |
| 2530 | 0.01 | 25 | 2530 | 0.00 | 25 |
| 2539 | 0.05 | 5 | 2539 | 0.00 | 5 |
| 2548 | OVER RANGE | 6 | 2548 | OVER RANGE | 6 |
| 2557 | 0.11 | 11 | 2557 | 0.00 | 11 |
| 2566 | OVER RANGE | 15 | 2566 | OVER RANGE | 15 |
| 2573 | 0.09 | 3 | 2573 | 0.03 | 3 |
| 2585 | 0.03 | 34 | 2585 | 0.14 | 34 |
| 2595 | 0.54 | 2 | 2595 | 0.00 | 2 |
| 2613 | 0.05 | 36 | 2613 | 0.02 | 36 |
| 2620 | 0.10 | 9 | 2620 | 0.00 | 9 |
| 2629 | 1.80 | 35 | 2629 | OVER RANGE | 35 |
| 2638 | 0.02 | 8 | 2638 | 0.11 | 8 |
| 2647 | 0.01 | 4 | 2647 | 0.00 | 4 |
| 2656 | 0.07 | 16 | 2656 | 0.00 | 17 |
| 2666 | 0.26 | 17 | 2666 | 0.31 | 16 |
| 2674 | 0.07 | 22 | 2674 | 0.19 | 22 |
| 2685 | 0.29 | 21 | 2685 | 0.00 | 20 |
| 2695 | 0.13 | 32 | 2695 | 0.00 | 32 |
| 2722 | 0.22 | 19 | 2722 | 0.02 | 19 |
| 2731 | OVER RANGE | 37 | 2731 | 0.39 | 37 |
| 2740 | 0.03 | 10 | 2740 | 0.03 | 10 |
| 2749 | 0.09 | 13 | 2749 | 0.05 | 13 |
| 2774 | 0.67 | 23 | 2774 | 0.00 | 23 |
| 2783 | 0.08 | 31 | 2783 | 0.03 | 31 |
| 2801 | 0.12 | 20 | 2801 | 0.00 | 21 |
| 2810 | 0.52 | 24 | 2810 | 0.01 | 24 |

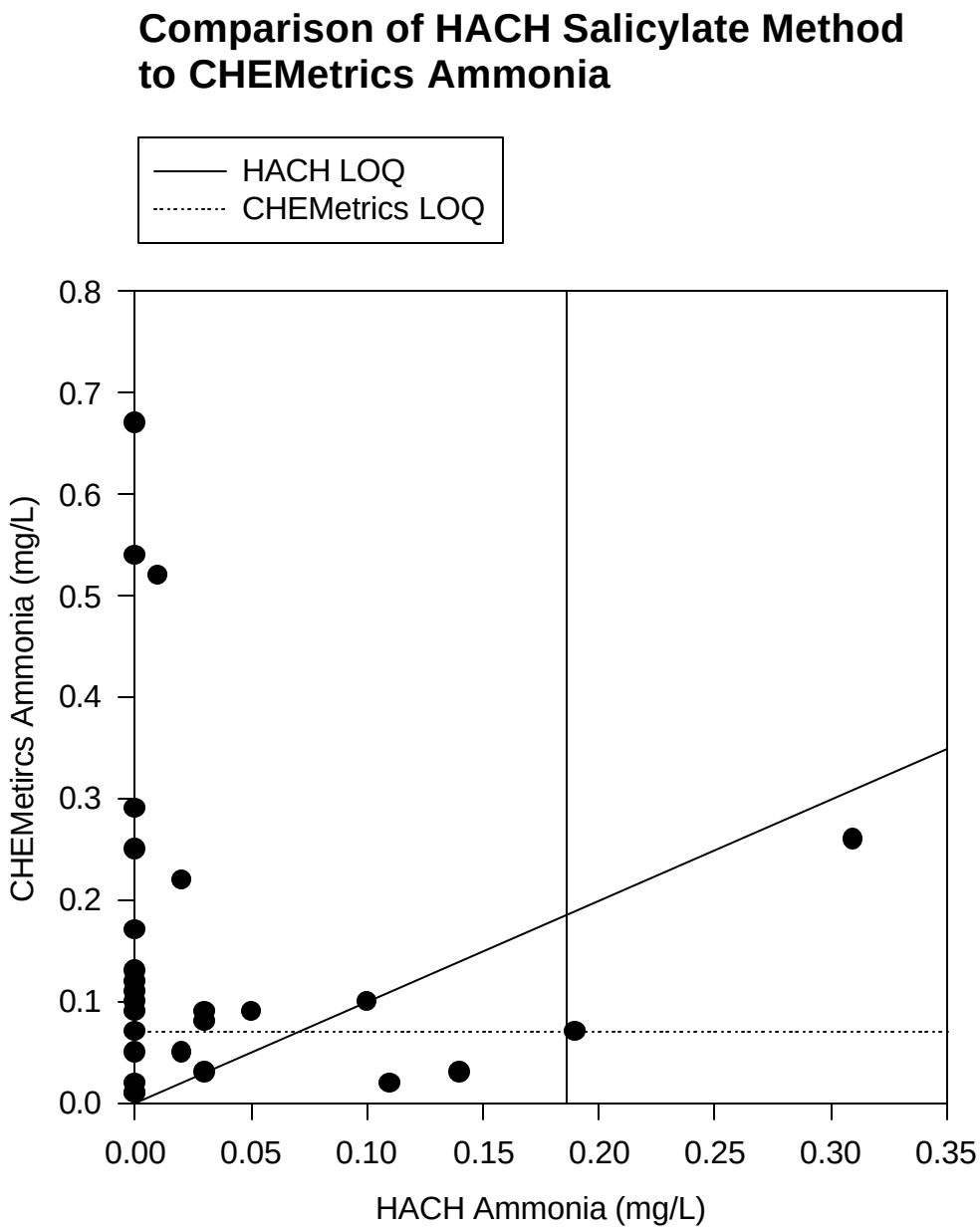



*Figure 3*

## 4.4 Conclusion

Based on these regressions, the HACH kit clearly has the lowest detection limit for both sample types. The detection limits and error plots for the La Motte methods both show large errors associated with those methods. Therefore, the HACH method has been selected for further more detailed study. In addition to its solid analytical performance, the

HACH method is preferable to the other Nessler methods since it uses no mercury. The CHEMetrics method was chosen for further evaluation due to its simplicity and quickness.

## 4.5 CHEMetrics Ammonia DCR Photometer

### *4.5.1 Method Summary*

The CHEMetrics Ammonia method uses a dedicated bichromatic spectrophotometer to determine ammonia concentrations in the sample. The user collects approximately 25 mL of sample in a small plastic cup specially designed for use with reagent ampoules. Careful measurement is not necessary, the test only requires about 1 mL that is automatically drawn up into the ampoule. The excess sample is to ensure the ampoule fills. The ampoule contains a buffer and Nessler's Reagent ($K_2HgI_4$). The buffer raises the pH of the sample in the ampoule to favor the reaction of Nessler's Reagent with ammonia. The reaction product is yellow. Therefore, the spectrophotometer can relate the absorbance of the sample cell (reacted ampoule) to the concentration of ammonia originally in the ampoule.

The procedure is quite simple. An ampoule containing all reagents is immersed in the sample cup and broken. The ampoule automatically draws in the required sample. Mix the contents by inverting the ampoule several times. An air bubble will be left in the ampoule after filling. This is normal; the air bubble enhances mixing of the reagents with the sample. There is a 2 minute reaction time (extend to 4 minutes for low concentrations, less than 0.1 mg/L). The ampoule is then placed in the spectrophotometer. The user must turn on the unit after placing the ampoule in the unit; if the unit is turned on before an ampoule is placed in the spectrophotometer, an error will result.

Nesslerization of samples to determine ammonia concentration is listed in Standard Methods prior to the 1995 edition. The method is most accurate when the sample is distilled before analysis, but direct Nesslerization (no distillation) will work for a wide range of ammonia concentrations. Standard Methods reports the precision associated with direct Nesslerization as varying from 38.1% (at 0.2 mg/L) to 5.3 % (at 1.5 mg/L), therefore, the analytical precision of the method improves as ammonia concentrations increases. The recommended range for Nesslerization is from 0.020 mg/L to 5 mg/L. However, direct Nesslerization is subject to a variety of interferences and should be periodically checked by other methods. CHEMetrics does not recommend using this method for ammonia concentrations in excess of 2.00 mg/L.

Samples absorbing color in the 400-425 nm region must be background corrected. The instructions provided with the kit describe a procedure for zeroing the DCR photometer, but a simple reagent blank will suffice. The DCR photometers are a unique design. The bichromatic chopped signal is supposed to alleviate the need to zero samples as long as the well windows remain intact.

Organic compounds such as ketones, alcohol, and aldehydes will unpredictably interfere with the final test results. However, glycine, hydrazine, and similar molecules with amino functional groups will always increase the reported ammonia concentration relative to the true value. Aromatic and aliphatic amines, iron, sulfide, calcium and magnesium will produce turbidity when exposed to Nessler's reagent and interfere with the test results. The stabilizing solution included with the kit will mask calcium and magnesium interference up to a total magnesium and calcium concentration of 1000 mg/L.

### *4.5.2 Observations*

The first attempt to evaluate the CHEMetrics system was unsuccessful. The expiration date on the ampoules had passed by about 6 weeks. After receiving a fresh supply of ampoules, the tests were successfully re-evaluated. There were no other problems identified with the test. The shelf life of the reagent ampoules is 6 months with refrigeration, 3 months without, which is apparently critical.

*Table 8*

| Sample ID | Spike Conc. (mg/L) as NH3 | Order | RO Response (mg/L) as N | RO Response (mg/L) as NH3 | RO Recovery (%) | Order | Runoff Response (mg/L) as N | Runoff Response (mg/L) as NH3 |
|---|---|---|---|---|---|---|---|---|
| NH3 X O | 0.000 | 1 | 0 | 0.00 | NA | 7 | 0.06 | 0.07 |
| NH3 X 1 | 0.100 | 4 | 0.06 | 0.07 | 73 | 11 | 0.23 | 0.28 |
| NH3 X 2 | 0.300 | 6 | 0.16 | 0.19 | 65 | 8 | 0.52 | 0.63 |
| NH3 X 3 | 0.600 | 3 | 0.41 | 0.50 | 83 | 10 | 0.7 | 0.85 |
| NH3 X 4 | 1.498 | 5 | 1.03 | 1.25 | 84 | 9 | 1.68 | 2.04 |
| NH3 X 5 | 2.494 | 2 | over-range | over-range | NA | not tested | over-range | over-range |

*Table 9*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.998970243 |
| R Square | 0.997941546 |
| Adjusted R Square | 0.997255395 |
| Standard Error | 0.026746384 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 1.040436138 | 1.040436 | 1454.404746 | 3.96615E-05 |
| Residual | 3 | 0.002146107 | 0.000715 | | |
| Total | 4 | 1.042582245 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | -0.019140362 | 0.01629978 | -1.174271 | 0.32501767 | -0.071013584 | 0.03273286 | -0.071013584 | 0.03273286 |
| Spike Conc. (mg/L) as NH3 | 0.845481718 | 0.02216979 | 38.13666 | 3.96615E-05 | 0.774927486 | 0.916035951 | 0.774927486 | 0.916035951 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L) as NH3* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | -0.019140362 | 0.019140362 | 0.715624 |
| 2 | 0.065399356 | 0.007457787 | 0.278833 |
| 3 | 0.234428083 | -0.040142369 | -1.500852 |
| 4 | 0.487844478 | 0.010012665 | 0.374356 |
| 5 | 1.247182731 | 0.003531555 | 0.132039 |

*Table 10*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.995860864 |
| R Square | 0.99173886 |
| Adjusted R Square | 0.988985147 |
| Standard Error | 0.080703663 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 2.345660348 | 2.345660348 | 360.1460264 | 0.000319469 |
| Residual | 3 | 0.019539244 | 0.006513081 | | |
| Total | 4 | 2.365199592 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.140656744 | 0.049182422 | 2.85989871 | 0.064582329 | -0.015863819 | 0.297177306 | -0.015863819 | 0.297177306 |
| Spike Conc. (mg/L) as NH3 | 1.269489375 | 0.066894399 | 18.9775137 | 0.000319469 | 1.056601342 | 1.482377408 | 1.056601342 | 1.482377408 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L) as NH3* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.140656744 | -0.067799601 | -0.840105617 |
| 2 | 0.267592988 | 0.011692727 | 0.144884706 |
| 3 | 0.521389337 | 0.110039235 | 1.363497394 |
| 4 | 0.901893627 | -0.051893627 | -0.643014512 |
| 5 | 2.042038734 | -0.002038734 | -0.02526197 |

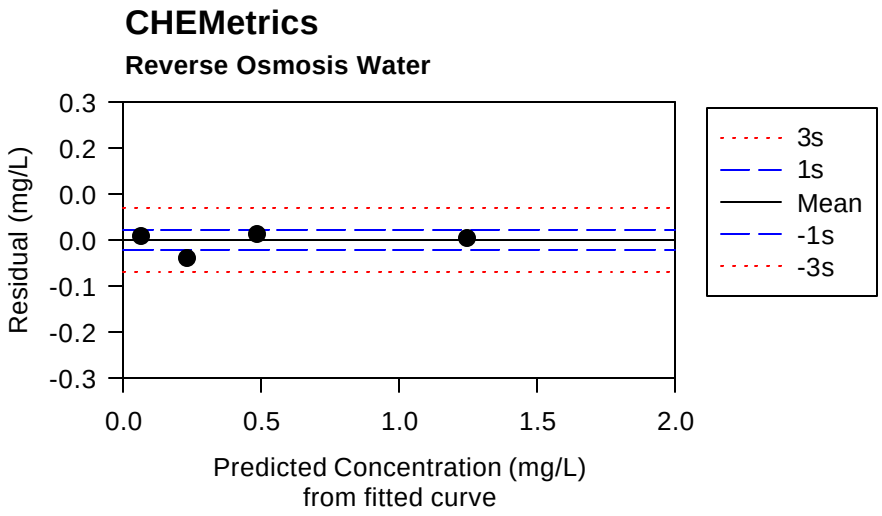



*Figure 4*

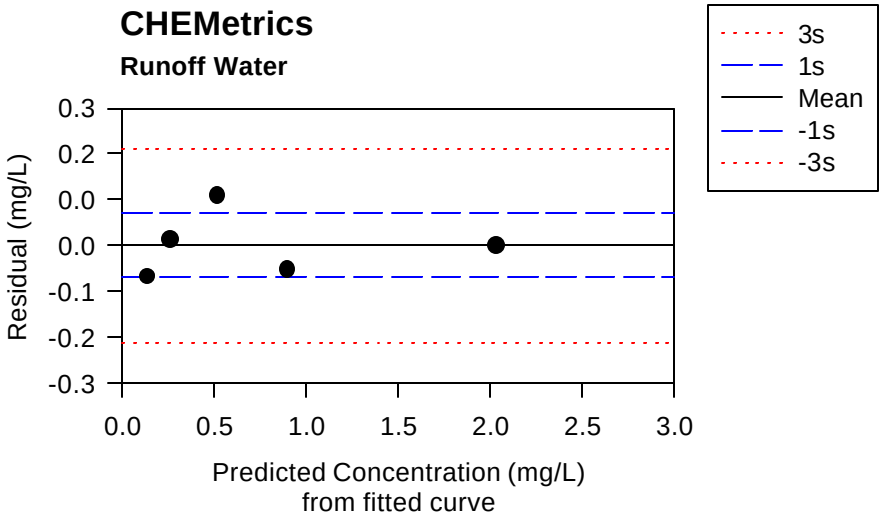



*Figure 5*

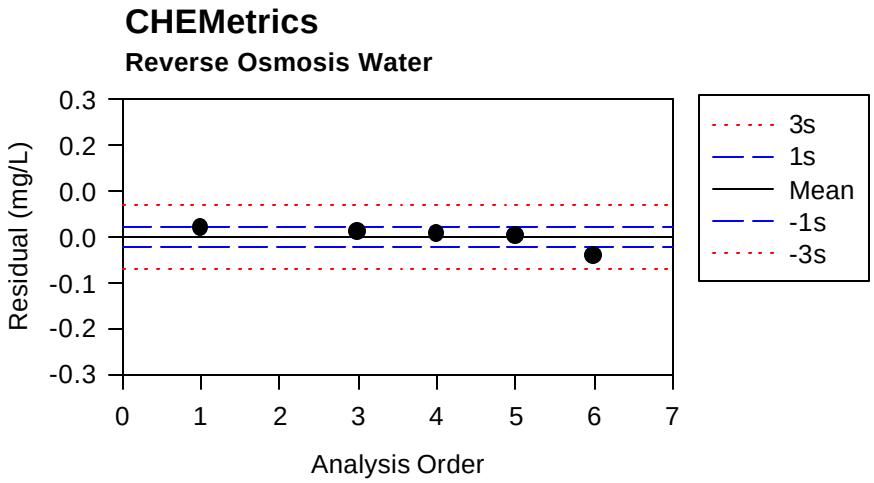



*Figure 6*

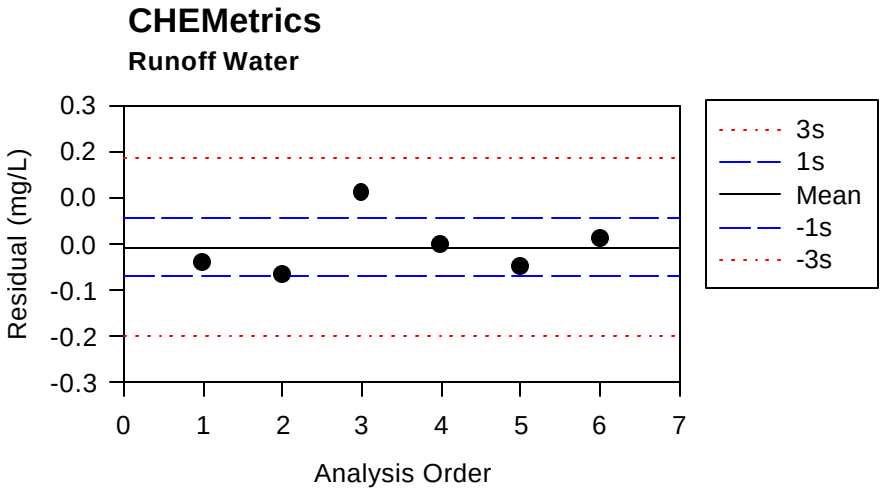



*Figure 7*

## 4.6 HACH Ammonia Salicylate

### *4.6.1 Method Summary*

The HACH Ammonia Salicylate method is adapted from the Phenate Method for determining ammonia concentrations described in Standard Methods (4500-$NH_3$ D) (1992). Ammonia in the sample is reacted with hypochlorite donated from the cyanurate reagent to form monochloramine. The monochloramine reacts with salicylate to form 5-aminosalicylate. The 5-aminosalicylate, in turn, oxidizes to form indosalicylate, a yellow compound. The oxidizing agent is nitroferricyanide (nitroprusside), a blue compound. The resulting color in a positive test is green.

The user collects 25 mL of sample and 25 mL of de-ionized water. One Ammonia Salicylate Powder Pillow is added to both. The user must shake the sample and blank until all crystals dissolve. After the crystals have dissolved, there is a 3 minute reaction time. The user then adds 1 Ammonia Cyanurate Powder pillow to both the sample and blank. After the crystals from the cyanurate dissolve, the sample and blank are allowed to stand for 15 minutes. After the 15 minute reaction time, the spectrophotometer is zeroed using the reagent blank (de-ionized water). The ammonia concentration of the sample may now be determined from the spectrophotometer.

HACH has used salicylate as the active reagent to eliminate the use of mercury (for Nessler's reaction) and phenol (the phenate method). The time required to complete the test is increased, but the reagent choice makes the waste products easier to dispose and the test safer to use. The more common interferences are listed below. Interferent concentrations exceeding those indicated will alter the test results.

*Table 11*

| | | |
|---|---|---|
| calcium | 1000 | mg/L as $CaCO_3$ |
| magnesium | 6000 | mg/L as $CaCO_3$ |
| nitrite | 12 | mg/L as N |
| nitrate | 100 | mg/L as N |
| orthophosphate | 100 | mg/L as P |
| sulfate | 300 | mg/L |

Other interferents include sulfide, glycine, hydrazine, color and turbidity. These interferences will intensify the color in the sample resulting in erroneously high ammonia concentrations. In addition, the pH of the sample should be approximately neutral before beginning the test.

### *4.6.2 Observations*

There are two principal problems with this method. First, the analysis time is long, requiring about 20 minutes (however, several samples can be evaluated at one time in duplicate glassware). Second, the upper limit of the test range is low, 0.5 mg/L as N (2.2 mg/L as $NO_3$). In actual water samples collected from manholes, several responses were "over range." Therefore, a second analysis would be needed, with a dilution step, if an initial analysis is over range. However, the method has provided a way to determine ammonia concentrations that does not require mercury or phenol. Mercury can be very difficult and expensive to dispose. Phenol is also a hazardous compound.

*Table 12*

| Sample ID | Spike Conc. (mg/L) as NH3 | Order | RO Response (mg/L) as N | RO Response (mg/L) as NH3 | RO Recovery (%) | Order | Runoff Response (mg/L) as N | Runoff Response (mg/L) as NH3 |
|---|---|---|---|---|---|---|---|---|
| NH3 X O | 0.000 | 5 | 0.00 | 0.00 | NA | 3 | 0.03 | 0.04 |
| NH3 X 1 | 0.100 | 6 | 0.14 | 0.17 | 170 | 7 | 0.15 | 0.18 |
| NH3 X 2 | 0.300 | 1 | 0.25 | 0.30 | 101 | 8 | 0.33 | 0.40 |
| NH3 X 3 | 0.600 | 10 | 0.59 | 0.72 | 119 | 4 | 0.58 | 0.70 |

*Table 13*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.9909692 |
| R Square | 0.982019955 |
| Adjusted R Square | 0.973029933 |
| Standard Error | 0.050198684 |
| Observations | 4 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 0.275260694 | 0.275260694 | 109.2344278 | 0.0090308 |
| Residual | 2 | 0.005039816 | 0.002519908 | | |
| Total | 3 | 0.28030051 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.011234214 | 0.037150786 | 0.302395059 | 0.790901124 | -0.148612829 | 0.171081258 | -0.148612829 | 0.171081258 |
| Spike Conc. (mg/L) as NH3 | 1.145589835 | 0.109609799 | 10.45152753 | 0.0090308 | 0.673976605 | 1.617203065 | 0.673976605 | 1.617203065 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L) as NH3* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.011234214 | -0.011234214 | -0.223794995 |
| 2 | 0.125781743 | 0.044218257 | 0.880864866 |
| 3 | 0.354808093 | -0.051236664 | -1.020677435 |
| 4 | 0.69817595 | 0.018252621 | 0.363607564 |

*Table 14*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.998044853 |
| R Square | 0.996093528 |
| Adjusted R Square | 0.994140292 |
| Standard Error | 0.022235749 |
| Observations | 4 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 0.252144179 | 0.252144179 | 509.9709173 | 0.001955147 |
| Residual | 2 | 0.000988857 | 0.000494429 | | |
| Total | 3 | 0.253133036 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.056910993 | 0.01645612 | 3.458348163 | 0.074400038 | -0.013894027 | 0.127716012 | -0.013894027 | 0.127716012 |
| Spike Conc. (mg/L) as NH3 | 1.09643155 | 0.048552189 | 22.58253567 | 0.001955147 | 0.887528194 | 1.305334905 | 0.887528194 | 1.305334905 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L) as NH3* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.056910993 | -0.020482421 | -0.921148232 |
| 2 | 0.166543184 | 0.015599673 | 0.701558229 |
| 3 | 0.385741808 | 0.014972478 | 0.67335161 |
| 4 | 0.714375444 | -0.010089729 | -0.453761606 |

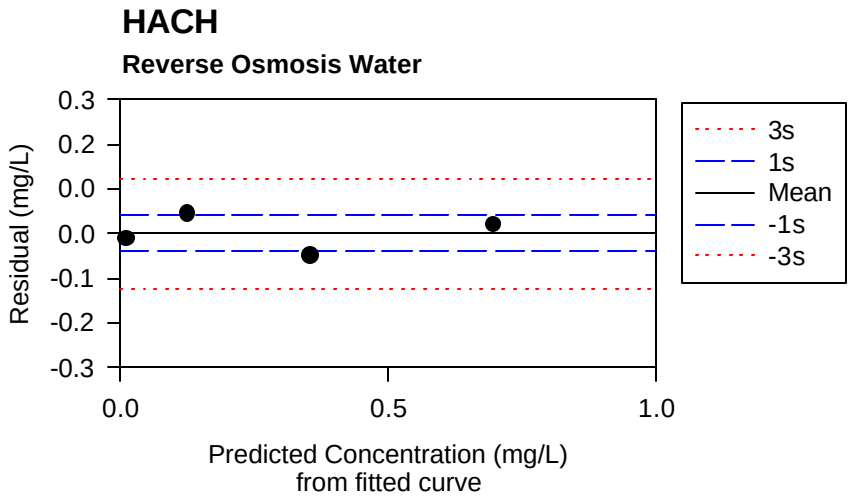

HACH
Reverse Osmosis Water
Residual (mg/L)
0.3
0.2
0.0
0.0
-0.1
-0.2
-0.3
0.0
0.5
1.0
Predicted Concentration (mg/L)
from fitted curve
3s
1s
Mean
-1s
-3s

*Figure 8*

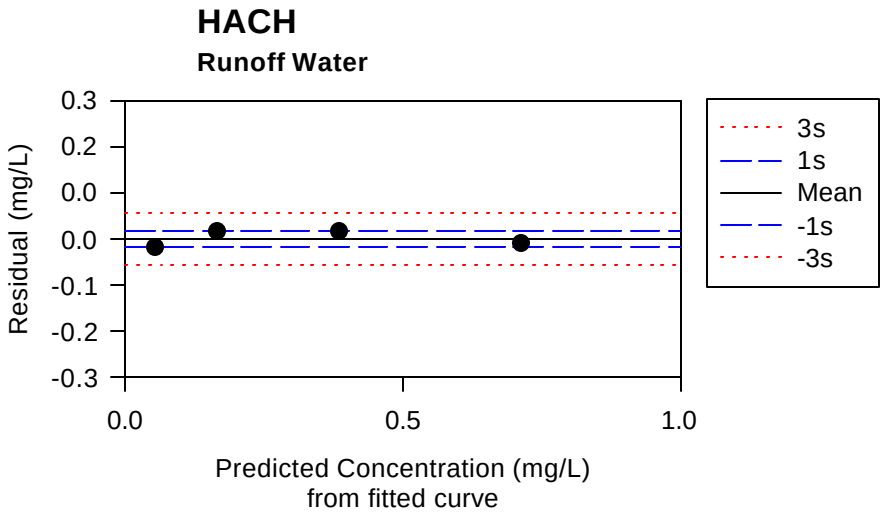

HACH
Runoff Water
0.3
0.2
0.0
0.0
-0.1
-0.2
-0.3
Residual (mg/L)
0.0
0.5
1.0
Predicted Concentration (mg/L)
from fitted curve
3s
1s
Mean
-1s
-3s

*Figure 9*

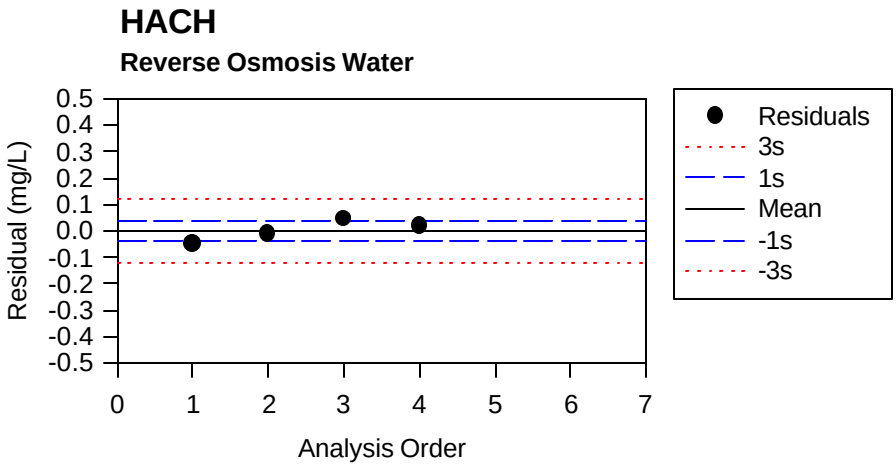
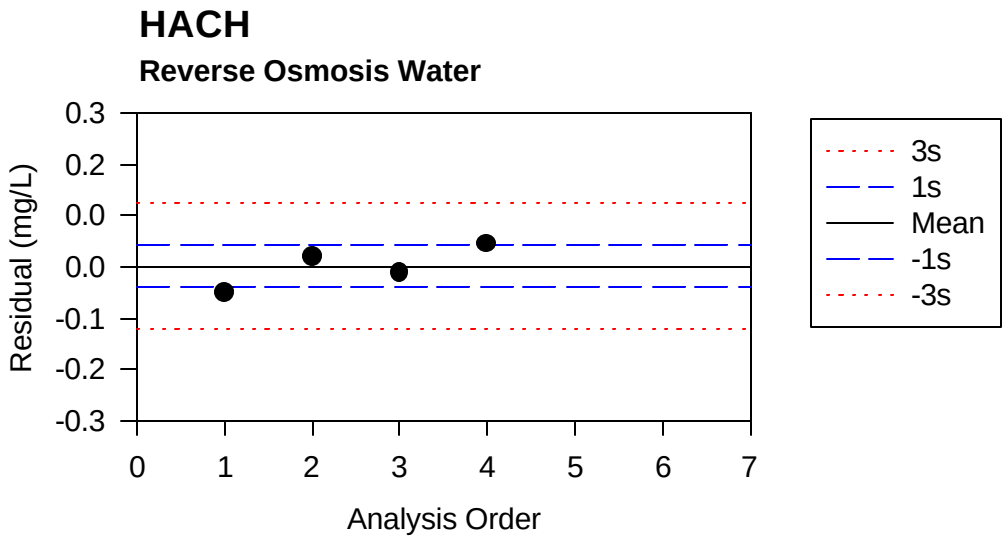



*Figure 10*




## 4.7 La Motte High Range Ammonia

### *4.7.1 Method*

The La Motte High Range Ammonia method uses a multi-parameter spectrophotometer, the Smart Colorimeter, to determine ammonia concentrations in the sample. The user collects 10 mL of sample in Smart Colorimeter cuvette. The user first zeroes the colorimeter using the sample before any reagents are added.

Eight drops of Ammonia Reagent #1 is then added and mixed thoroughly. This is a buffer to raise the pH of the sample high enough for the Nessler reaction. Then, 1.0 mL of Ammonia Reagent #2 is added to the sample. After 5 minutes, the absorbance of the sample is measured using the spectrophotometer. The manufacturer recommends using a reagent blank. A reagent blank is a volume of de-ionized water that has been treated in exactly the same manner as the sample. The response for the reagent blank should be subtracted from all sample measurements.

Nesslerization of samples to determine ammonia concentration was listed in Standard Methods prior to the 1995 edition. The method is most accurate when the sample is distilled before analysis, but direct Nesslerization (no distillation) will work on a wide range of ammonia concentrations. Standard Methods reports the precision associated with direct Nesslerization as varying from 38.1% (at 0.2 mg/L) to 5.3 % (at 1.5 mg/L), therefore, the analytical precision of the method increases as ammonia concentrations increases. The recommended range for Nesslerization is from 0.020 mg/L to 5 mg/L. However, direct Nesslerization is subject to a variety of interferences and should be periodically checked by other methods. La Motte does not recommend using this method for ammonia concentrations in excess of 2.00 mg/L.

Any Nessler ammonia test is subject to a variety of interferences. Samples absorbing color in the 400-425 nm region must be background corrected. Organic compounds such as ketones, alcohol, and aldehydes will unpredictably interfere with the final test results. However, glycine, hydrazine, and similar molecules with amino functional groups will always increase the reported ammonia concentration relative to the true value. Aromatic and aliphatic amines , iron, sulfide, calcium and magnesium will produce turbidity when exposed to Nessler's reagent and interfere with the test results. The stabilizing solution included with this kit will mask calcium and magnesium interference up to a total magnesium and calcium concentration of 1000 mg/L.

### *4.7.2 Observations*

The La Motte High Range Method utilizes the same chemical principles as the CHEMetrics ammonia method. However, the La Motte method does not utilize the glass ampoules. The reagents are stored in dropper bottles. The buffer reagent is in a bottle commonly used for eye drops. This is a good way to approximately measure small volumes without using standard glassware such as a pipette. The bottle containing Nessler's reagent is capped with a medicine dropper (like over the counter nose drops). The dropper has a calibration mark similar to a volumetric pipette for determining the required volume. Care should be taken using the medicine dropper. Users may be tempted to simply fill the dropper without using the calibration line on the dropper. This will result in a varying amount of reagent delivered to the sample. In particular, the dropper does not always fill to the calibration line.

*Table 15*

| Sample ID | spike conc. (mg/L) | Order | RO Response (mg/L) as N | RO Response (mg/L) as NH3 | RO Recovery (%) | Order | Runoff Response (mg/L) as N | Runoff Response (mg/L) as NH3 |
|---|---|---|---|---|---|---|---|---|
| NH3 X O | 0.000 | 1 | 0.07 | 0.09 | NA | 7 | 0.10 | 0.12 |
| NH3 X 1 | 0.100 | 3 | 0.19 | 0.23 | 231 | 12 | 0.25 | 0.30 |
| NH3 X 2 | 0.300 | 4 | 0.49 | 0.60 | 198 | 11 | 0.41 | 0.50 |
| NH3 X 3 | 0.600 | 6 | 0.63 | 0.77 | 128 | 8 | 0.60 | 0.73 |
| NH3 X 4 | 1.498 | 5 | 1.35 | 1.64 | 109 | 10 | 1.39 | 1.69 |
| NH3 X 5 | 2.494 | 2 | 2.70 | 3.28 | 131 | 9 | 2.68 | 3.25 |

*Table 16*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.991527545 |
| R Square | 0.983126873 |
| Adjusted R Square | 0.978908591 |
| Standard Error | 0.174155065 |
| Observations | 6 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 7.068808369 | 7.068808369 | 233.063352 | 0.00010737 |
| Residual | 4 | 0.121319947 | 0.030329987 | | |
| Total | 5 | 7.190128316 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.086273601 | 0.097236622 | 0.887254197 | 0.425070082 | -0.183699101 | 0.356246303 | -0.183699101 | 0.356246303 |
| spike conc. (mg/L) | 1.217362804 | 0.079741249 | 15.26641255 | 0.00010737 | 0.995965145 | 1.438760463 | 0.995965145 | 1.438760463 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L) as NH3* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.086273601 | -0.001273601 | -0.007313028 |
| 2 | 0.207997709 | 0.022716577 | 0.130438795 |
| 3 | 0.451372912 | 0.143627088 | 0.82470807 |
| 4 | 0.816253296 | -0.051253296 | -0.294296899 |
| 5 | 1.909582843 | -0.270297129 | -1.552048623 |
| 6 | 3.122091068 | 0.156480361 | 0.898511684 |

*Table 17*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.993860993 |
| R Square | 0.987759673 |
| Adjusted R Square | 0.984699592 |
| Standard Error | 0.14718074 |
| Observations | 6 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 6.992303104 | 6.992303104 | 322.7886675 | 5.64154E-05 |
| Residual | 4 | 0.086648681 | 0.02166217 | | |
| Total | 5 | 7.078951786 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.091768459 | 0.08217595 | 1.116731339 | 0.326659619 | -0.136389029 | 0.319925947 | -0.136389029 | 0.319925947 |
| spike conc. (mg/L) | 1.210757162 | 0.06739038 | 17.96632037 | 5.64154E-05 | 1.023651083 | 1.397863241 | 1.023651083 | 1.397863241 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L) as NH3* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.091768459 | 0.029660112 | 0.201521695 |
| 2 | 0.212832069 | 0.090739359 | 0.616516531 |
| 3 | 0.454886672 | 0.04297047 | 0.291957156 |
| 4 | 0.817787145 | -0.089215717 | -0.606164343 |
| 5 | 1.905184079 | -0.217326936 | -1.476599014 |
| 6 | 3.111113003 | 0.143172711 | 0.972767975 |

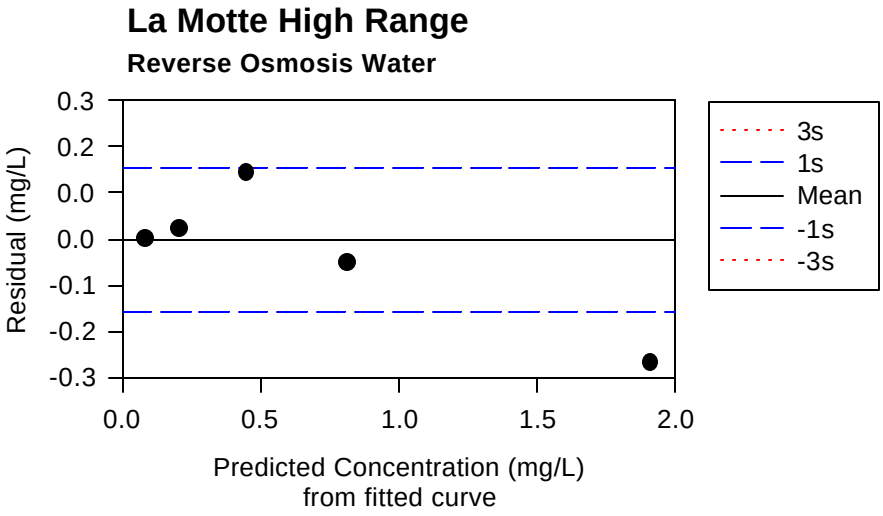



*Figure 11*

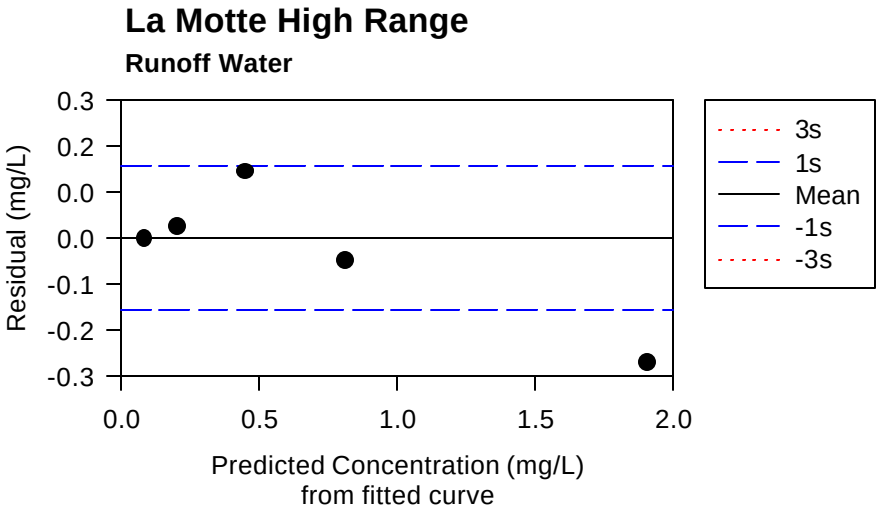



*Figure 12*

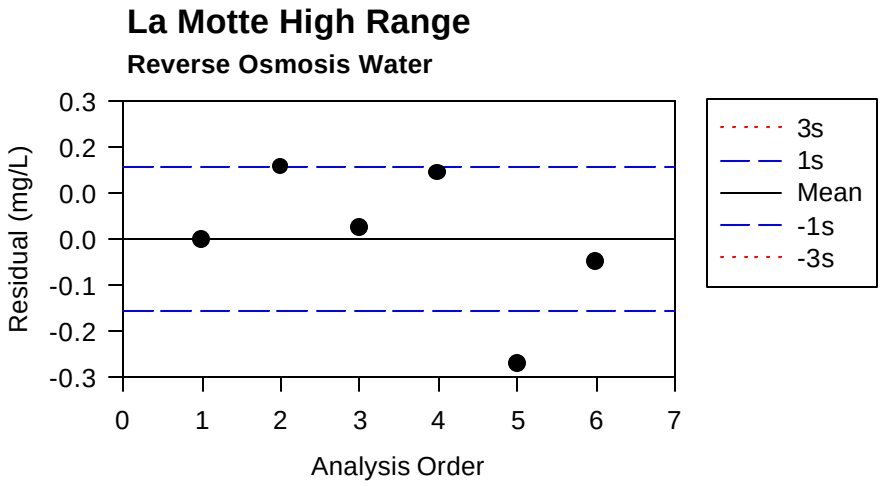

La Motte High Range
Reverse Osmosis Water
Residual (mg/L)
0.3
0.2
0.0
0.0
-0.1
-0.2
-0.3
0
1
2
3
4
5
6
7
Analysis Order
3s
1s
Mean
-1s
-3s

*Figure 13*

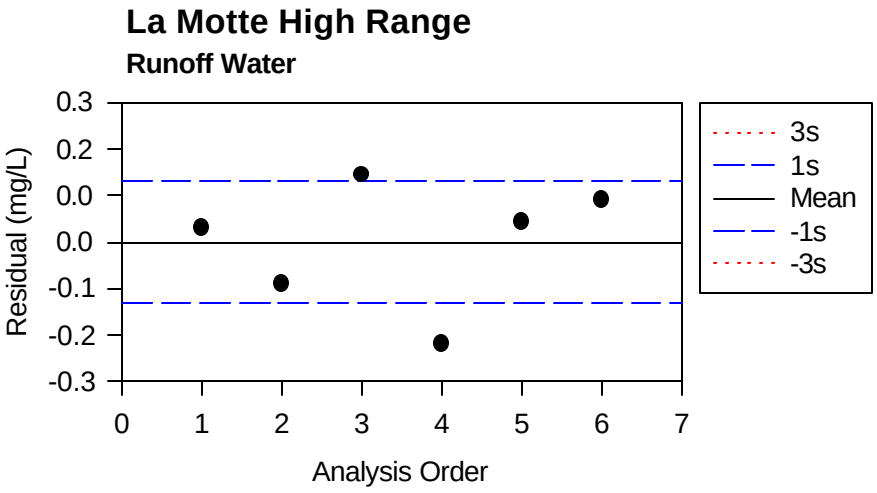



*Figure 14*

## 4.8 La Motte Ammonia low Range

### *4.8.1 Method Summary*

The La Motte Low Range Ammonia method is chemically identical to the HACH Salicylate Method. The only differences in the methods are the physical apparatus. Like most La Motte Methods, the reaction is carried out in the cuvette for the Smart Colorimeter. The user takes a 10 mL sample and zeroes the instrument. The user then adds 2.0 mL of a citrate buffer to adjust the pH to neutrality. Then, the user "spoons" 0.15 g of Salicylate Reagent into the cuvette with a small measuring scoop (provided). The sample is allowed to settle for 1.0 minutes. Then, 0.2 g of isocyanurate is added to initiate the desired reaction. The sample is allowed to develop for 12 minutes. After development the sample absorbance is measured using the Smart Colorimeter.

The La Motte Low Range Ammonia method is adapted from the Phenate Method for determining ammonia concentrations described in Standard Methods (4500-$NH_3$ D) (1992). Ammonia in the sample is reacted with hypochlorite donated from the cyanurate reagent to form monochloramine. The monochloramine reacts with salicylate to form 5-aminosalicylate. The 5-aminosalicylate, in turn, oxidizes to form indosalicylate, a yellow compound. The oxidizing agent is nitroferricyanide (nitroprusside), a blue compound. The resulting color in a positive test is green.

La Motte has used salicylate as the active reagent to eliminate the use of mercury (for Nessler's reaction) and phenol (the phenate method). The time required to complete the test is increased, but the reagent choice makes the waste products easier to dispose and the test safer to conduct. The more common interferences and the corresponding levels are listed below. La Motte maintains that there are few interferents for this method in most natural waters. The only interferent the La Motte company names are reducing agents.

These substances interfere by competing in the reaction with isocyanurate. The inteferenents previously associated with this reaction (in the HACH summary) are re-iterated below. The threshold levels are not reported since there may be some variation in the method.

*Table 18*

| | |
|---|---|
| calcium | nitrate |
| magnesium | orthophosphate |
| nitrite | sulfate |

Other interferents include sulfide, glycine, hydrazine, color and turbidity. These interferences will intensify the color in the sample resulting in erroneously high ammonia concentrations. In addition, the pH of the sample should be approximately neutral before beginning the test.

### *4.8.2 Observations*

This test is also quite long with an approximately 15-20 minute analysis time. This method also avoids the use of glass ampoules by using medicine droppers and calibrated scoops. In this case, special care should be taken to insure the user adds the correct amount of the reagent material. The required amount of citrate buffer (2.0 mL) and isocyanurate (0.2 g) are double the calibration marks. In addition, the use of a scoop to measure mass may be a problem. The users should be trained to measure “level,” not “heaping,” scoops of reagents. The residual plots in reverse osmosis water indicate a decreasing error associated with increasing analysis order. This is not observed in the runoff matrix.

*Table 19*

| Sample ID | spike conc. (mg/L) as NH3 | RO Response (mg/L) as N | RO Response (mg/L) as NH3 | RO Recovery (%) | Runoff Response (mg/L) as N | Runoff Response (mg/L) as NH3 |
|---|---|---|---|---|---|---|
| NH3 X O | 0.000 | 0.10 | 0.12 | NA | 0.00 | 0.00 |
| NH3 X 1 | 0.100 | 0.12 | 0.15 | 146 | 0.09 | 0.11 |
| NH3 X 2 | 0.300 | 0.27 | 0.33 | 109 | 0.13 | 0.16 |
| NH3 X 3 | 0.600 | 0.60 | 0.73 | 122 | 0.49 | 0.60 |

*Table 20*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.983834346 |
| R Square | 0.96793002 |
| Adjusted R Square | 0.95189503 |
| Standard Error | 0.061558514 |
| Observations | 4 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 0.228744951 | 0.228744951 | 60.36361814 | 0.016165654 |
| Residual | 2 | 0.007578901 | 0.003789451 | | |
| Total | 3 | 0.236323852 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.069933363 | 0.045557911 | 1.535043214 | 0.264540366 | -0.126086646 | 0.265953371 | -0.126086646 | 0.265953371 |
| spike conc. (mg/L) as NH3 | 1.044318109 | 0.134414208 | 7.769402689 | 0.016165654 | 0.465980048 | 1.622656171 | 0.465980048 | 1.622656171 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L) as NH3* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.069933363 | 0.051495209 | 0.836524559 |
| 2 | 0.174354732 | -0.028640446 | -0.465255641 |
| 3 | 0.383134835 | -0.055277692 | -0.897969895 |
| 4 | 0.696148499 | 0.032422929 | 0.526700977 |

*Table 21*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.962531802 |
| R Square | 0.92646747 |
| Adjusted R Square | 0.889701204 |
| Standard Error | 0.086830075 |
| Observations | 4 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 0.189985744 | 0.189985744 | 25.19884642 | 0.037468198 |
| Residual | 2 | 0.015078924 | 0.007539462 | | |
| Total | 3 | 0.205064668 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | -0.022289475 | 0.06426076 | -0.346859814 | 0.761793214 | -0.298781402 | 0.254202451 | -0.298781402 | 0.254202451 |
| spike conc. (mg/L) as NH3 | 0.951738326 | 0.189595152 | 5.019845259 | 0.037468198 | 0.135975659 | 1.767500992 | 0.135975659 | 1.767500992 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L) as NH3* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | -0.022289475 | 0.022289475 | 0.256702245 |
| 2 | 0.072874841 | 0.036410873 | 0.419334813 |
| 3 | 0.263146392 | -0.105289249 | -1.21258963 |
| 4 | 0.5484111 | 0.0465889 | 0.536552572 |

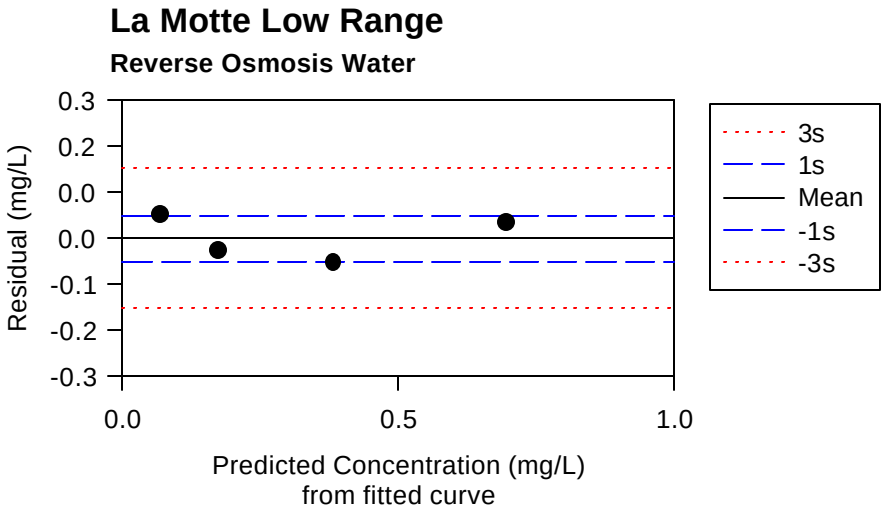

La Motte Low Range
Reverse Osmosis Water
Residual (mg/L)
0.3
0.2
0.0
0.0
-0.1
-0.2
-0.3
0.0
0.5
1.0
Predicted Concentration (mg/L)
from fitted curve
3s
1s
Mean
-1s
-3s

*Figure 15*

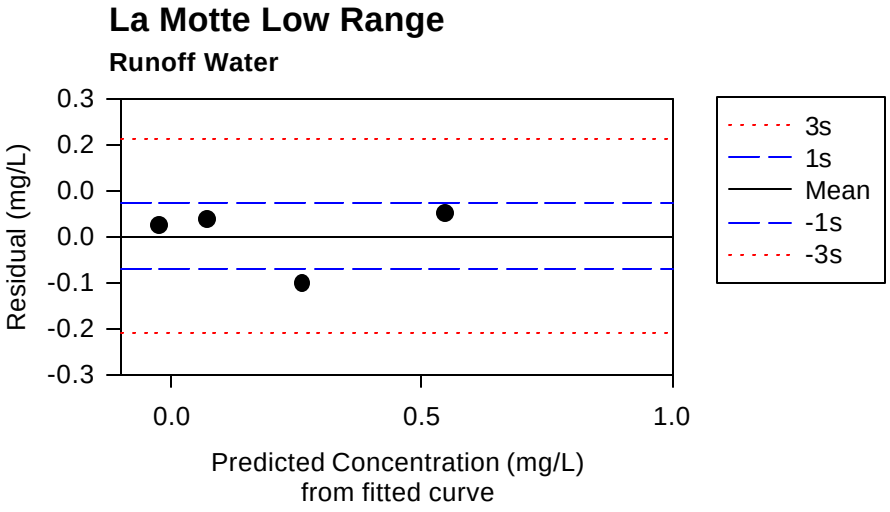

La Motte Low Range
Runoff Water
Residual (mg/L)
0.3
0.2
0.0
0.0
-0.1
-0.2
-0.3
0.0
0.5
1.0
Predicted Concentration (mg/L)
from fitted curve
3s
1s
Mean
-1s
-3s

*Figure 16*

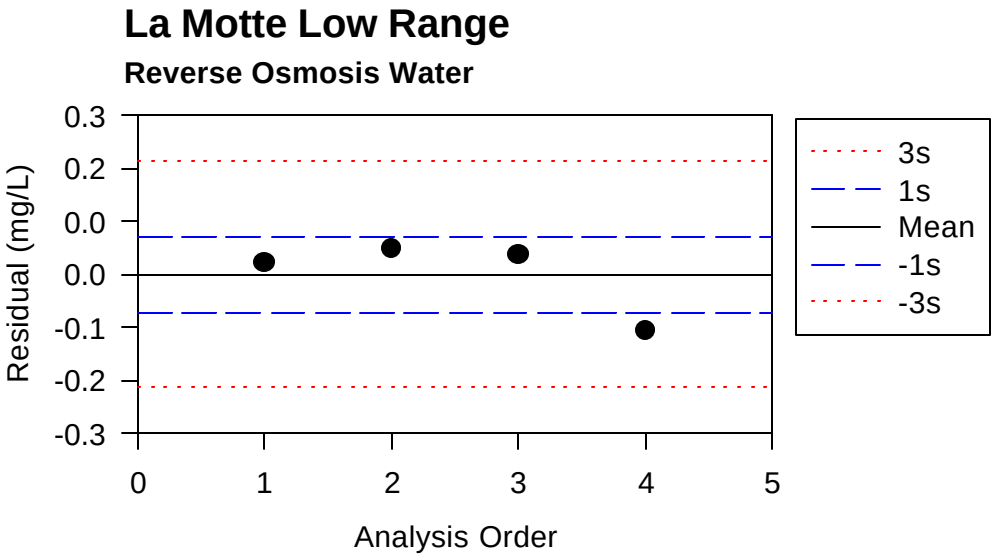



*Figure 17*

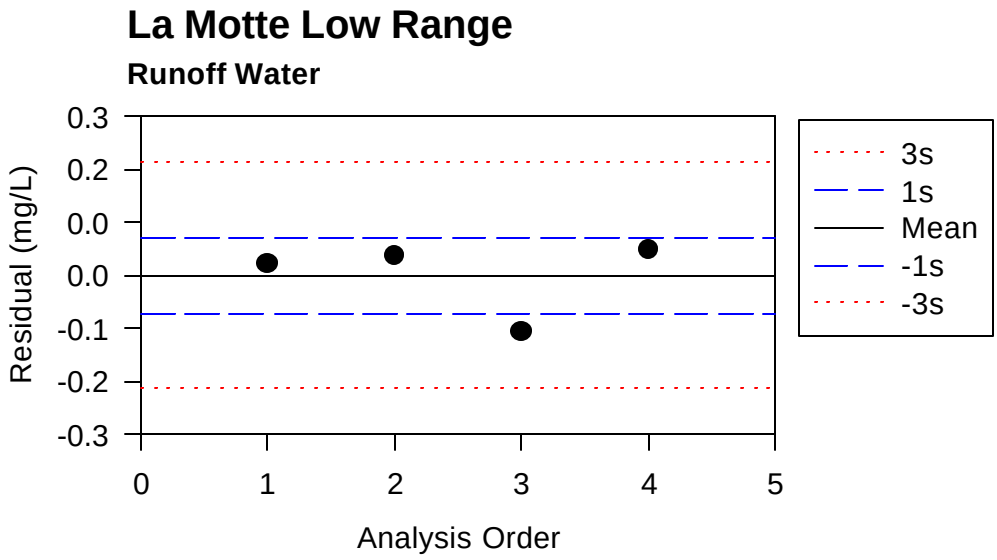

La Motte Low Range
Runoff Water
Residual (mg/L)
0.3
0.2
0.0
0.0
-0.1
-0.2
-0.3
0
1
2
3
4
5
Analysis Order
3s
1s
Mean
-1s
-3s

*Figure 18*

# Bacteria Summary

# 5 Bacteria

Comparison tests with standard bacteria cultures were not conducted because of problems in the manufacture of standard bacteria cultures from the supplier. Therefore, the evaluations were based on comparing the Kool Kount results with standard test results using the IDEXX methods.

# 6 IME.Test Kool Kount Assayer

## 6.1 Method

The user collects 20 mL of sample. The sample is allowed to stand for 15 minutes. After settling, use the ampoule to draw up a portion of sample. The reagents in the ampoule mix with the sample to initiate a reaction with bacteria in the sample. The ampoule is then placed in 95 °F environment (a shirt pocket is suggested). The length of time the sample requires to reach the target color is related to the number of bacteria in the sample. This test may be stopped (placed on ice) and re-started later.

The test was originally designed for determining bacterial counts in cooling waters. Therefore, it is sensitive to bacteria normally occurring under those conditions. The manufacturer, in conjunction with George Mason University, offers to develop other specific applications for this product.

The test is subject to interference from halogens. Halogens retard the color development, and thus, the counts made in the presence of halogens are less than the true value. The addition of sodium thiosulfate before snapping the ampoule will remove halogen interference. The manufacturer indicates that development times less than 15 minutes indicate a problem more often than a high bacterial count. If stratification occurs, gently mix the ampoule's contents. Other interferents are listed below.

*Table 22*

| compound | threshold (ppm) | compound | threshold (ppm) |
|---|---|---|---|
| chlorine | 0 | magnesium acetate (as Mg) | 9000 |
| bromine | 0 | sodium thiosulfate | 250,000 |
| iodine | 0 | EDTA | 6000 |
| fluorine | 0 | sodium nitrate | 3000 |
| astatine | 0 | hydrogen peroxide | 1500 |
| magnesium chloride (as Mg) | 1400 | isothasalons | 100 |
| sodium molybdate (as Mo) | 2500 | | |

The test method has been verified by the manufacturer to detect the species listed on Table 2.

*Table 23*

| | |
|---|---|
| *acinetobacter calcoaceticus* | *psuedomonas putida* |
| *aeromonas hydrofilia* | *psuedomonas maltophilia* |
| *alcaligenes faecalis* | *aspergillus* species |
| *bacillus* species | *penicillium* species |
| *citrobacter freundii* | sulfate reducing bacteria |
| nitrifying bacteria | iron reducing bacteria |
| *psuedomonas aeruginosa* | nitrate bacteria |
| *psuedomonas fluorescens* | |

(Source IME.Test Kool Kount Product Specifications, undated)

## 6.2

## 6.3 Observations

This test may or may not be very informative due to the typically long time period required for analyses. However, very high bacteria counts will be evident early. For example, a half-hour development time indicates a bacteria count of approximately $10^8$ CFU/mL. However, several hours would likely be needed to detect counts that may be of concern. This is the only bacteria test found that can be used in short period with out an incubator. The following chart indicates approximate count and development time.

*Table 24*

| Count (CFU/mL) | Time (hr) |
|---|---|
| $10^8$ | 0.5 |
| $10^7$ | 2.0 |
| $10^6$ | 4.0 |
| $10^5$ | 5.5 |
| $10^4$ | 7.0 |
| $10^3$ | 9.0 |
| $10^2$ | 10.5 |
| $10^1$ | 12.5 |

(Source IME.Test Kool Kount Product Specifications, undated)

Table 4 compares parallel analyses conducted using the Kool Kount test with the standard IDEXX tests for nine water samples collected from telecommunication manholes. The samples are sorted according to the Kool Kount results. The higher Kool Kount results may be associated with higher *E. coli* and Enterococci results, but are not related to the total coliform values. This test may be best used as an indicator of unusually high results, but may not be specific or repeatable enough to indicate moderate contamination levels. The likely presence of sanitary sewage (indicated by detergents, for example) may be a better (and certainly faster) indication of high bacteria values associated with sanitary wastewater contamination.

6.3.1.1

6.3.1.2 Table 4

| E. coli (MPN/100 mL) | Enterococci (MPN/100 mL) | Total Coliform (MPN/100 mL) | Kool Kount (CFU/mL) |
|---|---|---|---|

| | | | |
|---|---|---|---|
| 35 | 0.0 | 1,300 | 1,000 |
| 260 | 0.0 | 72,400 | 4,000 |
| 54 | 0.0 | 72,400 | 4,000 |
| 326 | 5.1 | 72,400 | 4,000 |
| 2,420 | 1.0 | 72,400 | 10,000 |
| 0.0 | 3.1 | 72,400 | 10,000 |
| 15 | 0.0 | 1,410 | 10,000 |
| 520 | 2,420 | 72,400 | 10,000 |
| 160 | 365 | 2,420 | 100,000 |

# 7 IDEXX Colilert and Enterolert

The IDEXX Colilert test is specific for total coliforms and *e. coli*, while the Enterolert test is specific for Enterococci. The tests are performed by adding 100 mL of water to the sample bottle. Add one correct Snap Pack to the sample bottle. Shake the bottle until all reagent is dissolved. Incubate the bottle at 35°C for 24 hr. For the Colilert test, the presence of total coliforms is indicated by a yellow color at the end of the incubation period. The presence of *e. coli* is indicated by a fluorescent color. The Enterolert test uses fluorescence measurements also. The fluorescent color requires a lamp emitting light at 365 nm to be visible. The Quantitray is used to quantify the bacterial population in the samples. After the Snap Pack reagent is added to the sample and dissolved, the mixture is poured into the Quantitray and sealed in the special thermal sealer. This forms numerous pockets that act as a multiple tube test. The positive pockets are counted after the correct incubation period and the MPN (most probably number) is read from a statistical chart.

The test is very simple, but like most bacteria tests, the analysis time is too long for use in the field. However, the 24 hr version of the Colilert test is EPA approved and was included in the 18$^{th}$ edition of Standard Methods. This test relies on the selective metabolism of coliforms and *e. coli* of ONPG and MUG, respectively. These substrates are cleaved by enzymes specific to coliforms (β-galactosidase) and *e. coli* (β-glucuronidase). The substrates have been specially designed to produce the indicating color when metabolized by the appropriate enzyme. In addition, the agar in the test is mixed with an anti-biotic that helps eliminate other bacteria species from the test.

# 8 Conductivity Summary

## 9 Conductivity

Four methods were evaluated for the determination of specific conductivity: YSI SCT Model 33, Horiba Twin, Horiba U-10, and a pocket TDSTestr3. All four instruments measure the conductance across a gap on the electrode. The YSI SCT Model 33 and Horiba U-10 are both designed to operate *in situ.* The Horiba Twin and the TDSTestr3 may also be used for *in situ* measurement, but only for the surface of a water body, as the probes should not be lowered more than 1" below the surface.

*Table 25*

| Kit Name | Method | Capital cost | Expendable Cost (per sample) | Time Required (min) | Sample Vol. (ml) | Expertise Required |
|---|---|---|---|---|---|---|
| TDSTestr 3 | pocket electronic probe | As part of GDS's AquaVats kit | $0.00 | 1 | *in situ* | none |
| YSI SCT | electronic probe | $600 for kit | $0.00 | 1 | *in situ* | none |
| Horiba Twin | electronic probe | $250 for kit | $0.00 | 1 | drops | none |
| Horiba U-10 | electronic probe | $3600 for kit | $0.00 | 1 | *in situ* | none |

*Table 26*

| Kit Name | Precision | Shelf Life | Regular Maintenance | Safety Hazards | Upper Limit of Useful Range |
|---|---|---|---|---|---|
| TDSTestr 3 | not evaluated | not applicable | Change batteries. One point calibration once per week. | None | 1900 µS/cm |
| YSI SCT | not evaluated | not applicable | Change batteries. | None | |
| Horiba Twin | 0.03990 | not applicable | Change batteries. One point calibration once per day. | None | 50 mS/cm |
| Horiba U-10 | not evaluated | not applicable | Change batteries. One point calibration once per day. | None | |

### 9.1 Spiked Samples

The following tables summarize the performance of the three kits in the spiked sample analyses. The Horiba Twin performance was not as consistent as the Horiba U-10 or the YSI SCT, but the performance is adequate for most applications, and is much less expensive and is easier to use if only conductivity measurements are needed.

Conductivity is a measure of the activity of all charged particles in a solution. This includes cations, anions and any associated particulates. Therefore, the expected response ratio is not 1:1 when comparing conductivity with sodium chloride concentrations. The expected ratio is the result of the activities of all ionic species in solution. This is seen in the regression analyses. The assumption that sodium chloride is representative of the types of water that will be measured in this application is justified by the excessive sodium chloride content found in the water samples obtained from northeastern manholes.

*Table 27 Reverse Osmosis*

| Kit Name | Adjusted $R^2$ | Standard Error | Intercept | p-Value | Slope | p-Value | Detection Limit ($\alpha$=0.05) | Limit of Quantification ($\alpha$=0.05) |
|---|---|---|---|---|---|---|---|---|
| YSI SCT | 0.9987 | 43.4881 | 23.9445 | 0.2051 | 1.8016 | 1.4652E-11 | 97.18 µS/cm | 170.4 µS/cm |
| Horiba Twin | 0.9995 | 31.6060 | 21.5637 | 0.1270 | 2.1523 | 4.5289E-13 | 74.79 µS/cm | 120 µS/cm |
| Horiba U-10 | 0.9987 | 45.8700 | 10.0700 | 0.5949 | 1.9080 | 1.4250E-11 | 87.32 µS/cm | 164.6 µS/cm |

*Table 28 Runoff*

| Kit Name | Adjusted $R^2$ | Standard Error | Intercept | p-Value | Slope | p-Value | Detection Limit ($\alpha$=0.05) | Limit of Quantification ($\alpha$=0.05) |
|---|---|---|---|---|---|---|---|---|
| YSI SCT | 0.9996 | 24.3200 | 44.8600 | 0.0051 | 1.8509 | 8.0600E-12 | 85.81 µS/cm | 126.8 µS/cm |
| Horiba Twin | 0.9982 | 60.2500 | 75.1000 | 0.0271 | 2.0385 | 1.1500E-09 | 176.6 µS/cm | 278.0 µS/cm |
| Horiba U-10 | 0.9996 | 27.5511 | 41.8100 | 0.0122 | 1.9290 | 1.4680E-11 | 88.21 µS/cm | 134.6 µS/cm |

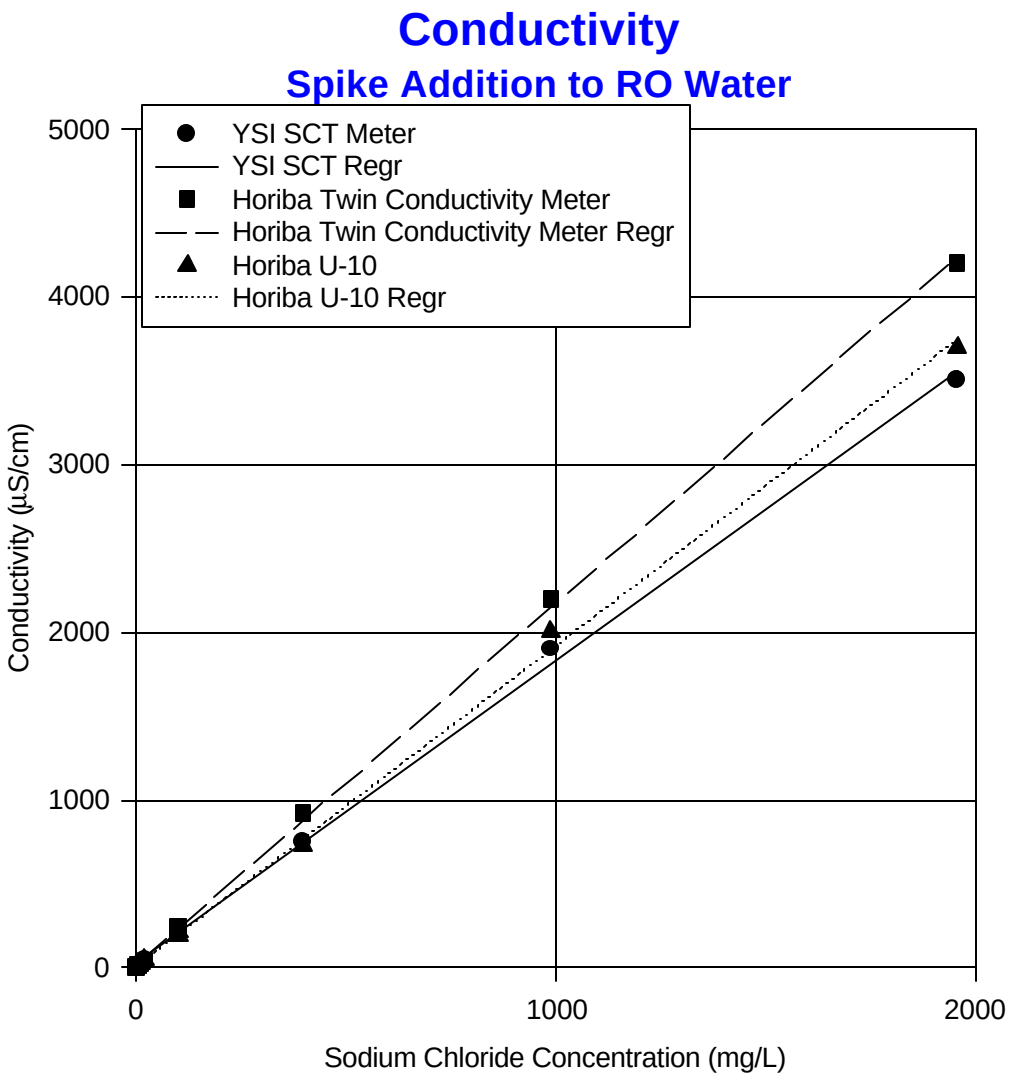

Conductivity
Spike Addition to RO Water
YSI SCT Meter
YSI SCT Regr
Horiba Twin Conductivity Meter
Horiba Twin Conductivity Meter Regr
Horiba U-10
Horiba U-10 Regr
5000
4000
3000
2000
1000
0
Conductivity (µS/cm)
0
1000
2000
Sodium Chloride Concentration (mg/L)

*Figure 19*

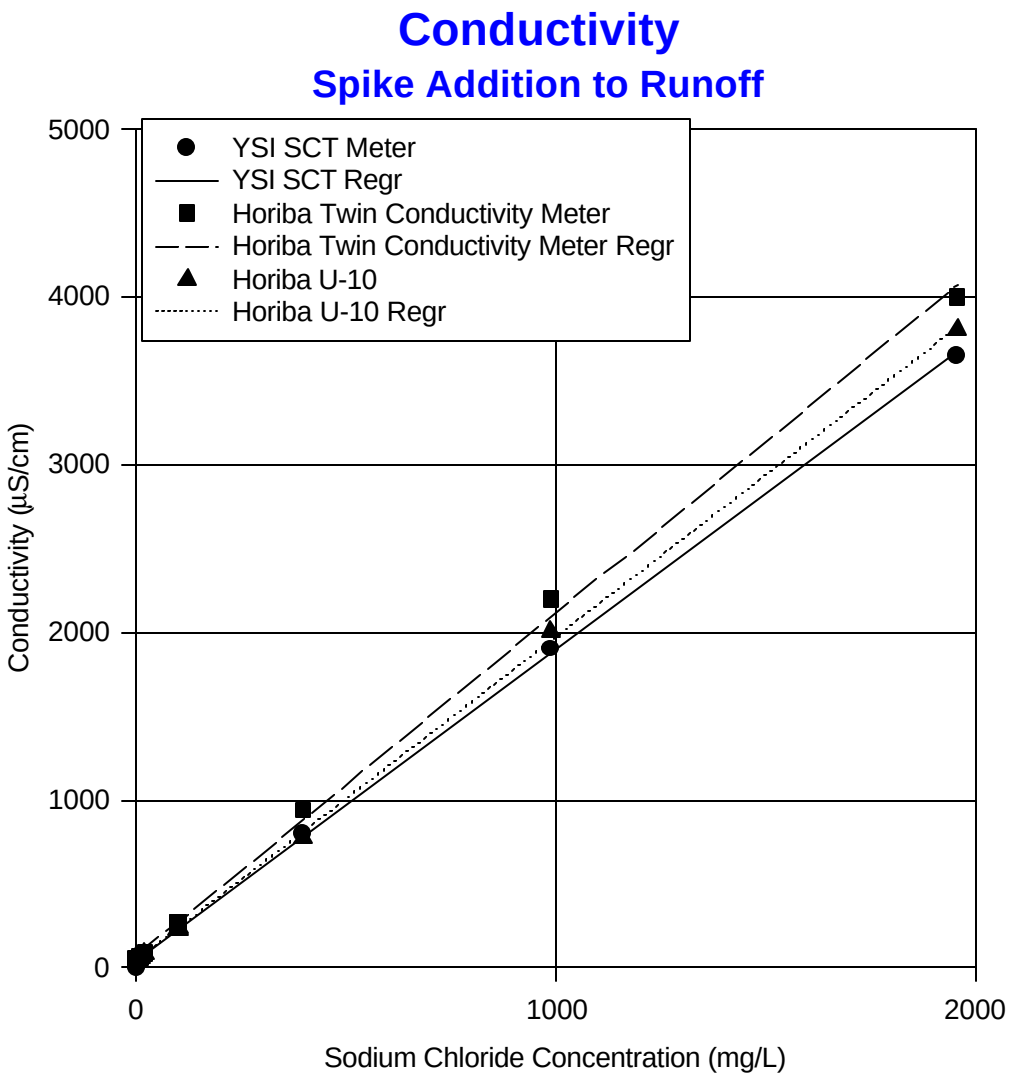



*Figure 20*

## 9.2 Parallel Analyses

The parallel analyses showed a good correlation between the measurements of the YSI SCT Model 33 and the Horiba Twin Conductivity meters. The data is presented below.

*Table 29*

| Sample ID | YSI Response (µS/cm) | Horiba Twin Response (mS/cm) | Horiba Twin Response (µS/cm) |
|---|---|---|---|
| 2464 | 1740 | 1.94 | 1940 |
| 2473 | 44000 | 50 | 50000 |
| 2491 | 900 | 0.92 | 920 |
| 2501 | 2550 | 2.7 | 2700 |
| 2511 | 2710 | 2.9 | 2900 |
| 2530 | 3120 | 3.3 | 3300 |
| 2539 | 1000 | 1.02 | 1020 |
| 2548 | 1760 | 1.85 | 1850 |
| 2585 | 149 | 0.163 | 163 |
| 2595 | 1900 | 2.8 | 2800 |
| 2613 | 3600 | 4.1 | 4100 |
| 2629 | 11500 | 13.3 | 13300 |
| 2638 | 1400 | 1.64 | 1640 |
| 2656 | 1290 | 1.56 | 1560 |
| 2666 | NA | 2.3 | 2300 |
| 2674 | 1390 | 1.5 | 1500 |
| 2695 | 980 | 1.05 | 1050 |
| 2722 | 17200 | 18.5 | 18500 |
| 2731 | 630 | 0.81 | 810 |
| 2740 | 520 | 0.64 | 640 |
| 2749 | 1020 | 1.27 | 1270 |
| 2774 | 150 | 0.2 | 200 |
| 2783 | 130 | 1.87 | 1870 |
| 2801 | 420 | 0.64 | 640 |
| 2810 | 110 | 0.24 | 240 |

*Table 30*

SUMMARY OUTPUT

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.999108814 |
| R Square | 0.998218423 |
| Adjusted R Square | 0.998137442 |
| Standard Error | 453.9271624 |
| Observations | 24 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 2539896540 | 2539896540 | 12326.61081 | 9.66052E-32 |
| Residual | 22 | 4533097.113 | 206049.8688 | | |
| Total | 23 | 2544429637 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 87.63126703 | 101.8713996 | 0.860214618 | 0.39894836 | -123.6373117 | 298.8998458 | -123.6373117 | 298.8998458 |
| YSI Response (mS/cm) | 1.126195226 | 0.010143594 | 111.025271 | 9.66052E-32 | 1.105158678 | 1.147231774 | 1.105158678 | 1.147231774 |

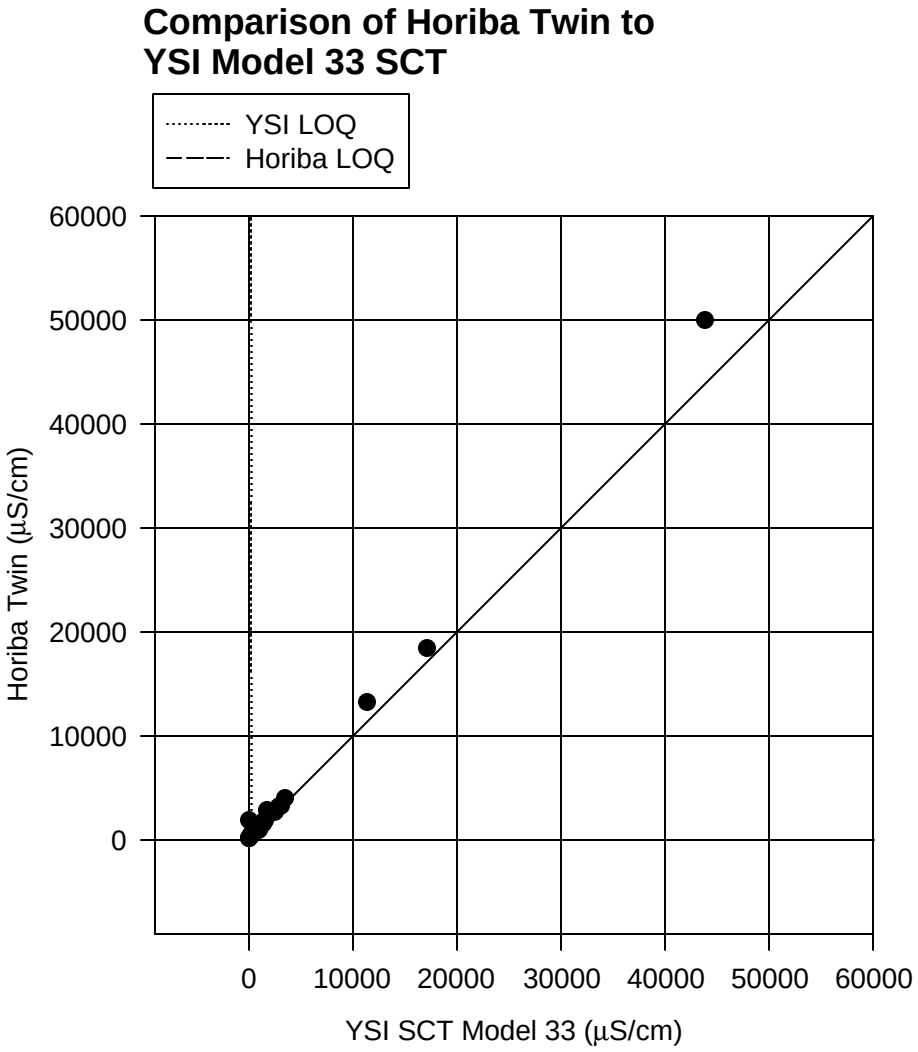

Comparison of Horiba Twin to
YSI Model 33 SCT
YSI LOQ
Horiba LOQ
60000
50000
40000
30000
20000
10000
0
Horiba Twin (µS/cm)
0
10000
20000
30000
40000
50000
60000
YSI SCT Model 33 (µS/cm)

*Figure 21*

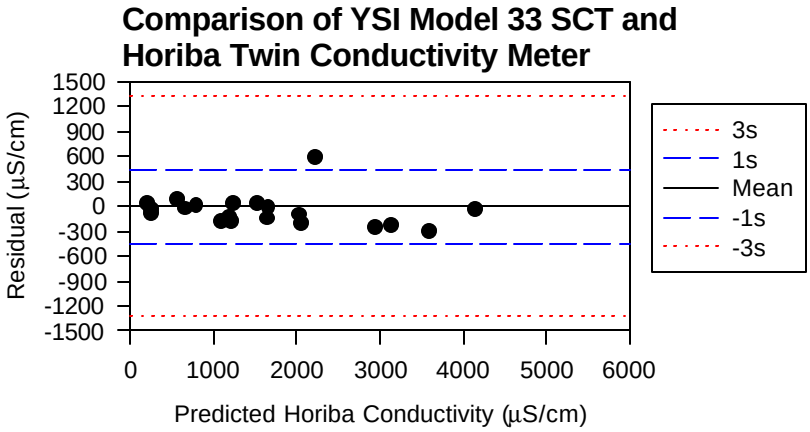



*Figure 22*

## 9.3 Conclusion

Although the Horiba Twin showed slightly more error and somewhat higher detection limits than the other instruments, it is our recommendation because of ease of use and lower cost. The meter should be sufficient for field needs since it is highly unlikely that water found in manholes will have a conductivity lower than the limit of detection of the meter. The Horiba Twin meets many other of the criteria for the evaluation of the methods. It is small, easy to use, safe and relatively inexpensive. The Horiba U-10 is much too expensive unless the other parameters were of great interest. The YSI SCT Model 33 is a good instrument, but its manual temperature compensation and lack of a calibration procedure make it subordinate to the Horiba instruments. YSI currently produces several modern updated SCT meters that were not investigated.

## 9.4 YSI Model 33 SCT

The YSI SCT meter uses a large probe to determine the conductance of samples. Those samples with sufficiently high salinity did follow a predictable trend. The only detriments to the instrument are there is no AC power option, the probe is large and temperature compensation must be performed manually. The device is best suited for taking measurements *in situ*.

### *9.4.1 Method*

The method for determining conductance with the YSI SCT is quite simple. Perform a voltage check and replace batteries if necessary. The machine does not have an AC option. Place the probe in the sample and measure the temperature. Use the temperature dial to compensate for the temperature of sample. Switch the selector to conductivity and select the appropriate scale. Record the measurement. Be sure to rinse the probe thoroughly between successive measurements.

### *9.4.2 Observations*

The YSI SCT Model 33 is our general field instrument for measuring conductivity. The device is rugged and reliable. The SCT was designed for *in situ* measurements, but it can be used to measure samples in the laboratory. If the device is used for benchtop work the samples must be placed in a relatively large container with a large mouth, otherwise, the probe will not reach the sample. The meter comes with cables in a variety of lengths. We have a 30 m cable that would make measurements easy from the surface of a manhole if *in situ* analysis is required. The meter is powered exclusively by D cell batteries. However, the meter is becoming outdated and newer versions of the instrument are now available (such as the YSI Model 30). The meter requires manual temperature compensation and has no internal calibration procedure. One procedural note, the YSI SCT Model 33 reports conductivity with µmho/cm units (these units are identical to the SI units, µS/cm that modern meters report).

*Table 31*

| Sample ID | NaCl Conc. (mg/L) | Analysis Order | Reverse Osmosis Response (µS/cm) | Analysis Order | Runoff Response (µS/cm) |
|---|---|---|---|---|---|
| Cl LR RO 0 | 0.00 | 12 | 0 | 10 | 3 |
| Cl LR RO 1 | 2.00 | 2 | 15 | 18 | 4.5 |
| Cl LR RO 2 | 9.99 | 4 | 25 | 16 | 60 |
| Cl LR RO 3 | 19.96 | 6 | 45 | 15 | 80 |
| Cl LR RO 4 | 99.01 | 17 | 200 | 1 | 240 |
| Cl HR RO 1 | 99.73 | 13 | 220 | 9 | 240 |
| Cl HR RO 2 | 397.73 | 3 | 750 | 14 | 800 |
| Cl HR RO 3 | 988.42 | 7 | 1900 | 5 | 1900 |
| Cl HR RO 4 | 1957.45 | 8 | 3500 | 11 | 3650 |

*Table 32*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.999428857 |
| R Square | 0.99885804 |
| Adjusted R Square | 0.998694903 |
| Standard Error | 43.48805981 |
| Observations | 9 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 11579533.74 | 11579533.74 | 6122.813172 | 1.46522E-11 |
| Residual | 7 | 13238.47942 | 1891.211346 | | |
| Total | 8 | 11592772.22 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 23.94445552 | 17.13903513 | 1.397071383 | 0.20508262 | -16.58289361 | 64.47180465 | -16.58289361 | 64.47180465 |
| NaCl Conc.(mg/L) | 1.801616517 | 0.023024322 | 78.24840683 | 1.46522E-11 | 1.747172686 | 1.856060348 | 1.747172686 | 1.856060348 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Conductivity (mmhos)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 23.94445552 | -23.94445552 | -0.550598385 |
| 2 | 27.54768855 | -12.54768855 | -0.288531809 |
| 3 | 41.94260452 | -16.94260452 | -0.389592099 |
| 4 | 59.9047212 | -14.9047212 | -0.342731344 |
| 5 | 202.3225069 | -2.322506862 | -0.053405622 |
| 6 | 203.6196708 | 16.38032925 | 0.376662682 |
| 7 | 740.5013928 | 9.498607199 | 0.218418739 |
| 8 | 1804.698253 | 95.30174681 | 2.191446278 |

*Table 33*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.999795372 |
| R Square | 0.999590786 |
| Adjusted R Square | 0.999532326 |
| Standard Error | 26.80224166 |
| Observations | 9 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 12283200.03 | 12283200.03 | 17098.94389 | 4.03487E-13 |
| Residual | 7 | 5028.521106 | 718.360158 | | |
| Total | 8 | 12288228.56 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 38.35860263 | 10.56300427 | 3.631410312 | 0.008382127 | 13.38108444 | 63.33612083 | 13.38108444 | 63.33612083 |
| NaCl Conc. (mg/L) | 1.855549655 | 0.014190181 | 130.7629301 | 4.03487E-13 | 1.821995233 | 1.889104077 | 1.821995233 | 1.889104077 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Conductivity (mmhos)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 38.35860263 | -35.35860263 | -1.319240498 |
| 2 | 42.06970194 | -37.56970194 | -1.401737303 |
| 3 | 56.89554369 | 3.104456314 | 0.115828234 |
| 4 | 75.39537375 | 4.604626254 | 0.171800042 |
| 5 | 222.076574 | 17.92342603 | 0.668728618 |
| 6 | 223.4125697 | 16.58743028 | 0.6188822 |
| 7 | 776.3663669 | 23.63363309 | 0.881778226 |
| 8 | 1872.420993 | 27.57900739 | 1.028981372 |

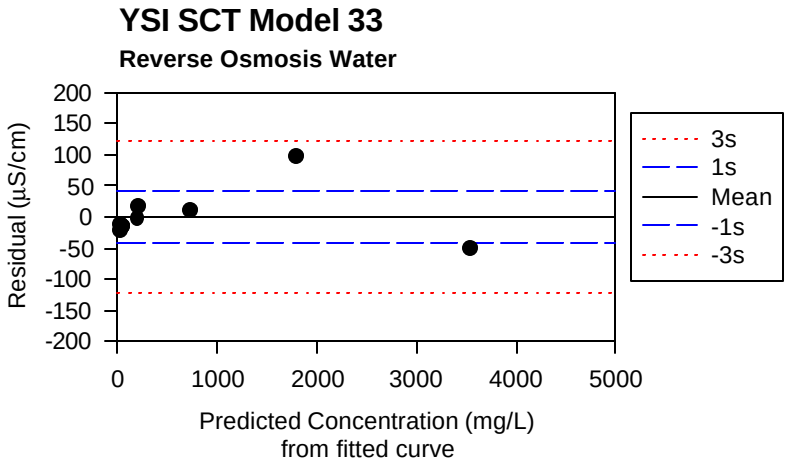



*Figure 23*

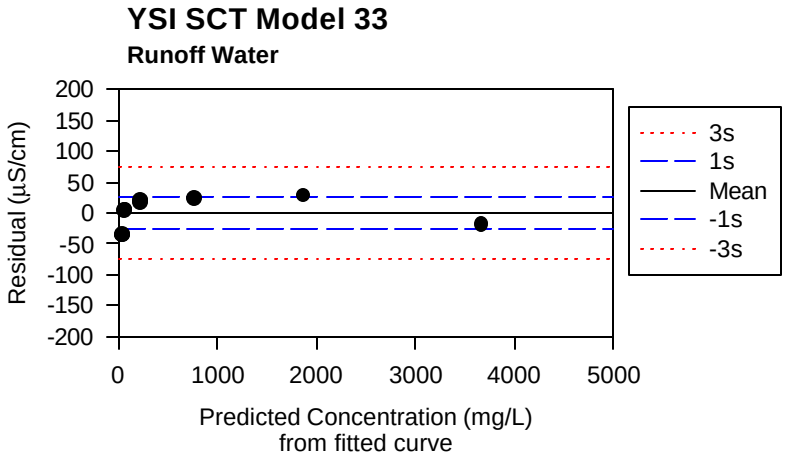



*Figure 24*

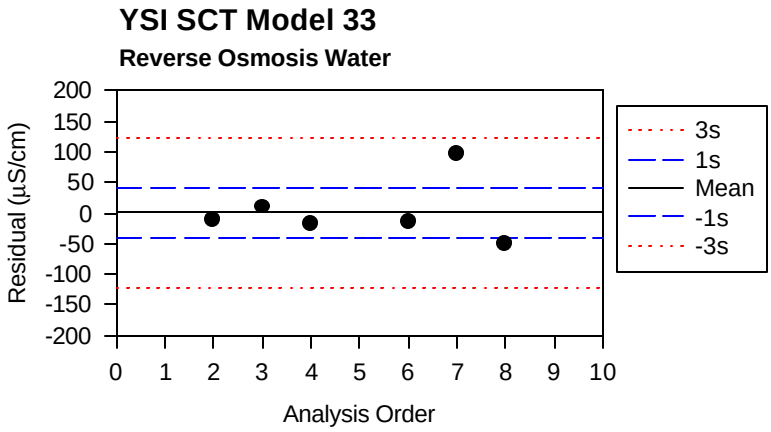



*Figure 25*

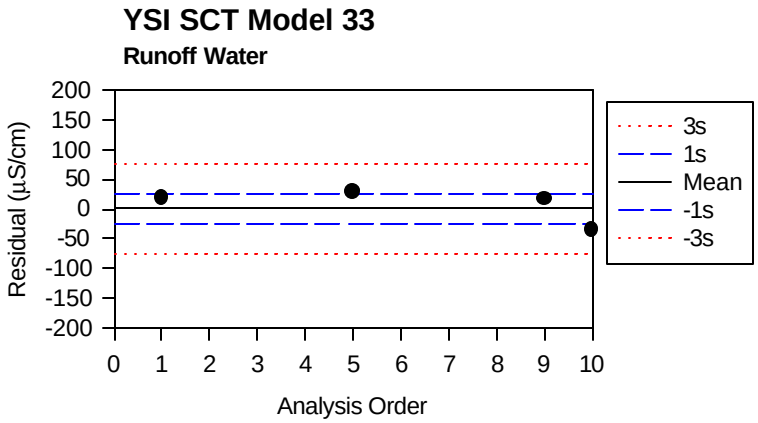



*Figure 26*

## 9.5 Horiba Twin Conductivity Meter

### *9.5.1 Method*

Measuring conductivity with the Horiba Twin Conductivity meter is extremely easy. The entire meter is the size of a magic marker. There are two options: the probe may be immersed in the sample (not entirely), or drops of the solution may be placed over the electrode. The meter displays the conductivity measurements on a real time basis until the meter comes to equilibrium. An LCD "smiley face" alerts the user that the instrument reading has been completed. The meter automatically compensates for temperature. In addition, the meter allows an internal 1 point calibration. The meter should be calibrated once daily.

### *9.5.2 Observations*

There is not much to comment about this instrument. It is extremely small, inexpensive (about $300), and easy to use. We have only encountered two problems with the instrument. The units of a sample reading automatically switch between µS/cm and mS/cm. However, the pointer that indicates µS/cm did not function correctly. Also, some of the northeastern winter manhole water samples exceeded the range of the instrument during the parallel analyses. Initially, the instrument readout would blink to signal an over-range response, but the meter continued to respond. One sample exceeded the range of the instrument so much that the meter "locked up." However, we rinsed the meter with tap water and turned it off. Ten minutes later, the meter had fully recovered and continued to function normally. The residual analyses against predicted concentration seem to indicate a quadratic error that may be eliminated by a multi-point calibration.

*Table 34*

| Sample ID | NaCl Conc.(mg/L) | Order | Reverse Osmosis (µmhos/cm) | Order | Runoff (µmhos/cm) |
|---|---|---|---|---|---|
| Cl LR X 0 | 0.00 | 6 | 3 | 16 | 3 |
| Cl LR X 1 | 2.00 | 17 | 13 | 7 | 47 |
| Cl LR X 2 | 9.99 | 15 | 25 | 4 | 68 |
| Cl LR X 3 | 19.96 | 8 | 46 | 9 | 92 |
| Cl LR X 4 | 99.01 | 2 | 230 | 12 | 270 |
| Cl HR X 1 | 99.73 | 18 | 250 | 5 | 270 |
| Cl HR X 2 | 397.73 | 3 | 920 | 1 | 940 |
| Cl HR X 3 | 988.42 | 1 | 2200 | 10 | 2200 |
| Cl HR X 4 | 1957.45 | 14 | 4200 | 13 | 4000 |

*Table 35*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.999788506 |
| R Square | 0.999577056 |
| Adjusted R Square | 0.999516635 |
| Standard Error | 31.60598901 |
| Observations | 9 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 16526085.43 | 16526085.43 | 16543.64583 | 4.52892E-13 |
| Residual | 7 | 6992.569789 | 998.9385412 | | |
| Total | 8 | 16533078 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 21.56368652 | 12.45620426 | 1.731160317 | 0.127035095 | -7.890535095 | 51.01790813 | -7.890535095 | 51.01790813 |
| NaCl Conc.(mg/L) | 2.152295091 | 0.016733477 | 128.6221047 | 4.52892E-13 | 2.112726733 | 2.191863449 | 2.112726733 | 2.191863449 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Conductivity (mmhos)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 21.56368652 | -18.56368652 | -0.587347117 |
| 2 | 25.8682767 | -12.8682767 | -0.407146781 |
| 3 | 43.06511448 | -18.06511448 | -0.57157251 |
| 4 | 64.52349654 | -18.52349654 | -0.586075523 |
| 5 | 234.6624235 | -4.662423493 | -0.147517089 |
| 6 | 236.212076 | 13.78792404 | 0.436244031 |
| 7 | 877.5960131 | 42.40398688 | 1.341644043 |

*Table 36*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.999125444 |
| R Square | 0.998251654 |
| Adjusted R Square | 0.99800189 |
| Standard Error | 61.14258492 |
| Observations | 9 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 14941637.09 | 14941637.09 | 3996.783216 | 6.50764E-11 |
| Residual | 7 | 26168.90984 | 3738.415691 | | |
| Total | 8 | 14967806 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 63.90504723 | 24.09684211 | 2.65200921 | 0.032845766 | 6.925110741 | 120.8849837 | 6.925110741 | 120.8849837 |
| NaCl Conc. (mg/L) | 2.046519609 | 0.032371335 | 63.22011718 | 6.50764E-11 | 1.96997362 | 2.123065599 | 1.96997362 | 2.123065599 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Conductivity (mmhos)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 63.90504723 | -60.90504723 | -0.99611502 |
| 2 | 67.99808645 | -20.99808645 | -0.343428176 |
| 3 | 84.34977813 | -16.34977813 | -0.267404104 |
| 4 | 104.7535786 | -12.75357863 | -0.208587495 |
| 5 | 266.5309538 | 3.469046238 | 0.05673699 |
| 6 | 268.0044479 | 1.995552119 | 0.03263768 |
| 7 | 877.8672915 | 62.1327085 | 1.016193682 |
| 8 | 2086.72596 | 113.2740404 | 1.852621058 |
| 9 | 4069.864857 | -69.86485679 | -1.142654614 |

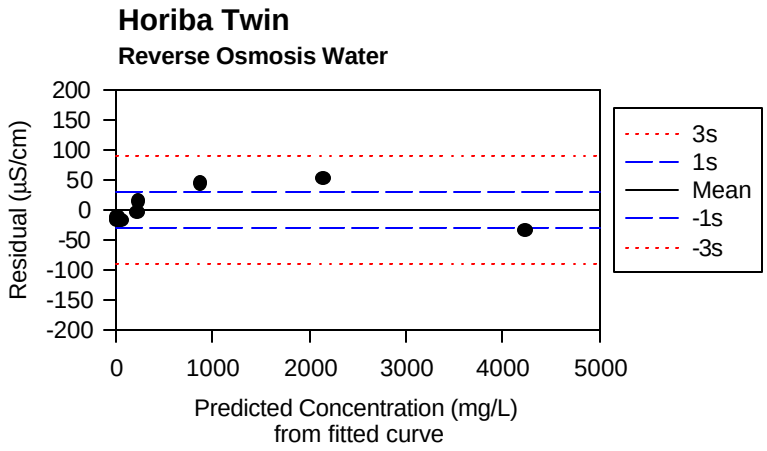



*Figure 27*

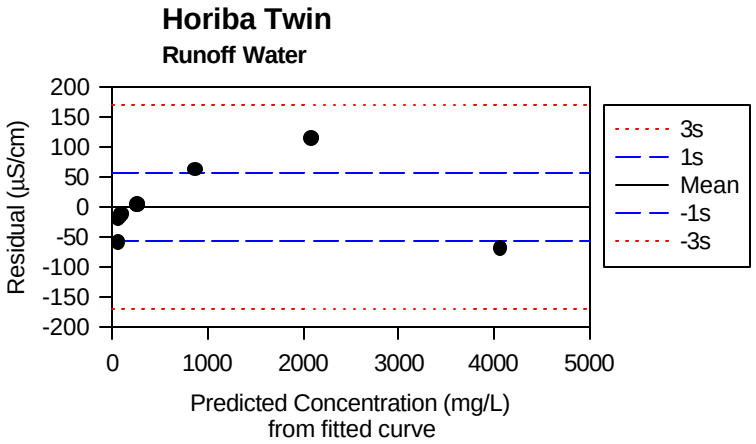



*Figure 28*

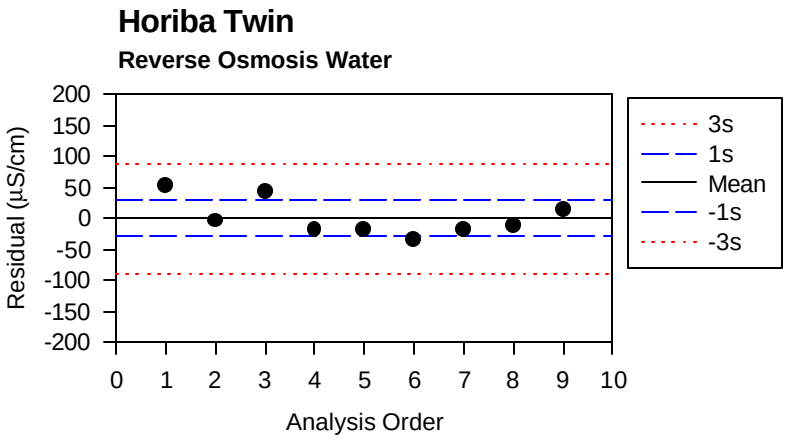



*Figure 29*

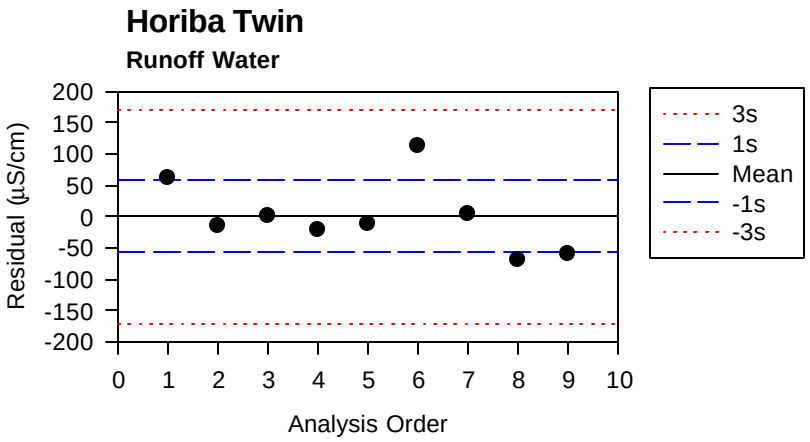



*Figure 30*

## 9.6 Horiba U-10

### *9.6.1 Method*

The Horiba U-10 is a multi-parameter instrument that measures conductivity, temperature, pH, DO and turbidity. The instrument is designed for *in situ* use. It has a large probe connected to the hand-held meter by a 30 m cable. The instrument probe is lowered into the test area and the desired parameter is selected from the hand held unit.

### *9.6.2 Observations*

This instrument is also quite easy to use. The meter calibrates all readings with a single buffered calibration solution (a special pH 4 buffer). A daily check is recommended with the calibration solution. This instrument is probably too expensive for many application unless the other parameters measured by the instrument (turbidity, DO, temperature, and pH, in addition to conductivity and calculated salinity) are needed. However it could be very useful for measuring standard water quality parameters *in situ* without sampling the water.

*Table 37*

| Sample ID | NaCl Conc.(mg/L) | Analysis Order | Reverse Osmosis (µmhos/cm) | Analysis Order | Runoff (µmhos/cm) |
|---|---|---|---|---|---|
| Cl LR RO 0 | 0.00 | 9 | 0 | 18 | 60 |
| Cl LR RO 1 | 2.00 | 13 | 10 | 4 | 50 |
| Cl LR RO 2 | 9.99 | 14 | 20 | 16 | 60 |
| Cl LR RO 3 | 19.96 | 2 | 50 | 12 | 80 |
| Cl LR RO 4 | 99.01 | 15 | 190 | 11 | 230 |
| Cl HR RO 1 | 99.73 | 10 | 210 | 7 | 240 |
| Cl HR RO 2 | 397.73 | 5 | 730 | 6 | 770 |
| Cl HR RO 3 | 988.42 | 17 | 2000 | 3 | 2000 |
| Cl HR RO 4 | 1957.45 | 1 | 3700 | 8 | 3800 |

**Table 14**

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.999433376 |
| R Square | 0.998867073 |
| Adjusted R Square | 0.998705226 |
| Standard Error | 45.87079733 |
| Observations | 9 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 12986026.65 | 12986026.65 | 6171.684427 | 1.42505E-11 |
| Residual | 7 | 14728.91033 | 2104.130047 | | |
| Total | 8 | 13000755.56 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 10.06913701 | 18.0780934 | 0.55698003 | 0.594892801 | -32.67873048 | 52.8170045 | -32.67873048 | 52.8170045 |
| NaCl Conc.(mg/L) | 1.907897168 | 0.024285839 | 78.56006891 | 1.42505E-11 | 1.850470325 | 1.96532401 | 1.850470325 | 1.96532401 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Conductivity (mmhos)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 10.06913701 | -10.06913701 | -0.219510835 |
| 2 | 13.88493134 | -3.884931345 | -0.084692911 |
| 3 | 29.12902971 | -9.129029713 | -0.199016155 |
| 4 | 48.15076447 | 1.849235527 | 0.040314004 |
| 5 | 198.9700356 | -8.970035566 | -0.195550025 |
| 6 | 200.3437215 | 9.656278473 | 0.210510369 |
| 7 | 768.8970774 | -38.89707745 | -0.84797038 |
| 8 | 1895.872855 | 104.1271447 | 2.270009477 |
| 9 | 3744.682448 | -44.68244758 | -0.974093545 |

*Table 15*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.999817637 |
| R Square | 0.999635308 |
| Adjusted R Square | 0.999583209 |
| Standard Error | 26.27831687 |
| Observations | 9 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 13249766.15 | 13249766.15 | 19187.26718 | 2.6961E-13 |
| Residual | 7 | 4833.849562 | 690.5499374 | | |
| Total | 8 | 13254600 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 44.63569858 | 10.3565208 | 4.309912512 | 0.003523482 | 20.14643585 | 69.12496131 | 20.14643585 | 69.12496131 |
| NaCl Conc. (mg/L) | 1.927173988 | 0.013912794 | 138.5181114 | 2.6961E-13 | 1.894275481 | 1.960072495 | 1.894275481 | 1.960072495 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Conductivity (mmhos)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 44.63569858 | 15.36430142 | 0.584676009 |
| 2 | 48.49004656 | 1.509953443 | 0.057460052 |
| 3 | 63.88816672 | -3.888166719 | -0.147961026 |
| 4 | 83.10209138 | -3.102091377 | -0.118047567 |
| 5 | 235.4451951 | -5.445195111 | -0.207212476 |
| 6 | 236.8327604 | 3.167239618 | 0.120526731 |
| 7 | 811.1306087 | -41.13060874 | -1.565191901 |
| 8 | 1949.493012 | 50.50698842 | 1.922002413 |
| 9 | 3816.982421 | -16.98242095 | -0.646252233 |

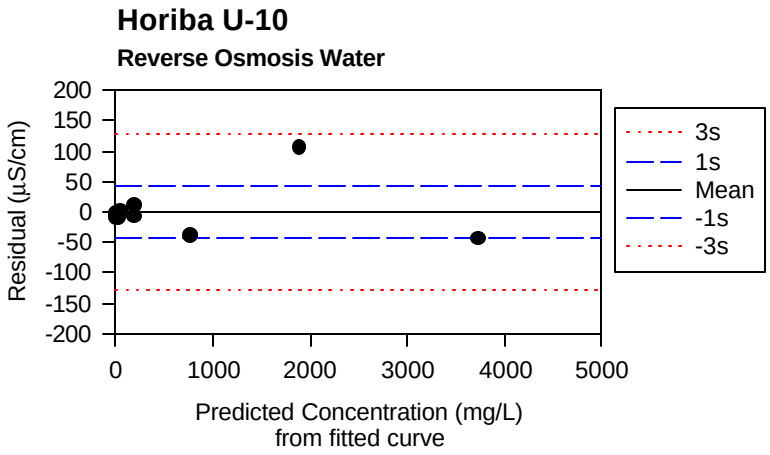



*Figure 31*

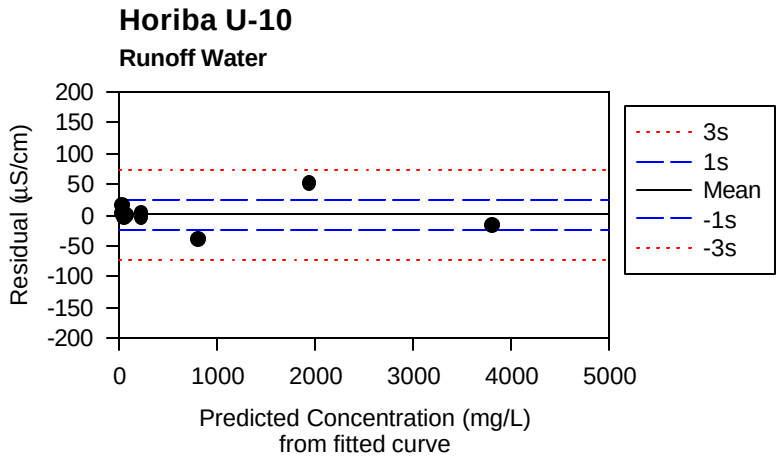



*Figure 32*

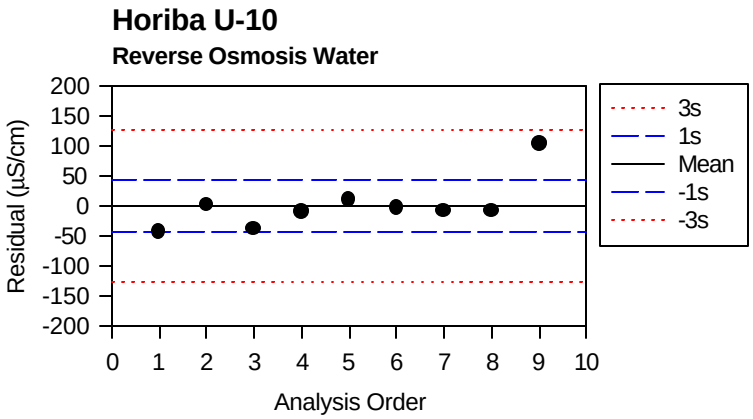



*Figure 33*

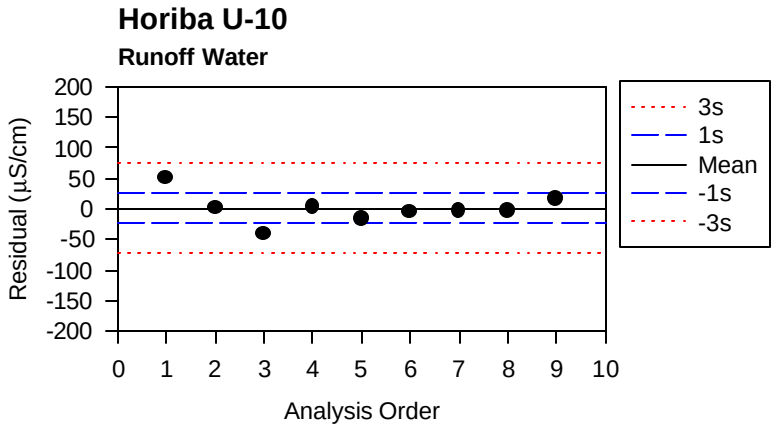



*Figure 34*

## 9.7 TDSTestr3 Conductivity Meter (as supplied in the GDS Aqua Vats test kit)

### *9.7.1 Method*

Measuring conductivity with the TDSTestr 3 conductivity meter, supplied by GDS in their Aqua Vacs test kit, is similar to the Horiba Twin and is also extremely easy to use. The entire meter is about 6 inches long and 1 thick and a little over one inch wide. The probe is immersed in the sample up to about one inch in depth. The meter displays the conductivity measurements continuously and the users selects an appropriate value when apparent stability occurs. The meter automatically compensates for temperature. In addition, the meter allows an internal 1 point calibration.

### *9.7.2 Observations*

The only reagent required for this meter is the calibration buffer, which is not hazardous and can be disposed of easily. Calibration is completed by submerging the bottom of the meter in a buffer solution, then using a small screwdriver or other thin, flat object to adjust the screw on the back until the meter reads within 10 µS/cm of the buffer amount. The meter has a tendency to drift, and several calibrations were required in the first day of use before a maintainable calibration was reached. The calibration buffer supplied with the kit is 1413 µS/cm. During testing against 445 and 1413 µS/cm buffers, the meter had an average recovery of 97.6%.

Additional tests were made to demonstrate the linearity of conductivity measurements using mixtures of sewage and spring water, ranging from 0.1 to 99.9%, as shown on the Figure 17. These tests were conducted to demonstrate the possible use of conductivity to help detect the presence of sanitary sewage contamination in water found in telecommunication manholes. Increasing amounts of sewage significantly increased the conductivity of the water, but the uncontaminated water conductivity would need to be well established before this technique would be useful. However, unusually high conductivity values could indicate potential problems in the water, especially in areas where road salting is used. The relatively low upper limit of the instrument may limit its usefulness in areas having relatively high conductivity values (areas potentially contaminated by snowmelt or intruding saline marine waters).

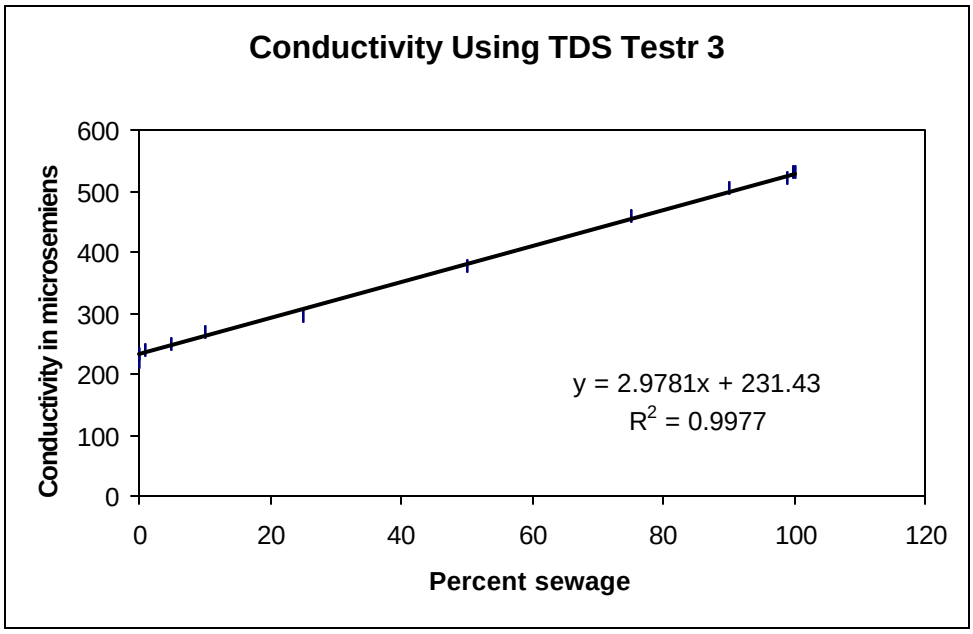

Conductivity Using TDS Testr 3
Conductivity in microsemiens
600
500
400
300
200
100
0
0
20
40
60
80
100
120
Percent sewage
y = 2.9781x + 231.43
R2 = 0.9977

**Figure 17**

# 10 Copper Summary

# 11 Copper

Eight methods for determining copper concentrations in the water column were evaluated: CHEMetrics DCR Photometer and CHEMetrics C3501, HACH Bicinchoate AccuVac, La Motte BCA and La Motte DDC, Palintest and Metalyzer. Four methods use a spectrophotometer/colorimeter to determine the concentration of an organo-copper complex. The HACH and La Motte BCA methods use the same ligand, bicinchoate. The last two tests are really laboratory methods modified for portable field use. Both the Palintest and Metalyzer are electro-chemical methods, well adopted for field use, but they are very expensive ($2300 to $4200) and were only examined in a preliminary manner. A comparison of each kit is summarized in the table below.

*Table 38*

| Kit Name | Method | Capital cost | Expendable Cost (per sample) | Time Required (min) | Sample Vol. (ml) | Expertise Required |
|---|---|---|---|---|---|---|
| CHEMetrics Copper 1 DCR Photometer Kit | colorimeter | $435 for kit | $0.63 | 15 | 25 | little |
| CHEMetrics Copper C3501 Comparator Kit | color comparator | Supplied as part of GDS's Aqua Vats test kit | na | 1 | 25 | none |
| La Motte Copper (Diethyldithiocarbamate) | colorimeter | $895 for Smart Colorimeter | $0.41 | 10 | 10 | none |
| La Motte Copper (Bicinchoninic Acid) | colorimeter | $895 for Smart Colorimeter | $0.23 | 20 | 10 | none |
| HACH Copper, Bicinchoate Method using AccuVac Ampoules | colorimeter | $1495 for DR 2000 | $0.28 | 2 | 25 | little |
| HACH Adaptation of La Motte DDC Method | colorimeter | $1495 for DR 2000 | $0.41 | 10 | 10 | little |
| Palintest SA-1000 Scanning Analyzer | anodic stripping voltametry | $2295 | $5.50 for both Cu and Pb | 5 | 25 | little |
| Environmental Technologies Group Metalyzer 3000 | anodic stripping voltametry | $4200 | $15.00 for both Cu and Pb | 5 | 25 | little |

*Table 39*

| Kit Name | Precision | Shelf Life | Regular Maintenance | Safety Hazards | Upper Limit of Useful Range (mg/L) |
|---|---|---|---|---|---|
| CHEMetrics Copper 1 DCR Photometer Kit | not evaluated | not indicated | Change Batteries | Sharps | <3.5 |
| CHEMetrics Copper C3501 Comparator Kit | not evaluated | not indicated | None | Sharps | <1.0 |
| La Motte Copper (Diethyldithiocarbamate) Note: Parallel and precision analyses completed with DR 2000 spectrophotometer. | 0.1457 | not indicated | Charge batteries. | | <3.5 |
| La Motte Copper (Bicinchoninic Acid) | not evaluated | not indicated | Charge batteries. | | <3.5 |
| HACH Copper, Bicinchoate Method using AccuVac Ampoules | not evaluated | not indicated | Change batteries. | Sharps | <5.0 |
| HACH Adaptation of La Motte DDC Method | 0.23 | not indicated | Change batteries. Check calibration | | unknown |
| Palintest SA-1000 Scanning Analyzer | not directly evaluated | about 1 year | Charge batteries | None | <2.0 |
| Environmental Technologies Group Metalyzer 3000 | not directly evaluated | about 1 year | Charge batteries | None | <2.5 |

## 11.1 Spiked Samples

The following tables and figures summarize the performance of each method with the reverse osmosis and runoff spikes. The CHEMetrics test clearly shows the lowest detection limit. However, the error associated with the measurements is the highest, and the method has the smallest working range. Therefore, the CHEMetrics test may be well suited when “detection” or “non-detection” is the only criteria for screening. The data also indicates that copper measurements significantly below 1 mg/L may be very difficult with any of these methods, except for the expensive stripping voltametry methods. However, more quantitative data may be found using the La Motte DDC or HACH bicinchoate method. These two methods were selected for further evaluation. The La Motte method was adapted for use with the DR 2000 spectrophotometer for further evaluation.

*Table 40 Reverse Osmosis*

| Kit Name | Adjusted $R^2$ | Standard Error | Intercept | p-Value | Slope | p-Value | Detection Limit ($\alpha$=0.05) (mg/L) | Limit of Quantification ($\alpha$=0.05) (mg/L) |
|---|---|---|---|---|---|---|---|---|
| CHEMetrics Copper 1 DCR Photometer Kit | 0.8957 | 0.1368 | 0.0649 | 0.4760 | 0.6423 | 9.5148E-03 | 0.2953 | 0.5256 |
| La Motte Copper (Diethyldithio-carbamate) | 0.9999 | 0.0169 | 0.0715 | 0.0057 | 1.1168 | 2.9490E-07 | 0.0999 | 0.1283 |
| La Motte Copper (Bicinchoninic Acid) | 0.8360 | 0.2564 | 0.2091 | 0.2567 | 0.9365 | 1.9026E-02 | 0.6409 | 1.0726 |
| HACH Copper, Bicinchoate Method using AccuVac Ampoules | 0.9708 | 0.2327 | 0.1482 | 0.2869 | 0.9722 | 2.0579E-04 | 0.5400 | 0.9319 |

*Table 41 Runoff*

| Kit Name | Adjusted $R^2$ | Standard Error | Intercept | p-Value | Slope | p-Value | Detection Limit ($\alpha$=0.05) (mg/L) | Limit of Quantification ($\alpha$=0.05) (mg/L) |
|---|---|---|---|---|---|---|---|---|
| CHEMetrics Copper 1 DCR Photometer Kit | 0.7790 | 0.1704 | 0.0776 | 0.4922 | 0.5230 | 3.0203E-02 | 0.3645 | 0.6515 |
| La Motte Copper (Diethyldithio-carbamate) | 0.9801 | 0.1823 | 0.2475 | 0.0590 | 0.9259 | 9.5526E-05 | 0.5545 | 0.8616 |
| La Motte Copper (Bicinchoninic Acid) | 0.8067 | 0.2784 | 0.2186 | 0.2714 | 0.9251 | 2.4527E-02 | 0.6875 | 1.1564 |
| HACH Copper, Bicinchoate Method using AccuVac Ampoules | 0.9665 | 0.2480 | 0.1259 | 0.3830 | 0.9644 | 2.7250E-04 | 0.5435 | 0.9611 |

# Copper

## Spike Addition to RO Water

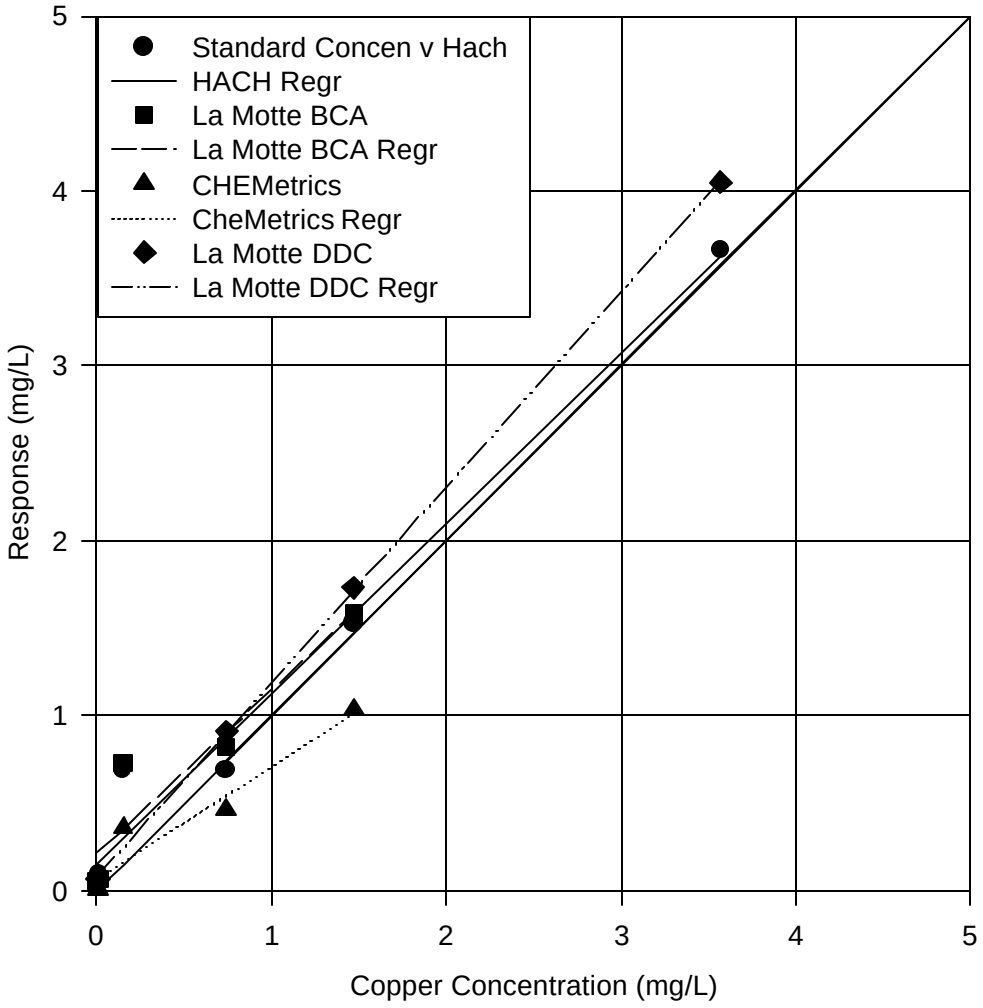



*Figure 35*

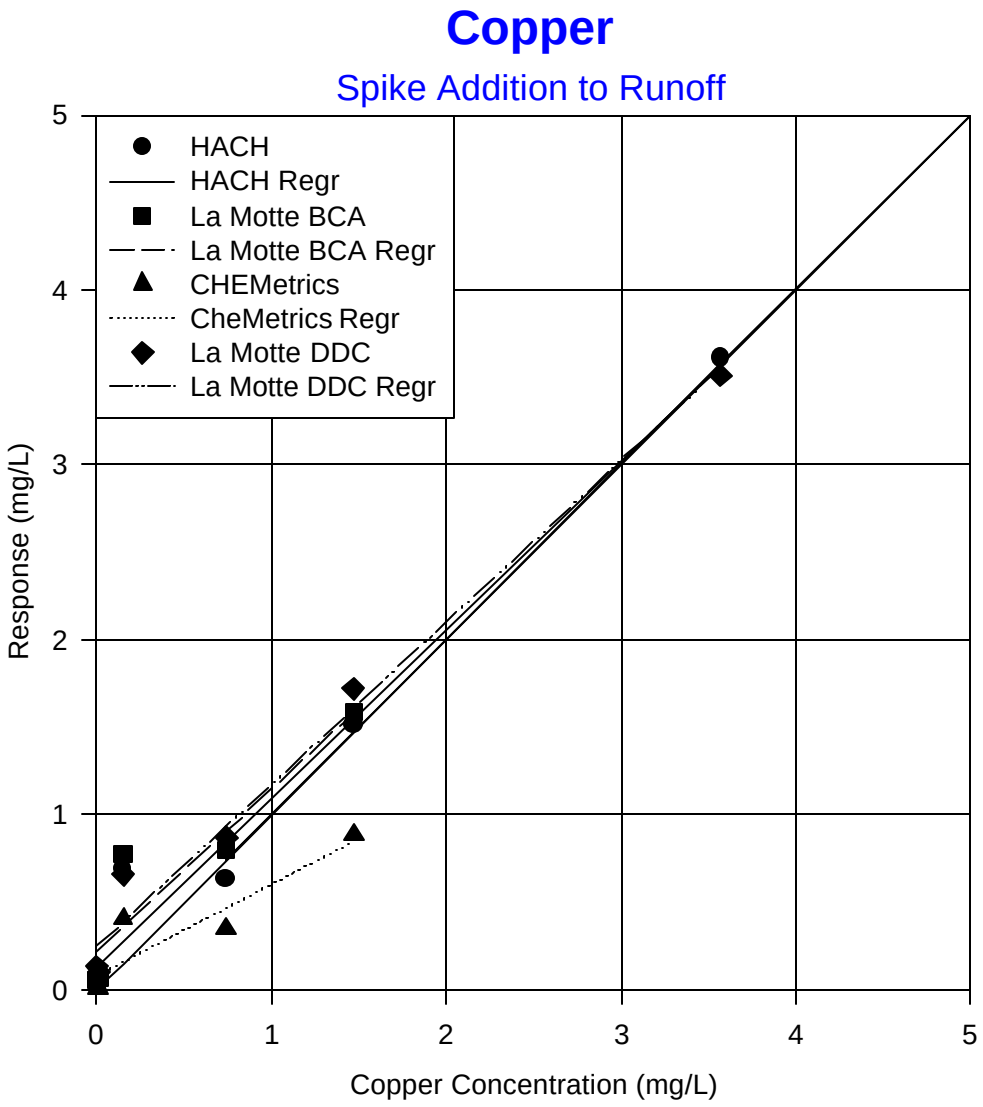



*Figure 36*

## 11.2 Conclusions

The wide variability in test comparisons shown in our evaluation is indicative of problems that will be faced by any field screening method. These methods only measure the amount of soluble copper. This form of copper is usually $Cu^{+}$ or $Cu^{2+}$. These charged species will most likely be associated with particulate surfaces in the natural environment and not be free ions in the solution. Therefore, none of these methods will detect the true amount of copper in the sample. In the laboratory, samples are digested to make all forms of copper available for analysis. In addition, each method uses a different method to prepare the free copper for complexation. Each of these will have varying success freeing copper for detection by the respective method.

None of these methods have great analytical capability. If a simple detection of copper is sufficient, the user may wish to consider the CHEMetrics DCR photometer. If a more quantitative analysis is required, we recommend the HACH bicinchoate method. The HACH method is very simple and provides answers comparable with the other methods. It also has the largest working range of any of the methods.

In these analyses we also explored adapting La Motte methods for use with the HACH DR 2000 spectrophotometer. There is no logical reason why the these methods cannot be adapted. In our limited explorations we encountered no difficulty. To adapt the methods, the user has to create an external calibration curve and make instrument readings in the absorbance mode.

# 12

# 13 CHEMetrics DCR Photometer, Copper

## 13.1 Method

This procedure uses the reaction of copper ions with an organic ligand to produce a colored complex. In this case the complex is the product of $Cu^{+}$ and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonicacid. The spectrophotometer included in the kit measures the absorbance of the complex to determine the copper concentration.

Place a ampoule in about 25 mL of sample. Break the ampoule tip under the surface of the sample. This draws a known volume of sample into the ampoule to react with the reagents. There is a one minute reaction time before measurement. The photometer reports the concentration in ppm. The ampoule contains a buffer to bring the solution to pH 7, where hydroxylamine reduces all soluble copper to $Cu^{+}$. The $Cu^{+}$ forms a colored complex with 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonicacid.

This method has problems common to all similar field screening methods for copper, specifically, the concentration determination must rely on a standard curve. The conditions under which the standard curve were derived may or may not be applicable to a desired use. The method depends on the formation of the copper complex. Any chemical agent interfering with this reaction will skew the results. Potential interferences of this type include any chelating agent, such as EDTA, that will selectively bind any copper ions before complexation with the bicinchoate which will lower the reported copper concentration from its true value. Other metal ions present in large concentrations may also compete with copper for bicinchoate ligands. The method has no means to determine the background absorbance in the range of interest. Therefore, any material present in the sample that absorbs over the same wavelength will contribute to the reported concentration which is larger than the true value. Any metallic or chelated copper will not be detected. This is important since relatively small electrical potentials or pH changes could release the copper at a later date. All materials required for the determination are included in the kit except for Kim Wipes to clean the ampoules before measurement.

### *13.1.1 Observations*

Since the path length utilized by the DCR photometer is longer than the other methods, the readings should be more accurate. Even though the residuals were very small for both sample types, the response factor (regression coefficient for the slope of the best fit line comparing spike concentrations to measured response) was very low (52% and 64%).

*Table 42*

| Sample ID | spike conc. (mg/L) | Order | RO Response (mg/L) | RO Percent Recovery | Order | Runoff Response (mg/L) |
|---|---|---|---|---|---|---|
| Cu X 0 | 0.000 | 9 | 0.00 | NA | 5 | 0.00 |
| Cu X 1 | 0.015 | 1 | 0.00 | 0.00 | 8 | 0.00 |
| Cu X 2 | 0.150 | 7 | 0.36 | 240.00 | 11 | 0.40 |
| Cu X 6 | 0.740 | 14 | 0.46 | 62.16 | 16 | 0.35 |
| Cu X 7 | 1.470 | 17 | 1.03 | 70.07 | 15 | 0.88 |
| Cu X 3 | 3.571 | 13 | | | 3 | |

*Table 43*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.960086313 |
| R Square | 0.921765729 |
| Adjusted R Square | 0.895687639 |
| Standard Error | 0.136797798 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 0.661459087 | 0.661459087 | 35.3463661 | 0.009514791 |
| Residual | 3 | 0.056140913 | 0.018713638 | | |
| Total | 4 | 0.7176 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.064884131 | 0.079853239 | 0.81254225 | 0.475970723 | -0.189244754 | 0.319013015 | -0.189244754 | 0.319013015 |
| spike conc. (mg/L) | 0.642349198 | 0.108043539 | 5.945280994 | 0.009514791 | 0.298506115 | 0.986192282 | 0.298506115 | 0.986192282 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.064884131 | -0.064884131 | -0.474306835 |
| 2 | 0.074519369 | -0.074519369 | -0.544740994 |
| 3 | 0.161236511 | 0.198763489 | 1.452972868 |
| 4 | 0.540222538 | -0.080222538 | -0.586431496 |
| 5 | 1.009137452 | 0.020862548 | 0.152506457 |

*Table 44*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.913377769 |
| R Square | 0.83425895 |
| Adjusted R Square | 0.779011933 |
| Standard Error | 0.170391937 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 0.438419763 | 0.438419763 | 15.10052486 | 0.030203203 |
| Residual | 3 | 0.087100237 | 0.029033412 | | |
| Total | 4 | 0.52552 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.077596126 | 0.09946321 | 0.780149026 | 0.492197698 | -0.238940495 | 0.394132748 | -0.238940495 | 0.394132748 |
| spike conc. (mg/L) | 0.522955524 | 0.134576346 | 3.885939379 | 0.030203203 | 0.094673126 | 0.951237922 | 0.094673126 | 0.951237922 |

RESIDUAL
OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.077596126 | -0.077596126 | -0.455397876 |
| 2 | 0.085440459 | -0.085440459 | -0.501434872 |
| 3 | 0.156039455 | 0.243960545 | 1.431761087 |
| 4 | 0.464583214 | -0.114583214 | -0.67246852 |
| 5 | 0.846340746 | 0.033659254 | 0.19754018 |

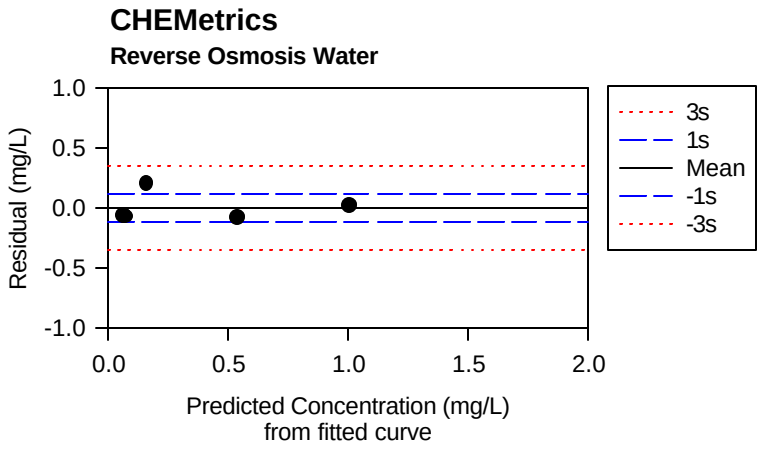

CHEMetrics
Reverse Osmosis Water
Residual (mg/L)
1.0
0.5
0.0
-0.5
-1.0
0.0
0.5
1.0
1.5
2.0
Predicted Concentration (mg/L)
from fitted curve
3s
1s
Mean
-1s
-3s

*Figure 37*

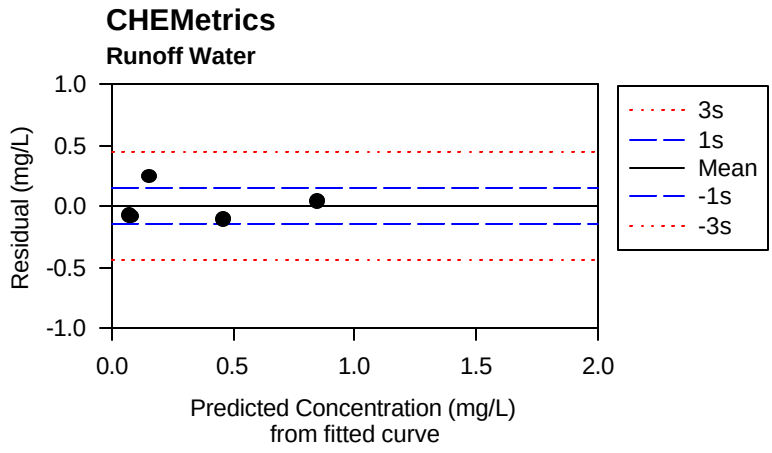



*Figure 38*

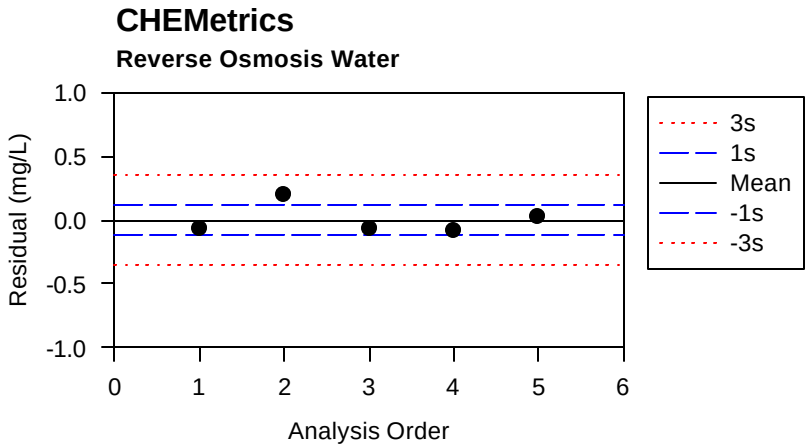



*Figure 39*

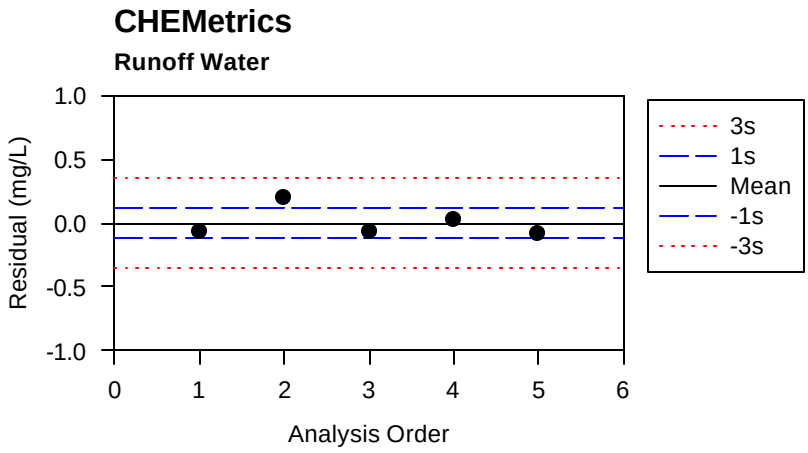



*Figure 40*

## 13.2 HACH Bicinchoate Method

### *13.2.1 Method*

The HACH Bicinchoate method uses the HACH DR2000 spectrophotometer to detect the presence of a copper bicinchoate complex in the sample solution.

A sample blank is scanned by the DR2000. An AccuVac ampoule is immersed in approximately 50 mL of sample and the tip is broken. A known volume is drawn into the ampoule. After a two minute reaction time, the ampoule is scanned to determine the copper complex concentration.

This method (as for most field screening methods) is susceptible to many interferences. The conditions under which the standard curve were derived may or may not be applicable to the desired uses. The method depends on the formation of the copper bicinchoate complex. Any chemical agent interfering with this reaction will skew the results. Potential interferences of this type include any chelating agent, such as EDTA, that will selectively bind any copper ions before complexation with the bicinchoate. Chelation will lower the reported copper concentration from its true value. Other metal ions present in large concentrations may also compete with copper for bicinchoate ligands. This interference will most likely produce a reported concentration larger than the true value if the metal complex absorbs in the same range as the copper complex. The most important potential error associated with this method is it

only indicates the presence of ionized copper. Any metallic or chelated copper will not be detected. This is important since small electrical potentials or pH changes could release the ionized copper at a later date.

The required materials include the HACH DR2000, AccuVac CuVer II reagent ampoules, a 100 mL beaker, and Kim Wipes. The procedure was tested using equipment in a lab, but a complete kit excluding Kim Wipes is available.

### *13.2.2 Observations*

*Table 45*

| Sample ID | spike conc. (mg/L) | Order | RO Response (mg/L) | RO Percent Recovery | Order | Runoff Response (mg/L) |
|---|---|---|---|---|---|---|
| Cu X 0 | 0.000 | 8 | 0.01 | NA | 5 | 0.02 |
| Cu X 1 | 0.015 | 2 | 0.09 | 600 | 4 | 0.03 |
| Cu X 2 | 0.150 | 6 | 0.69 | 460 | 9 | 0.69 |
| Cu X 6 | 0.740 | 14 | 0.69 | 93 | 15 | 0.63 |
| Cu X 7 | 1.470 | 12 | 1.53 | 104 | 13 | 1.51 |
| Cu X 3 | 3.571 | 11 | 3.66 | 102 | 3 | 3.61 |

*Table 46*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.988264199 |
| R Square | 0.976666126 |
| Adjusted R Square | 0.970832658 |
| Standard Error | 0.23269452 |
| Observations | 6 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 9.065496374 | 9.065496374 | 167.4246021 | 0.000205785 |
| Residual | 4 | 0.216586959 | 0.05414674 | | |
| Total | 5 | 9.282083333 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.148187154 | 0.120702108 | 1.227709745 | 0.286862767 | -0.186936317 | 0.483310625 | -0.186936317 | 0.483310625 |
| spike conc. (mg/L) | 0.972229579 | 0.075137924 | 12.9392659 | 0.000205785 | 0.763612825 | 1.180846332 | 0.763612825 | 1.180846332 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.148187154 | -0.138187154 | -0.593856502 |
| 2 | 0.162770598 | -0.072770598 | -0.312730173 |
| 3 | 0.294021591 | 0.395978409 | 1.701709213 |
| 4 | 0.867637042 | -0.177637042 | -0.763391601 |
| 5 | 1.577364635 | -0.047364635 | -0.203548562 |
| 6 | 3.62001898 | 0.03998102 | 0.171817625 |

*Table 47*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.98649117 |
| R Square | 0.973164829 |
| Adjusted R Square | 0.966456036 |
| Standard Error | 0.247983945 |
| Observations | 6 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 8.920499186 | 8.920499186 | 145.0581152 | 0.0002725 |
| Residual | 4 | 0.245984147 | 0.061496037 | | |
| Total | 5 | 9.166483333 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.125923352 | 0.12863296 | 0.978935354 | 0.383040058 | -0.231219739 | 0.483066442 | -0.231219739 | 0.483066442 |
| spike conc. (mg/L) | 0.964423123 | 0.080074936 | 12.04400744 | 0.0002725 | 0.742098999 | 1.186747247 | 0.742098999 | 1.186747247 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.125923352 | -0.105923352 | -0.427137942 |
| 2 | 0.140389699 | -0.110389699 | -0.445148571 |
| 3 | 0.27058682 | 0.41941318 | 1.69129167 |
| 4 | 0.839596463 | -0.209596463 | -0.845201745 |
| 5 | 1.543625343 | -0.033625343 | -0.135594837 |
| 6 | 3.569878324 | 0.040121676 | 0.161791425 |

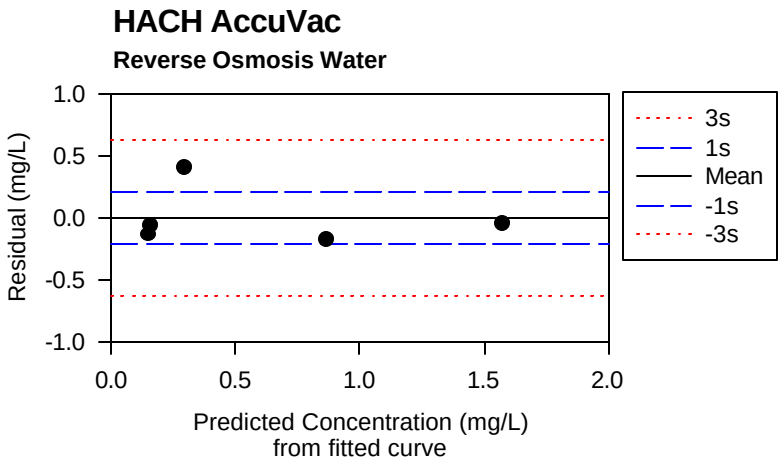



*Figure 41*

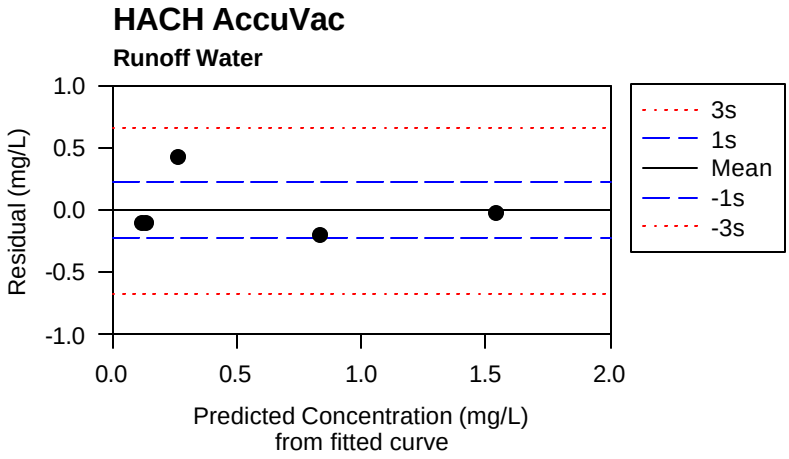



*Figure 42*

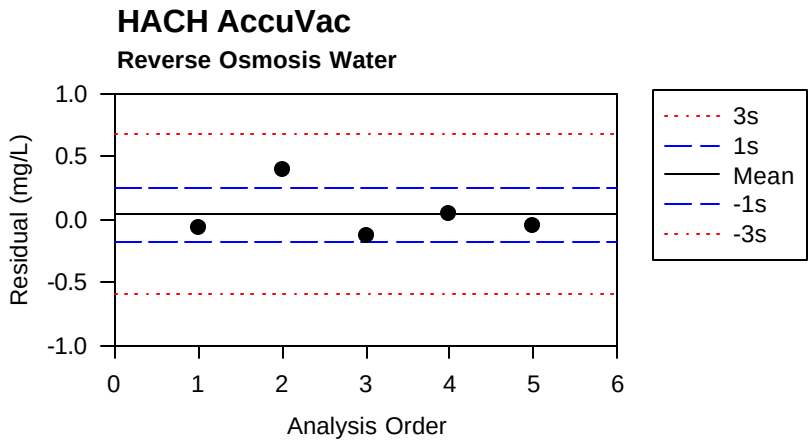



*Figure 43*

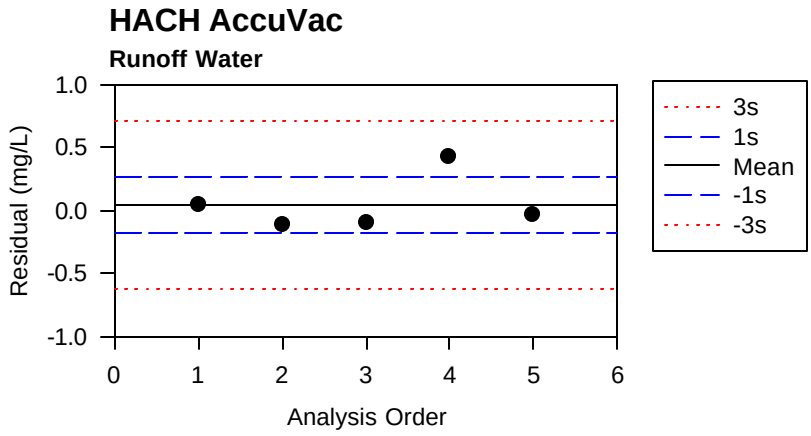



*Figure 44*

## 13.3 La Motte Copper, BCA Method

### *13.3.1 Method*

The La Motte BCA method has a reported range of 0-3.0 ppm. This method uses the La Motte Smart Colorimeter to detect the presence of a copper bicinchoate complex in the sample solution.

Approximately 10 mL of sample is collected. The sides of the cuvette must be cleaned with a soft cloth such as a Kim Wipe. The sample is then scanned by the Smart Colorimeter to detect any background absorbance in the same range of wavelengths used to detect the copper complex. One pre-packaged tablet containing all reagents is added to the sample. A two minute reaction time after dissolution of the tablet is required before proceeding. The sample is scanned again to determine the concentration of the copper complex in the sample solution. The Smart Colorimeter automatically adjusts for background and converts the reading to ppm.

This method (as for most field screening methods) is susceptible to many interferences. The conditions under which the standard curve were derived may or may not be applicable to the desired use. The method depends on the formation of the copper bicinchoate complex. Any chemical agent interfering with this reaction will skew the results. Potential interferences of this type include any chelating agent, such as EDTA, that will selectively bind any copper ions before complexation with the bicinchoate. Chelation will lower the reported copper concentration from its true value. Other metal ions present in large concentrations may also compete with copper for bicinchoate ligands. This interference will most likely produce a reported concentration larger than the true value if the metal complex absorbs in the same range as the copper complex. This is very likely since the Smart Colorimeter uses glass filters which select relatively broad wavelength ranges. The most important potential error associated with this method is it only indicates the presence of ionized copper. Any metallic or chelated copper will not be detected. This is important since relatively small electrical potentials or pH changes could release the ionized copper at a later date.

The required materials are the Smart Colorimeter, the Copper BCA tablets, and Kim Wipes. The Kim Wipes must be provided by the user.

### *13.3.2 Observations*

The Smart Colorimeter is easy to use and to misuse. The simplicity of the controls means all commands are entered through menus. However, the device defaults to the next menu selection after executing a command. This is annoying when replicate procedures are used. The user must select previous item after each measurement or risk making the wrong measurement.

The method as published by the manufacturer is unclear whether the two minute reaction time begins after placing the pill into solution or after dissolution of the pill. We assumed the two minute reaction time should begin after dissolution so that all relevant reactions can proceed to completion. The time required for dissolution was approximately 5 minutes. Therefore, the sample run time was 10-15 minutes.

There are no manufacturers suggestions for the disposal of the sample after the determination; nor, is there any indication of the possibly hazardous nature of the sample after determination.

*Table 48*

| Sample ID | Spike Conc. (mg/L) | Order | RO Response (mg/L) | RO Percent Recovery | Order | Runoff Response (mg/L) |
|---|---|---|---|---|---|---|
| Cu X 0 | 0.000 | 4 | 0.06 | NA | 9 | 0.06 |
| Cu X 1 | 0.015 | 1 | 0.07 | 467 | 8 | 0.07 |
| Cu X 2 | 0.150 | 9 | 0.73 | 487 | 5 | 0.77 |
| Cu X 6 | 0.740 | 11 | 0.82 | 111 | 3 | 0.80 |
| Cu X 7 | 1.470 | 2 | 1.59 | 108 | 10 | 1.59 |
| Cu X 3 | 3.571 | 6 | NA | NA | 7 | |

*Table 49*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.936496157 |
| R Square | 0.877025052 |
| Adjusted R Square | 0.836033402 |
| Standard Error | 0.25636445 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 1.406151806 | 1.406151806 | 21.39521253 | 0.019026248 |
| Residual | 3 | 0.197168194 | 0.065722731 | | |
| Total | 4 | 1.60332 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.209133803 | 0.149648109 | 1.397503818 | 0.256679557 | -0.267113714 | 0.68538132 | -0.267113714 | 0.68538132 |
| Spike Conc. (mg/L) | 0.936560414 | 0.202477838 | 4.625495923 | 0.019026248 | 0.292184962 | 1.580935866 | 0.292184962 | 1.580935866 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.209133803 | -0.149133803 | -0.581725754 |
| 2 | 0.223182209 | -0.153182209 | -0.59751736 |
| 3 | 0.349617865 | 0.380382135 | 1.483755389 |
| 4 | 0.90218851 | -0.08218851 | -0.32059246 |
| 5 | 1.585877612 | 0.004122388 | 0.016080185 |

*Table 50*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.924689461 |
| R Square | 0.8550506 |
| Adjusted R Square | 0.806734133 |
| Standard Error | 0.278446526 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 1.372082596 | 1.372082596 | 17.69687762 | 0.024527295 |
| Residual | 3 | 0.232597404 | 0.077532468 | | |
| Total | 4 | 1.60468 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.21855611 | 0.162538121 | 1.344645237 | 0.271367119 | -0.298713217 | 0.73582543 7 | -0.298713217 | 0.73582543 7 |
| Spike Conc. (mg/L) | 0.925145032 | 0.219918364 | 4.206765695 | 0.024527295 | 0.225265988 | 1.62502407 5 | 0.225265988 | 1.62502407 5 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.21855611 | -0.15855611 | -0.569431094 |
| 2 | 0.232433286 | -0.162433286 | -0.583355403 |
| 3 | 0.357327865 | 0.412672135 | 1.482051656 |
| 4 | 0.903163433 | -0.103163433 | -0.370496392 |
| 5 | 1.578519306 | 0.011480694 | 0.041231233 |

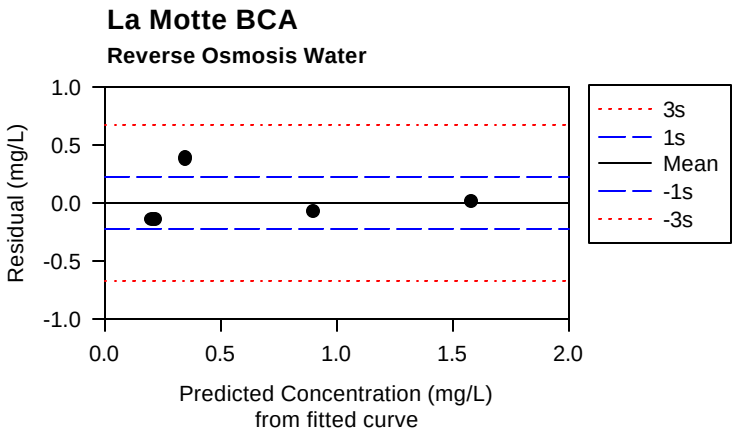



*Figure 45*

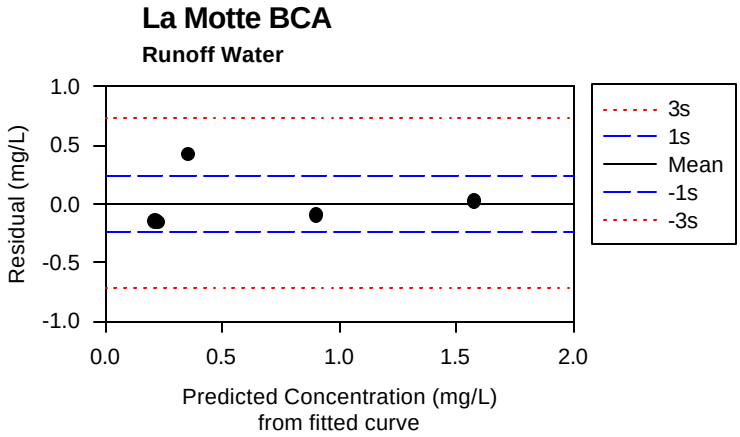



*Figure 46*

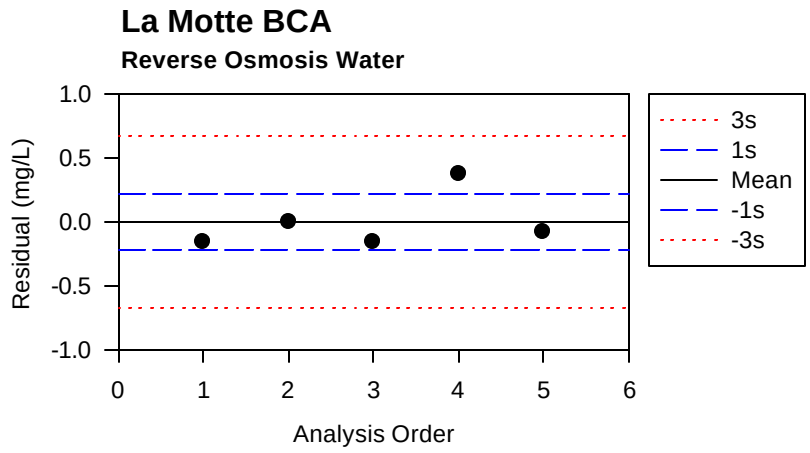



*Figure 47*

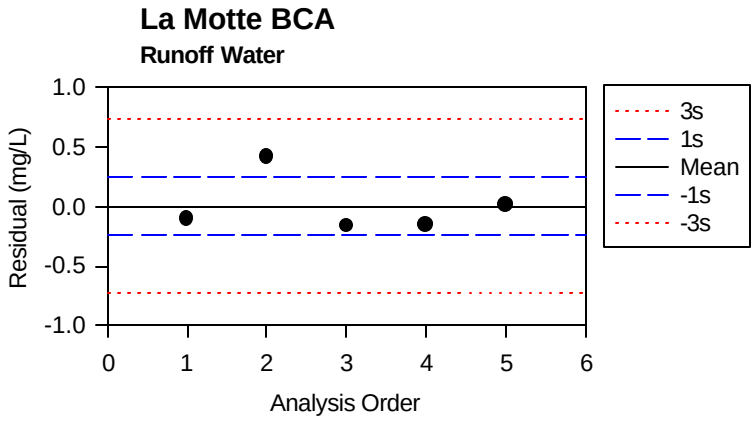



*Figure 48*

## 13.4 La Motte Copper, DDC Method

### *13.4.1 Method*

A solution containing diethyldithiocarbamate (DDC) is added to the sample. The DDC reacts with ionized copper to form a complex as in the BCA method. The Smart Colorimeter then detects the absorbance of the copper complex which should be proportional to the copper concentration in the sample. The reported range of the method is 0 to 5.0 ppm.

Collect 10 mL of sample in a Smart Colorimeter cuvette. Scan the sample to record background absorbance. Add 5 drops of DDC solution to the sample and scan again. The Smart Colorimeter reports the result in ppm. The method is dependent upon the same physical and chemical principles as the BCA method except the complex is now with DDC.

This method has a similar set of potential errors as for most of the other copper field screening methods. The concentration determination must rely on a standard curve. The conditions under which the standard curve were derived may or may not be applicable to the desired use. The method depends on the formation of the copper bicinchoate complex. Any chemical agent interfering with this reaction will skew the results. Potential interferences of this type include any chelating agent, such as EDTA, that will selectively bind any copper ions before complexation with the bicinchoate which will lower the reported copper concentration from its true value. Other metal ions present in large concentrations may also compete with copper for bicinchoate ligands. This interference will most likely produce a reported concentration larger than the true value if the metal complex absorbs in the same range as the copper complex. This is very likely since the Smart Colorimeter uses glass filters which select relatively broad wavelength ranges. The most important potential error associated with this method is it only indicates the presence of ionized copper. Any metallic or chelated copper will not be detected. This is important since small electrical potential or pH could change the copper to a free ionized state at a later date.

### *13.4.2 Observations*

During our evaluations, the bottom of the cuvette sheared. The sample then flooded the chamber of the unit and spilled into the main body of the Smart Colorimeter. The colorimeter then malfunctioned and was sent back to La Motte for repair. The service department was helpful and expedient. The instrument was returned in a few days with the necessary repairs and a free update of the instruction guide and software.

The runoff samples appear to show a trend of decreasing error with increasing concentration. This was not observed in the reverse osmosis samples. This may be indicative of a matrix interference.

*Table 51*

| Sample ID | spike conc. (mg/L) | Order | RO Response (mg/L) | RO Percent Recovery | Order | Runoff Response (mg/L) |
|---|---|---|---|---|---|---|
| Cu X 0 | 0.000 | 2 | 0.07 | NA | 7 | 0.13 |
| Cu X 1 | 0.015 | 1 | 0.07 | 467 | 12 | 0.10 |
| Cu X 2 | 0.150 | NA | NA | | 13 | 0.66 |
| Cu X 6 | 0.740 | 16 | 0.91 | 123 | 17 | 0.87 |
| Cu X 7 | 1.470 | 15 | 1.73 | 118 | 14 | 1.72 |
| Cu X 3 | 3.571 | 6 | 4.05 | 113 | 5 | 3.51 |

*Table 52*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.999960775 |
| R Square | 0.999921552 |
| Adjusted R Square | 0.999895403 |
| Standard Error | 0.016885494 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 10.90266464 | 10.90266464 | 38238.87724 | 2.94898E-07 |
| Residual | 3 | 0.00085536 | 0.00028512 | | |
| Total | 4 | 10.90352 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.071451771 | 0.010042407 | 7.11500479 | 0.005713366 | 0.039492321 | 0.10341122 | 0.039492321 | 0.10341122 |
| spike conc. (mg/L) | 1.116760032 | 0.005710936 | 195.5476342 | 2.94898E-07 | 1.098585268 | 1.134934797 | 1.098585268 | 1.134934797 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.071451771 | -0.001451771 | -0.085977381 |
| 2 | 0.088203171 | -0.018203171 | -1.07803606 |
| 3 | 0.897854194 | 0.012145806 | 0.719304146 |
| 4 | 1.713089018 | 0.016910982 | 1.001509482 |
| 5 | 4.059401846 | -0.009401846 | -0.556800186 |

*Table 53*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.992009124 |
| R Square | 0.984082103 |
| Adjusted R Square | 0.980102628 |
| Standard Error | 0.182336825 |
| Observations | 6 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 8.22156313 | 8.22156313 | 247.2894687 | 9.5526E-05 |
| Residual | 4 | 0.13298687 | 0.033246718 | | |
| Total | 5 | 8.35455 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.247462363 | 0.094580822 | 2.616411626 | 0.059021213 | -0.015136642 | 0.510061368 | -0.015136642 | 0.510061368 |
| spike conc. (mg/L) | 0.925870471 | 0.058877237 | 15.72544018 | 9.5526E-05 | 0.762400716 | 1.089340227 | 0.762400716 | 1.089340227 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.247462363 | -0.117462363 | -0.644205377 |
| 2 | 0.26135042 | -0.16135042 | -0.884903092 |
| 3 | 0.386342934 | 0.273657066 | 1.500832688 |
| 4 | 0.932606512 | -0.062606512 | -0.343356378 |
| 5 | 1.608491956 | 0.111508044 | 0.611549776 |
| 6 | 3.553745816 | -0.043745816 | -0.239917616 |

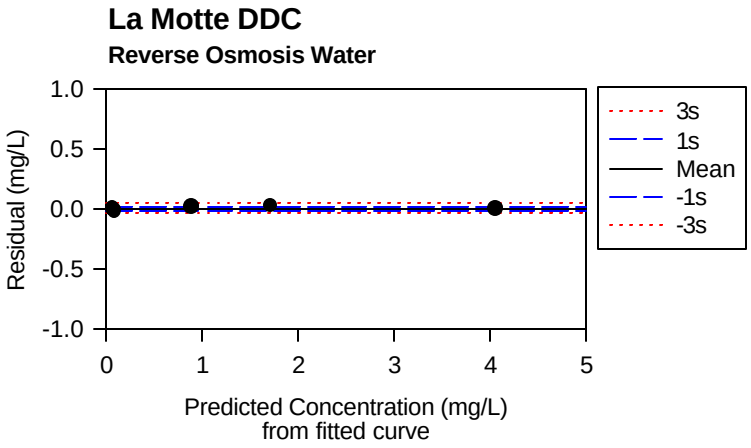



*Figure 49*

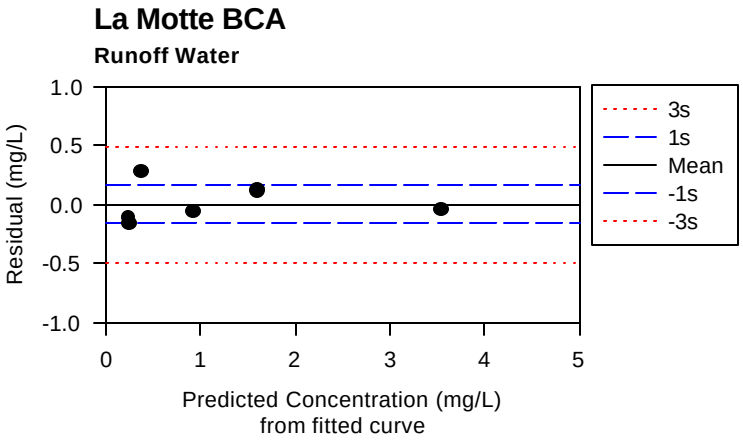



*Figure 50*

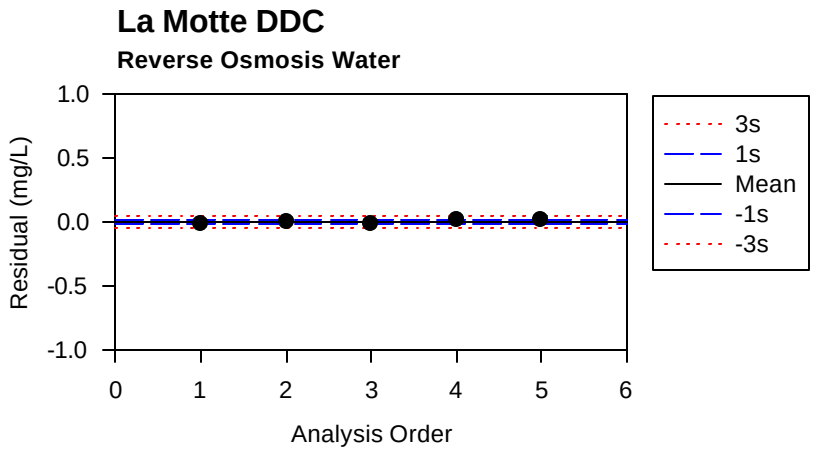



*Figure 51*

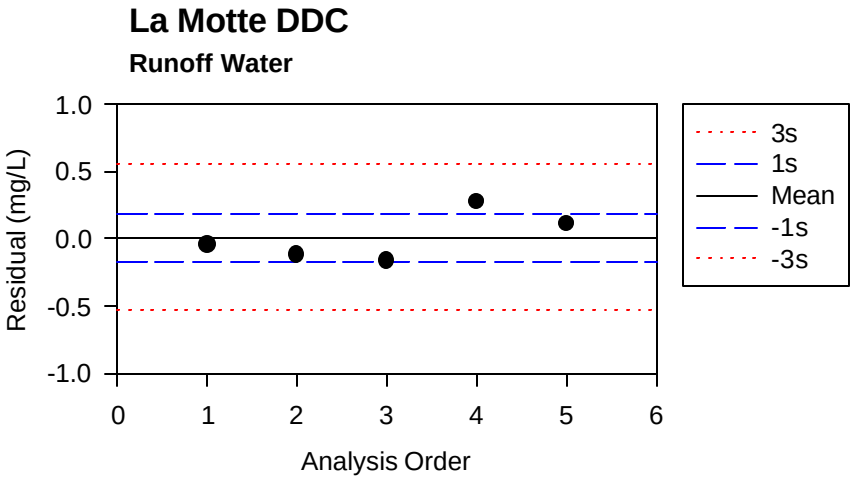



*Figure 52*

# 14 Adaptation of La Motte DDC Method

The adaptation of the La Motte DDC method for use with the HACH DR 2000 spectrophotometer was attempted to take advantage of the superior capabilities of the DR 2000 compared to the La Motte Smart Colorimeter. The procedure is quite simple.

In this case, the spectrophotometer must measure the absorbance of the copper-DDC complex. The first task is to determine the wavelength of maximum absorbance ($\lambda_{max}$). Many times this information will be available in the directions for the method or the literature. We determined $\lambda_{max}$ by scanning the solution with the SPEC 2000 UV-Vis Spectrometer. The printout clearly shows $\lambda_{max}$ occurring at approximately 450 nm. The second task was to create an external calibration curve of absorbance (abs) versus concentration. The DR 2000 method for absorbance measurements is coded 0. We used our reverse osmosis spikes to create the calibration curve. A regression line for this curve is then used to calculate the copper concentrations for other absorbance measurements within the calibration range.

A new set of calibration standards were prepared to determine the response of the DR 2000 to the La Motte DDC reagent system. The calibration data is presented below.

*Table 54*

| Sample ID | Spike Concentration (mg/L) | Response (abs) |
|---|---|---|
| CuRO0 | 0 | 0.042 |
| CuRO1 | 0.999 | 0.341 |
| CuRO2 | 1.996 | 0.680 |
| CuRO3 | 2.991 | 0.991 |
| CuRO4 | 4.975 | 1.545 |
| CuRO5 | 5.964 | 1.782 |

*Table 55*

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.998824825 |
| R Square | 0.99765103 |
| Adjusted R Square | 0.997063788 |
| Standard Error | 0.124760184 |
| Observations | 6 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 26.44315442 | 26.44315442 | 1698.874316 | 2.07074E-06 |
| Residual | 4 | 0.062260414 | 0.015565103 | | |
| Total | 5 | 26.50541483 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | -0.220602063 | 0.08966136 | -2.460391653 | 0.069662098 | -0.469542423 | 0.028338298 | -0.469542423 | 0.028338298 |
| Response (abs) | 3.391305032 | 0.082278474 | 41.21740307 | 2.07074E-06 | 3.162862892 | 3.619747172 | 3.162862892 | 3.619747172 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Spike Concentration (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | -0.078167251 | 0.078167251 | 0.626540047 |
| 2 | 0.935832953 | 0.063167047 | 0.506307742 |
| 3 | 2.085485359 | -0.089485359 | -0.717258955 |
| 4 | 3.140181224 | -0.149181224 | -1.195743862 |
| 5 | 5.018964211 | -0.043964211 | -0.352389762 |
| 6 | 5.822703504 | 0.141296496 | 1.132544791 |

## Calibration Curve: HACH Adaptation of La Motte DDC Method

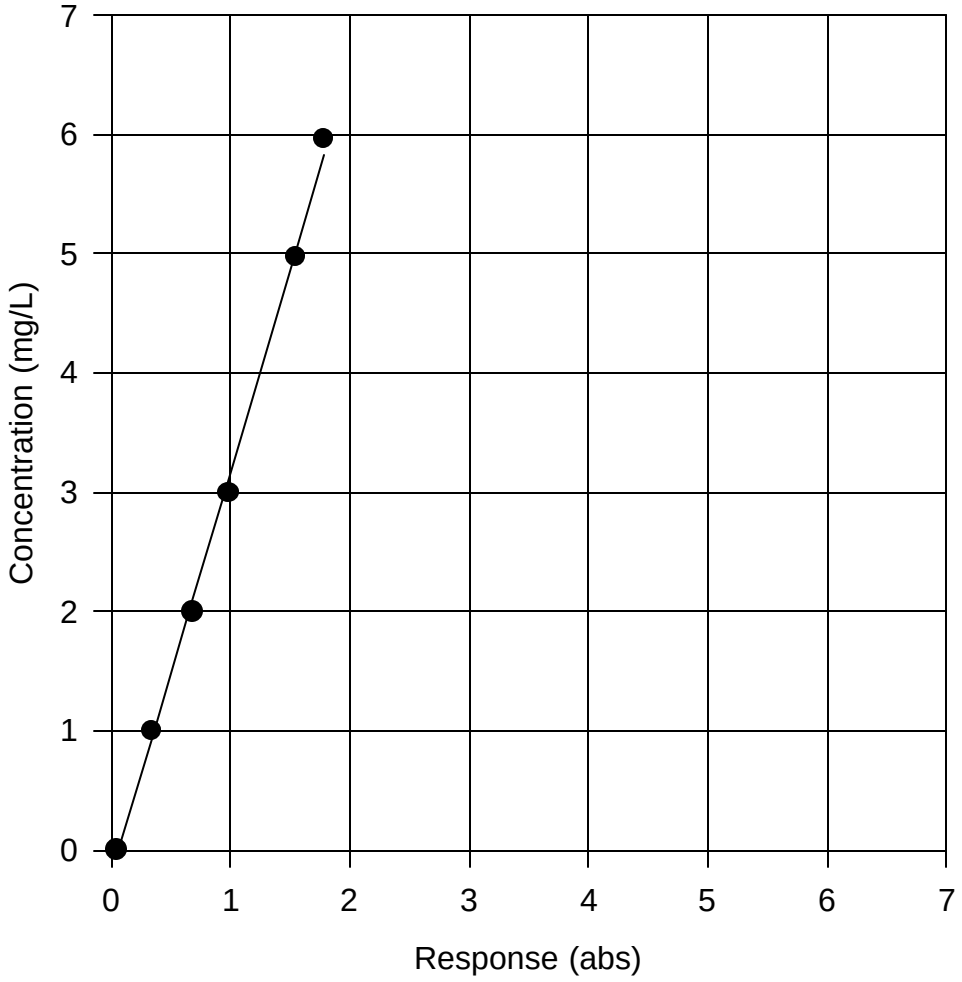



*Figure 53*

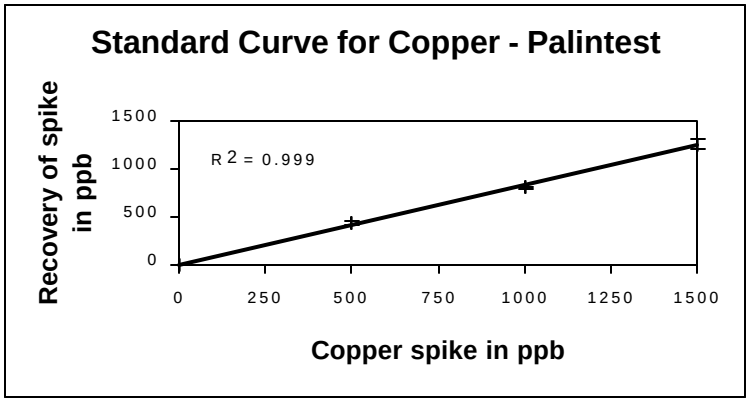
# 15 Field-Adapted Stripping Voltametry Methods

Due to the cost of these instruments and supplies for analyses, complete evaluations were not conducted. Comparisons with four standard solutions and with two previously evaluated samples (using a graphite furnace atomic absorption spectrophotometer) were made. We have also used the Palintest instrument for numerous field measurements (with few detectable results) and in laboratory treatability analyses (frequently in the range of detection). These are the only field measurement methods evaluated that provided consistent low-level analyses of copper in a relatively rapid manner. The reported detection limits for both of these instruments is 70 µg/L for copper. They also simultaneously evaluate lead using the same sample and supplies.

## 15.1 Palintest

The test supplies for the Palintest are relatively expensive, at about $5 per analysis (simultaneous with lead). The only reagent is a buffer pill that must be crushed in the bottom of the sample vial. The metals in the sample are electroplated on to an expendable electrode, which must be carefully inserted into the test tube holder. Touching the electrode, bending it, or prematurely inserting it into the sample will ruin the electrode. This makes the test a little difficult and expensive to do (new users probably ruin about half of the electrodes, while more experienced users may still ruin up to about one-fourth of the electrodes). The instrument automatically begins the analysis, taking about 5 minutes to return the results. The lowest reported value is 70 µg/L, while the highest value that can be reported is 2,000 µg/L.

Figure 20 shows a plot of Palintest results for different prepared standards over the range of detection. Three replicate analyses were made for each of three levels of standards, plus the blank. The regression line for this series of standard analyses showed excellent precision of the instrument ($R^2$=0.999), but with a bias of about 80-85% (results were about 15 to 20% low). This bias could be easily corrected by adjusting the analysis results.



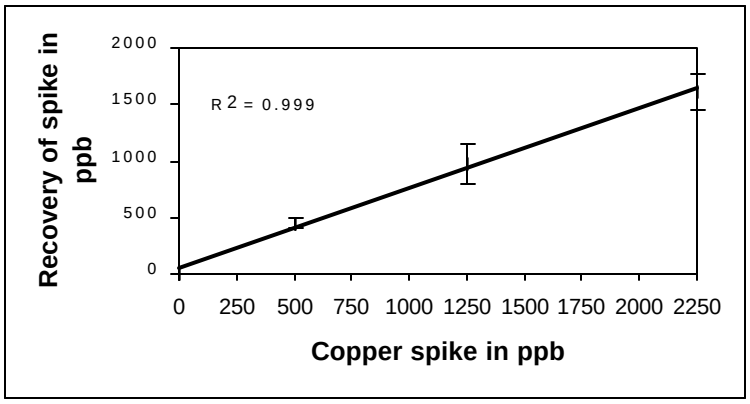

15.1.1.1 Figure 20

## 15.2 Metalyzer

The test supplies for the Metalyzer are also expensive (about $15 per test for both copper and lead), plus the instrument is expensive to purchase (over $4,000). Because of these high costs, a full evaluation was not conducted with the Metalyzer. The detection limit of the Metalyzer was reported to be 50 to 2,500 µg/L for copper.

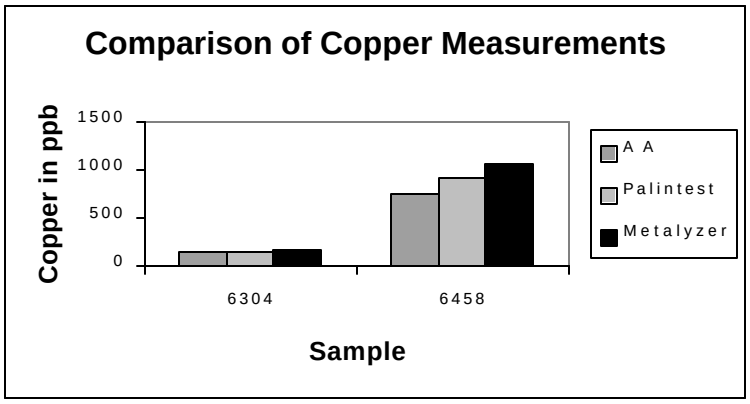
The reagent package contains a glass vial and disposal electrode enclosed in a plastic capsule. The glass shards and reagents are completely enclosed in the plastic capsule, minimizing any potential safety problems. The vial is inserted into the machine for use, and no contact is made with the reagents. The reagent vials are well packed in foam for shipment.

Again, three separate analyses were conducted for each of three standards and the blank. Figure 21 is a plot of the Metalyzer results compared to the standard concentrations. The regression line showed excellent precision of the instrument ($R^2$=0.999), but with a bias of 72-89% (results were 11 to 18% low). Again, this bias could be easily corrected by adjusting the analysis results.




15.2.1.1 Figure 21

Two previously analyzed samples of water from telecommunication manholes (using a TJA graphite furnace atomic absorption spectrophotometer) within the reported range of these instruments were also analyzed with the Palintest and Metalyzer (Figure 22). It is not unusual for different metal analytical methods to produce somewhat different results due to the methods used, although the Metalyzer produced a higher value than should be expected for the high concentration sample.




15.2.1.2 Figure 22

## 16 CHEMetrics Copper (as supplied by GDS in the Aqua Vats test kit)

The small number of reagents supplied with this test limited a complete evaluation. The reported range of the test is 0.1 to 1 mg/L. The test is simple to use. The vacuole is removed from the package and its tip is inserted into the water sample that is in a 25 mL plastic graduated cup. The tip is snapped off (while under water) and a vacuum draws sample up into the vacuole that contains the reagent. Color is immediately developed in the vacuole, which is placed in the comparator for reading.

The results of the tests are shown in Table 19. Three samples with previously calculated copper levels within the reported range of the test had non-detectable results. Standard solutions prepared using de-ionized water read at 0.4 mg/L for a spike level of 0.5 mg/L, and 1.0 mg/L at a spike level of 1.0 mg/L. The actual detection limit for this test appeared to be closer to 0.5 mg/L than the reported 0.1 mg/L. The ampoules produce a waste glass which can be dangerous if not properly handled and disposed.

**Table 19**

| Sample # | CHEMetrics C3501 tested value (mg/L) | Previously Measured Value using graphite furnace AAS | |
|---|---|---|---|
| | | (µg/L) | (mg/L) |
| 6237 | nd (< 0.1 mg/L) | 89 | 0.089 |
| 6290 | nd (< 0.1 mg/L) | 21.9 | 0.022 |
| 6304 | nd (< 0.1 mg/L) | 147 | 0.147 |
| 6327 | nd (< 0.1 mg/L) | 12.8 | 0.128 |
| 6458 | 1.0 mg/L | 754 | 0.754 |
| 0.5 mg/L standard | 0.4 mg/L | | |
| 1.0 mg/L standard | 1.0 mg/L | | |

# 17 Detergents Summary

# 18 Detergents

Three methods were chosen for evaluation: general fluorescence, CHEMetrics detergents and HACH anionic surfactants. The fluorescence method was only examined briefly due to the high capital cost of the fluorometer making it an unusual choice for these analyses, unless it was also being used for low-level hydrocarbon analyses or tracer analyses. The HACH method was rejected due to the use of a large amount of benzene in an uncontrolled environment. The CHEMetrics method uses hazardous materials as well (chloroform), however, the manufacturer has devised a system that minimizes exposure to the operator using glass ampoules. The method is quick and relatively inexpensive compared to other detergent methods, but is not as sensitive as the HACH method. The CHEMetrics method consistently over-predicted the spike concentrations of the detergent standards in these tests. However, this can be compensated for in quantitative analyses. Currently, we have no lab procedure to evaluate the method using parallel analyses.

*Table 56*

| Kit Name | Method | Capital cost | Expendable Cost (per sample) | Time Required (min) | Sample Vol. (ml) | Expertise Required |
|---|---|---|---|---|---|---|
| Turner 10-AU Fluorometer | fluorometric | $10,500 for 10-AU | $0 | 1 | 25 | little |
| CHEMetrics Detergents (Anionic Surfactants) | colorimetric | $59.5 for 1st 30 tests and standards | $2.38 | 10 | 5 | little |
| HACH Surfactants, Anionic, Crystal Violet Method | colorimetric | $1495 for DR 2000 | $1.10 | 30 | 25 | extensive |

*Table 57*

| Kit Name | Precision | Shelf Life | Regular Maintenance | Safety Hazards | Upper Limit of Useful Range (mg/L) |
|---|---|---|---|---|---|
| Turner 10-AU Fluorometer | NA | no reagents used | minimal | none | Multi-scaling |
| CHEMetrics Detergents (Anionic Surfactants) | 0.1813 | not indicated | none | Sharps, chloroform extraction | 3 |
| HACH Surfactants, Anionic, Crystal Violet Method | NA | not indicated | Charge batteries. | benzene extraction | N/A |

*Table 58 – RO water matrix tests*

| Kit Name | Adjusted $R^2$ | Standard Error | Intercept | p-Value | Slope | p-Value | Detection Limit ($\alpha$=0.05) (mg/L) | Limit of Quantification ($\alpha$=0.05) (mg/L) |
|---|---|---|---|---|---|---|---|---|
| CHEMetrics Detergents (Anionic Surfactants) | 0.9874 | 0.1308 | -0.0655 | 0.3503 | 1.6649 | 3.8733E-06 | 0.1547 | 0.3750 |

*Table 59 – Stormwater matrix tests*

| Kit Name | Adjusted $R^2$ | Standard Error | Intercept | p-Value | Slope | p-Value | Detection Limit ($\alpha$=0.05) (mg/L) | Limit of Quantification ($\alpha$=0.05) (mg/L) |
|---|---|---|---|---|---|---|---|---|
| CHEMetrics Detergents (Anionic Surfactants) | 0.9795 | 0.1832 | 0.0137 | 0.8836 | 1.8224 | 1.3108E-05 | 0.3223 | 0.6309 |

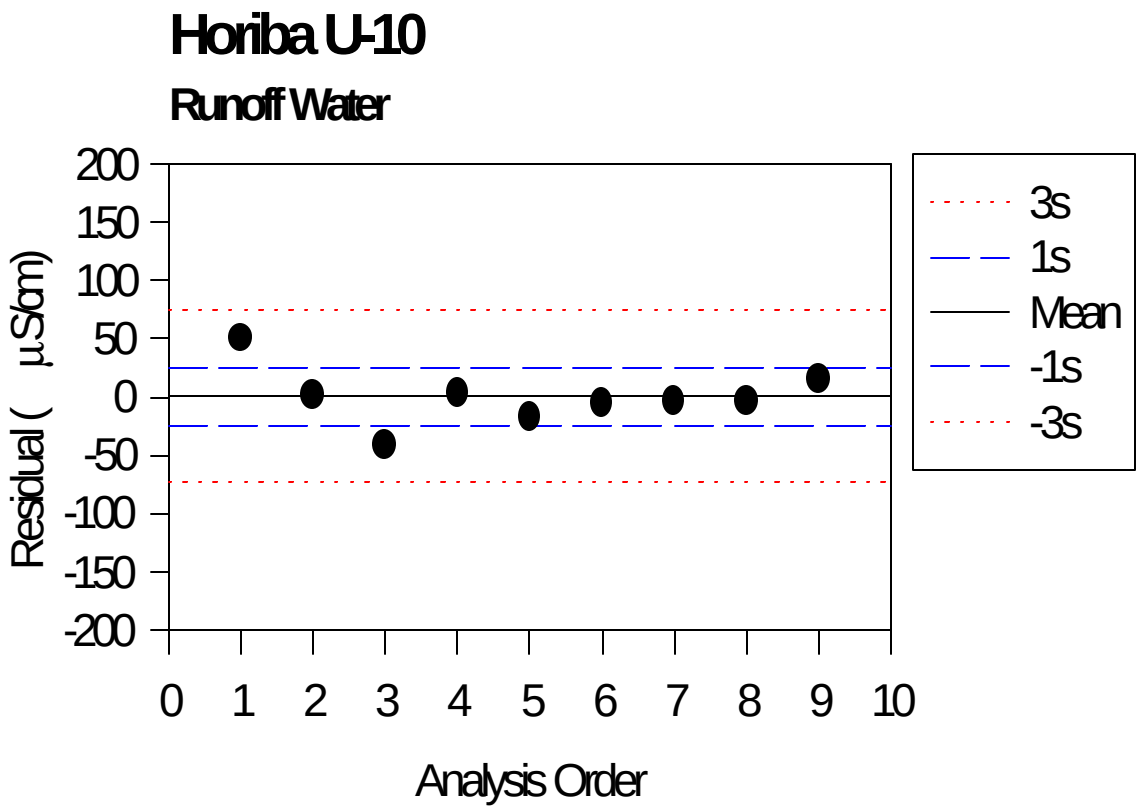

Horiba U-10
Runoff Water
Residual ( µS/cm)
200
150
100
50
0
-50
-100
-150
-200
0 1 2 3 4 5 6 7 8 9 10
Analysis Order
3s
1s
Mean
-1s
-3s

*Figure 54*

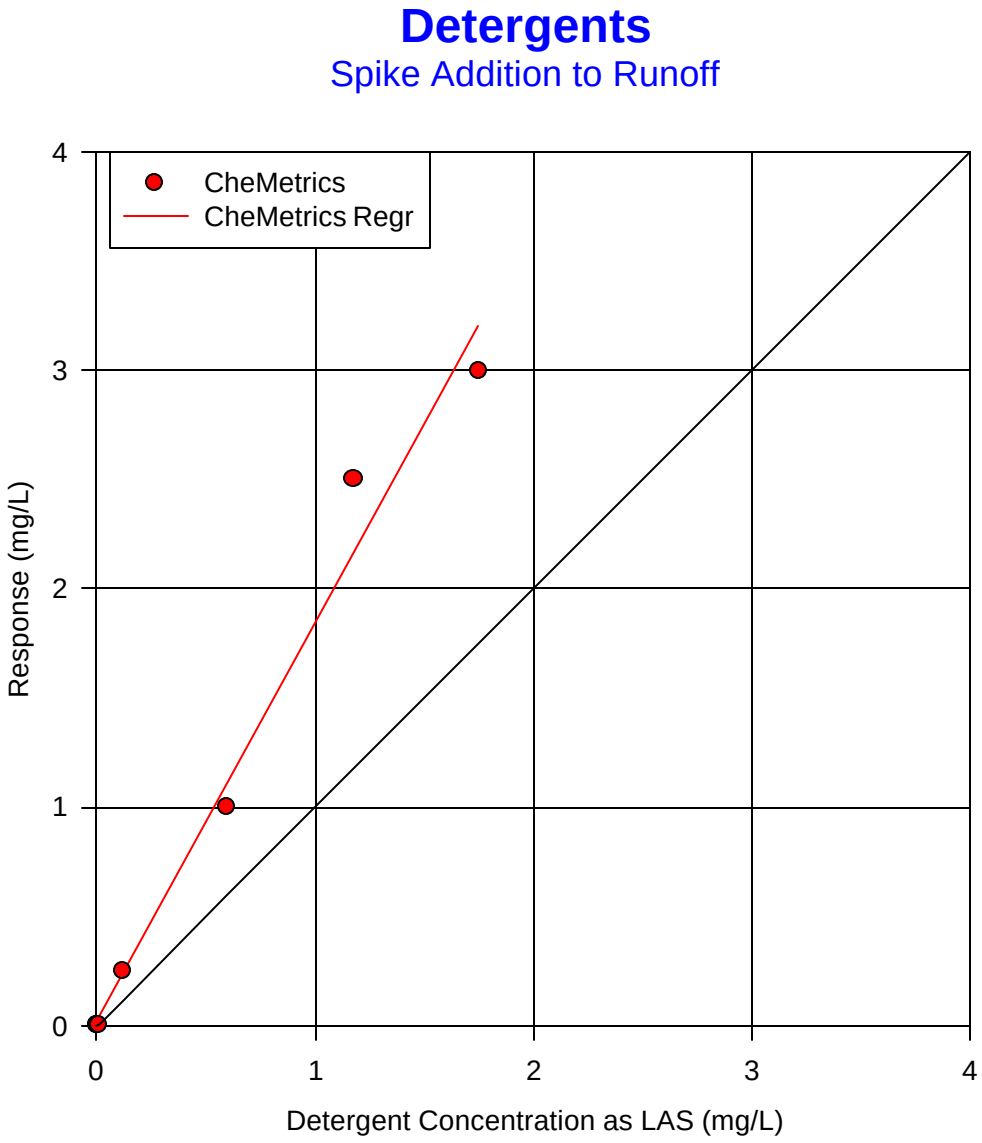



*Figure 55*

## 18.1 CHEMetrics Detergents

### *18.1.1 Method*

The CHEMetrics procedure uses a visual comparator to determine the concentration of the detergent in the samples. A small volume of sample (5 mL) is required. An ampoule containing methylene blue and chloroform are mixed with the sample. Anionic detergents complex with the methylene blue and are extracted into the chloroform layer. Cationic detergents and sulfides interfere with the reaction and lead to diminished results. The directions do not explicitly require rinsing of the cap between sample measurements, but the caps do become contaminated and must be cleaned.

### *18.1.2 Observations*

The method is very quick and easy. However, some concerns must be addressed. The method uses chloroform, a known carcinogen, and there is nothing in the experimental procedure to bring this to the operators attention. Users must seek well ventilated areas to perform this test. Furthermore, the waste must be disposed properly.

The kit also does not contain a few items required to complete the test. For example, a transfer pipette or medicine dropper is required to accurately measure 5 mL. A small cup should be used as a test tube holder for the reaction vessel. Finally, the reagent packs likely have a limited, but unspecified, shelf life. The user must insure that the reagents are still fresh for testing.

*Table 60*

| Sample ID | Spike Conc. (mg/L) | Analysis Order | RO Response (mg/L) | RO Percent Recovery | Analysis Order | Runoff Response (mg/L) |
|---|---|---|---|---|---|---|
| det X 0 | 0.000 | n.t | 0 | NA | 4 | 0 |
| det X 1 | 0.001 | n.t | 0 | 0 | 14 | 0 |
| det X 2 | 0.012 | 1 | 0 | 0 | 10 | 0 |
| det X 3 | 0.120 | 9 | 0.12 | 100 | 7 | 0.25 |
| det X 4 | 0.594 | 6 | 0.75 | 126 | 13 | 1 |
| det X 5 | 1.176 | 11 | 1.75 | 149 | 12 | 2.5 |
| det X 6 | 1.748 | 3 | 3 | 172 | 5 | 3 |
| det X 7 | 2.857 | 8 | >3 | NA | 2 | >3 |

*Table 61*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.994723537 |
| R Square | 0.989474914 |
| Adjusted R Square | 0.987369897 |
| Standard Error | 0.130798302 |
| Observations | 7 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 8.041801878 | 8.041801878 | 470.0555185 | 3.87331E-06 |
| Residual | 5 | 0.085540979 | 0.017108196 | | |
| Total | 6 | 8.127342857 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | -0.065525856 | 0.063626121 | -1.029857792 | 0.350294327 | -0.229081739 | 0.098030027 | -0.229081739 | 0.098030027 |
| Spike Conc. (mg/L) | 1.664908151 | 0.076791951 | 21.68076379 | 3.87331E-06 | 1.467508479 | 1.862307823 | 1.467508479 | 1.862307823 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | -0.065525856 | 0.065525856 | 0.500968706 |
| 2 | -0.063528006 | 0.063528006 | 0.485694426 |
| 3 | -0.045550953 | 0.045550953 | 0.348253399 |
| 4 | 0.133864342 | -0.013864342 | -0.105997871 |
| 5 | 0.923528491 | -0.173528491 | -1.326687639 |
| 6 | 1.893189615 | -0.143189615 | -1.094736038 |
| 7 | 2.844022368 | 0.155977632 | 1.192505017 |

*Table 62*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.991401393 |
| R Square | 0.982876722 |
| Adjusted R Square | 0.979452067 |
| Standard Error | 0.183231699 |
| Observations | 7 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 9.635702151 | 9.635702151 | 287.0001666 | 1.31075E-05 |
| Residual | 5 | 0.167869278 | 0.033573856 | | |
| Total | 6 | 9.803571429 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.01373277 | 0.089132061 | 0.154072175 | 0.883578547 | -0.215388111 | 0.242853652 | -0.215388111 | 0.242853652 |
| Spike Conc. (mg/L) | 1.822448557 | 0.107575706 | 16.94107926 | 1.31075E-05 | 1.545916854 | 2.098980261 | 1.545916854 | 2.098980261 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.01373277 | -0.01373277 | -0.074947569 |
| 2 | 0.015919665 | -0.015919665 | -0.086882701 |
| 3 | 0.03559778 | -0.03559778 | -0.194277411 |
| 4 | 0.231990083 | 0.018009917 | 0.098290402 |
| 5 | 1.096375478 | -0.096375478 | -0.525976009 |
| 6 | 2.157789897 | 0.342210103 | 1.86763592 |
| 7 | 3.198594327 | -0.198594327 | -1.083842632 |

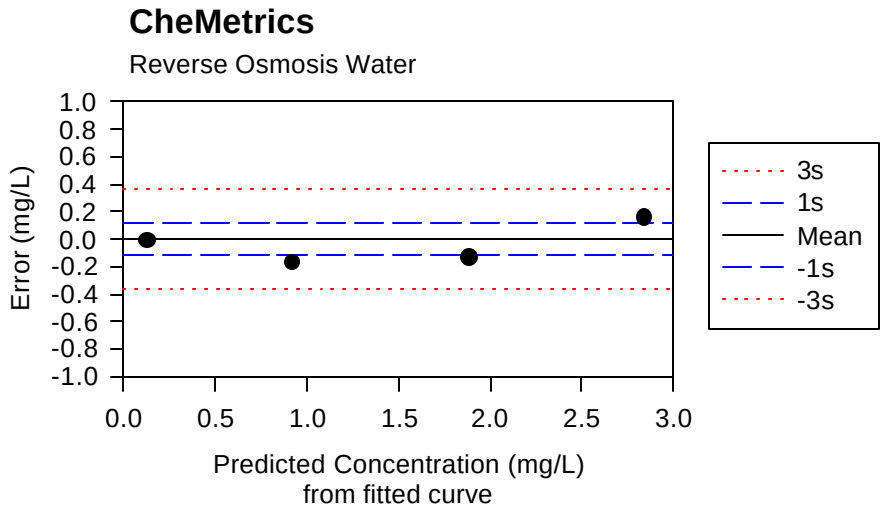

CheMetrics
Reverse Osmosis Water
Error (mg/L)
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Predicted Concentration (mg/L)
from fitted curve
3s
1s
Mean
-1s
-3s

*Figure 56*

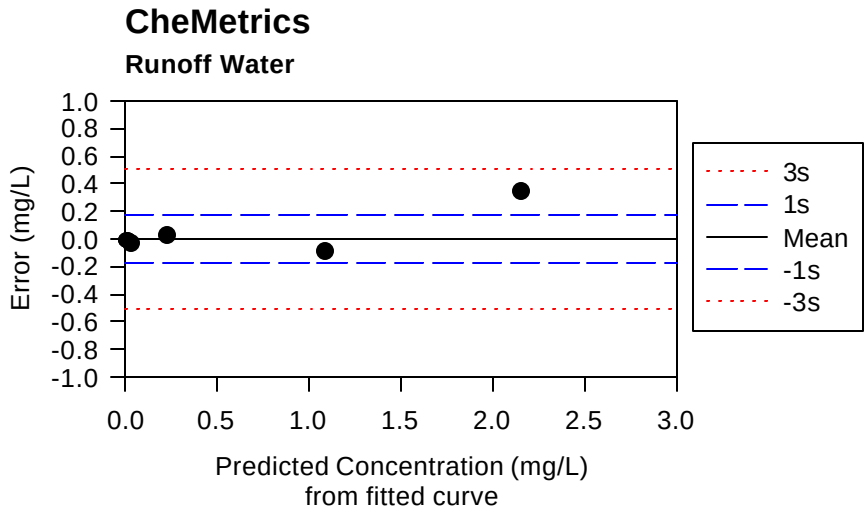

CheMetrics
Runoff Water
Error (mg/L)
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Predicted Concentration (mg/L)
from fitted curve
3s
1s
Mean
-1s
-3s

*Figure 57*

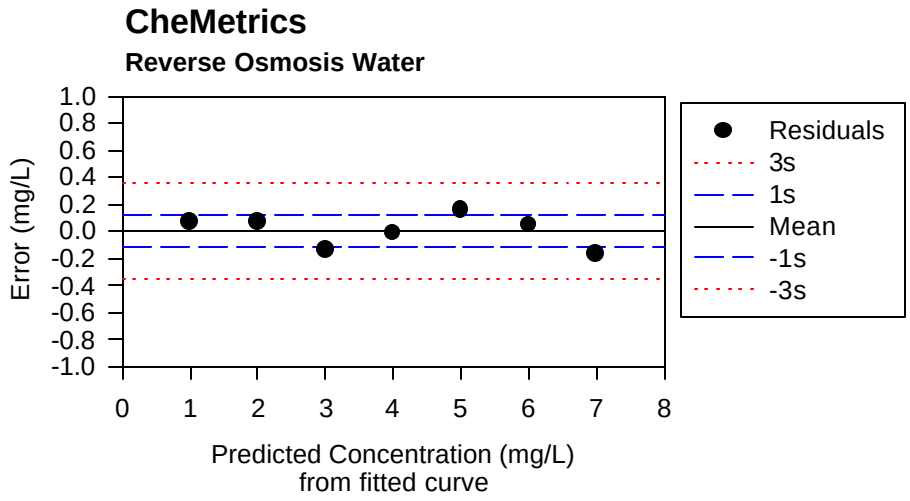

CheMetrics
Reverse Osmosis Water
Error (mg/L)
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
0
1
2
3
4
5
6
7
8
Predicted Concentration (mg/L)
from fitted curve
Residuals
3s
1s
Mean
-1s
-3s

*Figure 58*

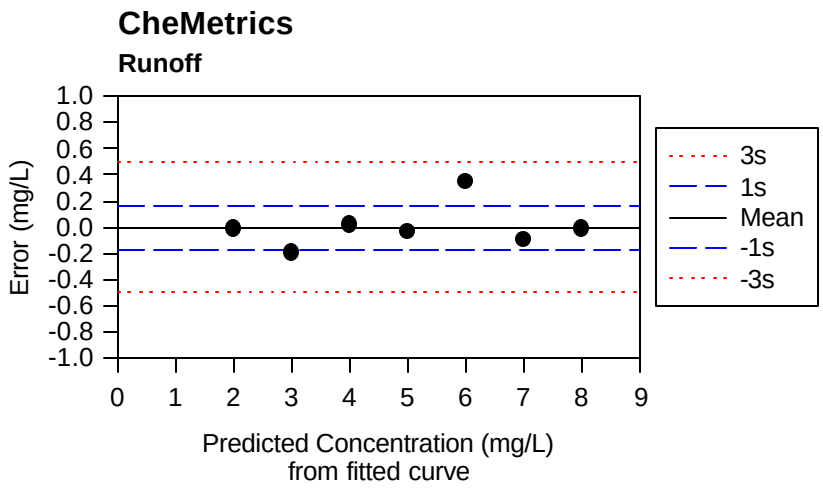



*Figure 59*

## 18.2 Turner Model 10-AU

### *18.2.1 Method*

The Turner Model 10-AU is a multi-purpose fluorometer. The instrument was configured using a 049 (near UV) lamp with a 300 to 400 nanometer excitation filter and a 410 to 500 nanometer emission filter set for detecting the fluorescence of brightening agents commonly added to laundry detergents. The instrument is capable of single sample analysis or continuos flow-through monitoring. It was configured for single sample analyses for these tests.

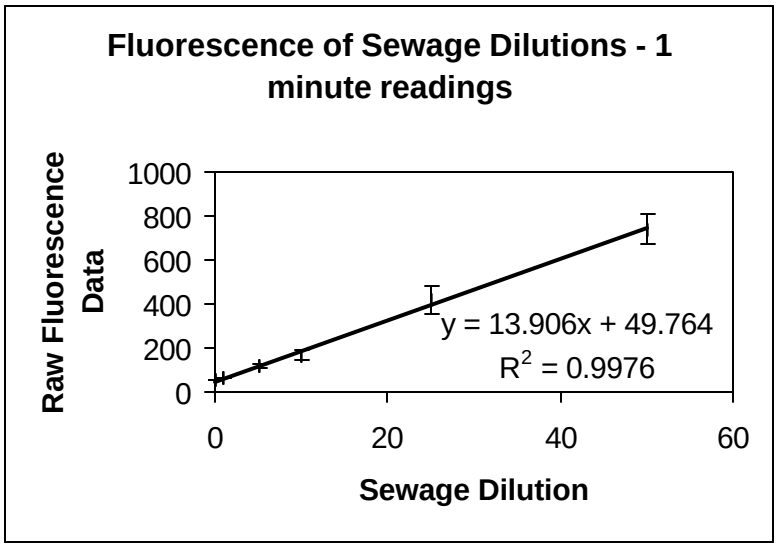
The instrument may be internally calibrated with a single standard representing 85% of the maximum concentration to be measured. A blank is measured and subtracted from the 85% concentration. The user may enter the concentration of the 85% standard so that output will be in desired units. The user may opt to have output in raw form from the detector with an adjustable scan. Once the instrument is set up correctly, actual measurements are quite simple: fill the cuvette and read.

Because of the lack of a suitable “brightener” standard, the instrument, using the relative raw fluorescence signal, was compared to mixtures of commercial laundry detergents and to dilutions of sanitary sewage. Unfiltered mixtures of sewage from 0.1% in spring water to 50% in spring water were

analyzed in triplicate. Mixtures of unfiltered sewage above 50% in spring water exceeded the upper-limit measurement capabilities of the instrument. The manufacturers of the fluorometer recommend an 8 second time constant for stable readings. It was found that using a 1 minute time constant with unfiltered sewage resulted in slightly less scatter among the data points and allowed a statistically significant difference to be measured between spring water and 0.1% sewage diluted in spring water. However, filtering the sanitary sewage samples improved the precision of the results and the use of an 8 second time constant was suitable and allowed similar detection limits. The laundry detergent tests indicated the variability between two commonly used brands, but also indicated the relatively strong signals associated with very low detergent concentrations.

This equipment requires no reagents and the equipment is easy to use. The only specific accessories required are the filters and the lamp needed for the specific analysis. The potential problems involved with using this piece of equipment include the variability of the fluorescence signal in the background water (reduced by using an appropriate selective filter-lamp combination), and the high cost of the instrument (about $10,500). The advantages are the rapid analysis time, sensitivity of the method, and ease of use.

18.2.1.1




18.2.1.2 Figure 7 – Fluorescence of unfiltered sanitary sewage samples

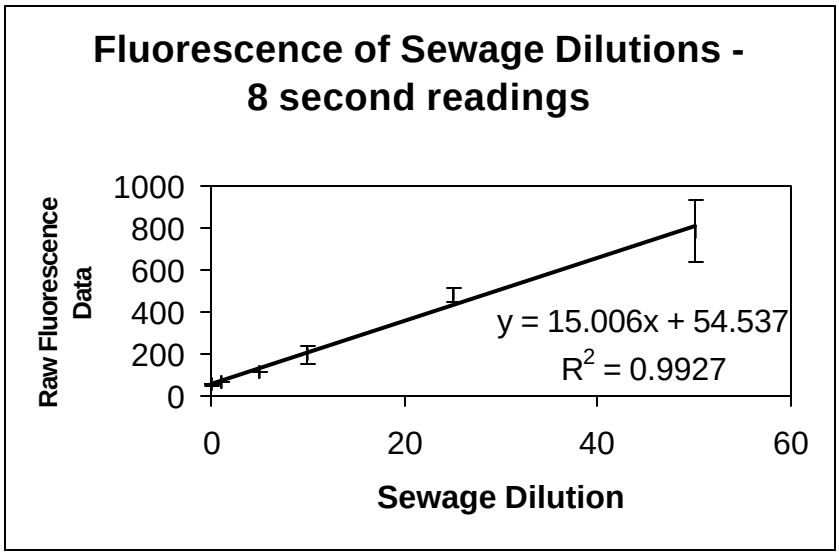



**Figure 8 – Fluorescence of unfiltered sanitary sewage samples**

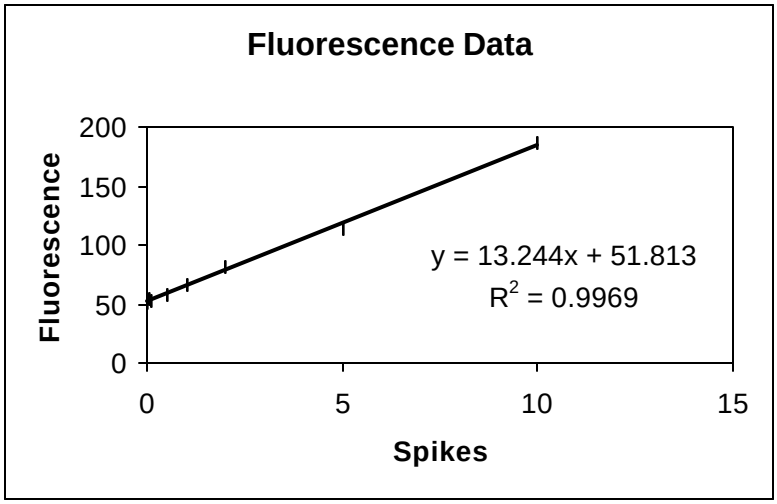



**Figure 9 – Fluorescence of Tide laundry detergent (mg/L)**

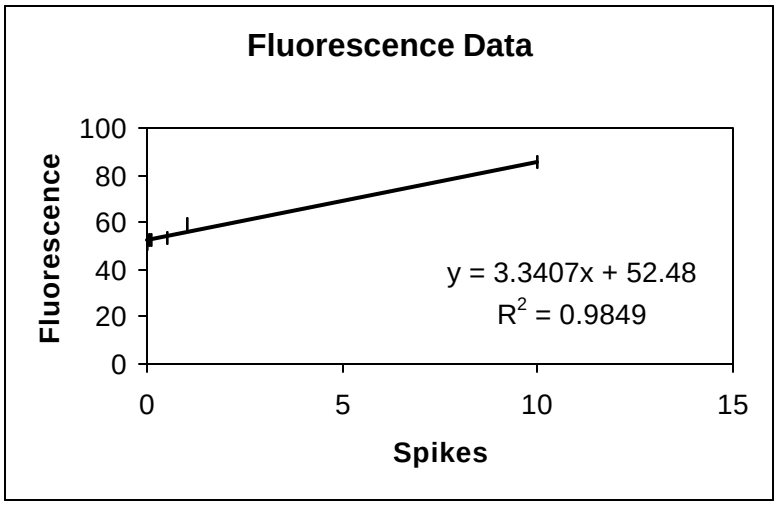



**Figure 10 – Fluorescence of Cheer laundry detergent (mg/L)**

# 19 Fluoride Summary

# 20 Fluoride

Three methods for the determination of fluoride concentration were evaluated. The HACH Company produces two methods for the determination of fluoride using SPADNS reagents. The difference between the HACH methods is the packing of the reagent. The other method evaluated for fluoride is the Fluoride Ion Tester by Cole-Parmer. Detailed descriptions of each method are included in this document. Table 1 summarizes the important factors for each method.

*Table 63*

| Method | Reagents Used | Analysis Time (min.) | Capital Cost | Expendable Cost | Sample Volume (ml) |
|---|---|---|---|---|---|
| HACH SPADNS Reagent | SPADNS Reagent | 5 | $1,495.00 | $0.18 | 25 |
| HACH SPADNS Reagent, AccuVac | SPADNS Reagent in AccuVac Ampoule | 2 | $1,495.00 | $1.20 | 25 |
| Cole-Parmer ISE | TISAB Buffer | 5 | $400.00 | $0.40* | 10 |

*Does not include the cost for the electrodes that periodically need replacement

Our analyses did provide a benchmark of the relative performance of each method. Figures 1 and 2 shows the relative performance of all methods in the reverse osmosis and runoff trials. All methods show good correlation with the expected concentration for fluoride concentrations less than 2.00 mg/L. There is no evidence of any significant matrix interference. Tables 2 and 3 summarize the regression analyses of each method. Although the Cole-Parmer ISE had a slightly lower detection limit and better correlation coefficient with the reverse osmosis samples, we believe the HACH AccuVac method is superior. The Cole-Parmer ISE probe also showed promise, so both methods were evaluated in the parallel analysis.

The HACH SPADNS Reagent method without ampoules was not tested further for two reasons: the chemical principles are identical to those as the AccuVac method, and the measuring and glassware cleaning are not as critical for the Cole-Parmer ISE and AccuVac methods.

We also measured the correlation of the responses between the two methods. Figure 3 shows that there is only a weak correlation (adjusted $r^2$=0.42) between the measurements made with the Cole-Parmer and HACH AccuVac methods. This poor correlation is likely due to the Cole-Parmer detection limit being greater than most of the fluoride concentrations of the samples.

The final piece of evidence to consider in the comparison of these two methods is the precision of each method. Table 4 presents the fluoride concentrations measured on a composite of 5 manholes. The precision represented by the coefficient of variation (COV) for the HACH method is four times better than the Cole-Parmer ISE with these samples. When all factors are considered, the HACH AccuVac is the preferred method for the determination of fluoride. However, because of the sodium arsenite in the

HACH reagents, the procedure requires special care in its use and in waste disposal. The waste material is classified as a hazardous waste under EPA RCRA regulations.

# 21 Cole-Parmer Fluoride Tester

## 21.1 Method

The Cole-Parmer Fluoride Tester is a small ion selective electrode capable of making fluoride determinations. A 10 mL sample is mixed with 10 mL of TISAB (Total Ionic Strength Adjusting Buffer). The probe is placed in the mixture. The solution must be stirred constantly until the reported fluoride concentration stabilizes.

Before measuring, the meter must be calibrated. The meter can be purchased with a kit including three calibration standards and approximately 250 mL of TISAB solution. The calibration standards are pre-mixed with the buffering solution. The meter is programmed to automatically recognize standard concentrations of 0.5, 1.0 and 2.0 ppm. Best results will be obtained if the instrument is calibrated at approximately the same temperature as the samples.

Standard Methods (1992) lists an ion selective electrode method (4500-$F^-$ C for the determination of fluoride in concentrations of 0.1-10 mg/L. Cole-Parmer states the effective range for this electrode is 0.20 to 20 ppm. Our tests show the lower detection limit to be higher than the value reported by the manufacturer. Standard Methods (1992) lists some common interfering materials producing a 0.1 mg/L error at a sample concentration of 1.0 mg/L with $F^-$ ion selective electrodes (Table 2).

*Table 64*

| | |
|---|---|
| Alkalinity | 5000 mg/L (as $CaCO_3$) |
| Aluminum ($Al^{3+}$) | 3.0 mg/L |
| Chloride ($Cl^-$) | 20,000 mg/L |
| Chlorine | 5,000 mg/L |
| Iron | 200 mg/L |
| hexametaphosphate $[Na(PO_3)]_6$ | 50,000 mg/L |
| phosphate ($PO_4^{3-}$) | 50,000 mg/L |
| sulfate ($SO_4^{2-}$) | 50,000 mg/L |

Cole-Parmer advises that the TISAB Buffer will remove interferences from iron, aluminum and silicon. The buffer also controls pH influences on fluoride reactions.

## 21.2 Observations

Initial evaluations of the ISE seemed to indicated a tendency to report reduced fluoride concentrations when compared to the other field methods. The standards are labeled as 0.5 ppm, 1.0 ppm and 2.0 ppm. However, the procedure requires a 1:1 dilution in a stabilizing buffer. This reduces the concentration of the calibration standards by one half. Thus, the instrument reports the fluoride concentration in the buffered sample which is approximately 50% of the original concentration. In light

of the very good regression results (high correlation and low standard error), this approach may be appropriate for some uses. However, the poor detection limit is very limiting. We unsuccessfully attempted to check the concentrations of the calibration standards shipped with the probe. The calibration standards are pre-mixed with the TISAB buffer, and this reagent interferes with the detection of fluoride by our Dionex ion chromatograph as well as the HACH SPADNS reagent methods.

The most problematic feature of the electrode is calibration. First, electrodes are notoriously temperature dependent. Therefore, the calibration must be performed at a temperature close to the sample temperature. The meter will give erroneous results if it is calibrated at room temperature (about 70° F) and used at cooler temperatures. Cole-Parmer reports that a 1°C temperature difference between the calibration standards and the measured samples will produce a 2% error. The instrument may not operate in cold temperatures at all. Second, the calibration routine can be lengthy. We have not yet successfully calibrated the instrument on the first try. Calibration took 2-3 attempts each time the instrument was used (about 30-45 minutes). Furthermore, the manufacturer recommends re-calibration every hour.

From experience we feared the electrode performance would degrade with time and use. Therefore, the instrument was calibrated and used to prepare a standard curve and then stored for one month. The instrument was then re-calibrated and used to measure fluoride in water samples obtained from manholes. A second standard curve was prepared immediately after the manhole testing to observe any degradation in performance. There was little or no degradation in performance observed.

One other potential problem is the method requires constant stirring for 5 minutes or longer if the fluoride concentration is low. This can become very tiring if the stirring is done by hand. A magnetic stirrer was used in the lab analyses and would be of great benefit to the user. However, the hand-held probe is not well designed for mechanized stirring. Care must be taken to secure the instrument to prevent entering calibration mode or damaging the LCD display. If the calibration mode button is pushed, all previous calibration data is lost from memory and the instrument must then be re-calibrated.

Cole-Parmer, unlike many of the manufacturers evaluated in this report, does two very nice things with this instrument package. First, the instrument manual states that disposal of chemical wastes must be in accordance with federal state, and local regulations. Second, the recipe for the standards and TISAB buffer are included with the manual for the instrument. They also sell the standards and buffers ready to use if convenience is a factor.

*Table 65*

Reverse Osmosis Measurements

| Method | n | Adjusted $R^2$ | Standard Error | Intercept | p-Value | Slope | p-Value | Lower Detection Limit, $\alpha$=0.05 (mg/L) | Upper Limit without Dilution (mg/L) |
|---|---|---|---|---|---|---|---|---|---|
| HACH SPADNS Reagent | 5 | 0.9814 | 0.1200 | 0.0785 | 0.3761 | 1.0935 | 6.89E-04 | 0.28 | 2.00 |
| HACH SPADNS Reagent, AccuVac | 5 | 0.9983 | 0.0320 | 0.0499 | 0.0898 | 0.9714 | 1.89E-05 | 0.10 | 2.00 |
| Cole-Parmer ISE, First Evaluation | 6 | 0.9995 | 0.0886 | -0.0533 | 0.3305 | 0.9683 | 6.91E-08 | 0.09 | 20.00 mg/L* |
| Cole-Parmer ISE, Second | 7 | 0.9963 | 0.0897 | 0.1432 | 0.0297 | 0.8187 | 1.79E-07 | 0.29 | 20.00 mg/L* |

*Table 66*

Runoff Measurements

| Method | n | Adjusted $R^2$ | Standard Error | Intercept | p-Value | Slope | p-Value | Lower Detection Limit, $\alpha$=0.05 (mg/L) | Upper Limit without Dilution |
|---|---|---|---|---|---|---|---|---|---|
| HACH SPADNS Reagent | 5 | 0.9725 | 0.1437 | 0.1055 | 0.3290 | 1.0670 | 1.26E-03 | 0.34 | 2.00 |
| HACH SPADNS Reagent, AccuVac | 5 | 0.9970 | 0.0416 | 0.0790 | 0.0572 | 0.9420 | 4.55E-05 | 0.15 | 2.00 |
| Cole-Parmer ISE, First Evaluation | 6 | 0.9948 | 0.2723 | -0.0842 | 0.6002 | 0.9571 | 6.43E-06 | 0.36 | 20.00 mg/L* |
| Cole-Parmer ISE, Second Evaluation | 7 | 0.9950 | 0.1181 | 0.1315 | 0.0755 | 0.8694 | 3.81E-07 | 0.33 | 20.00 mg/L* |

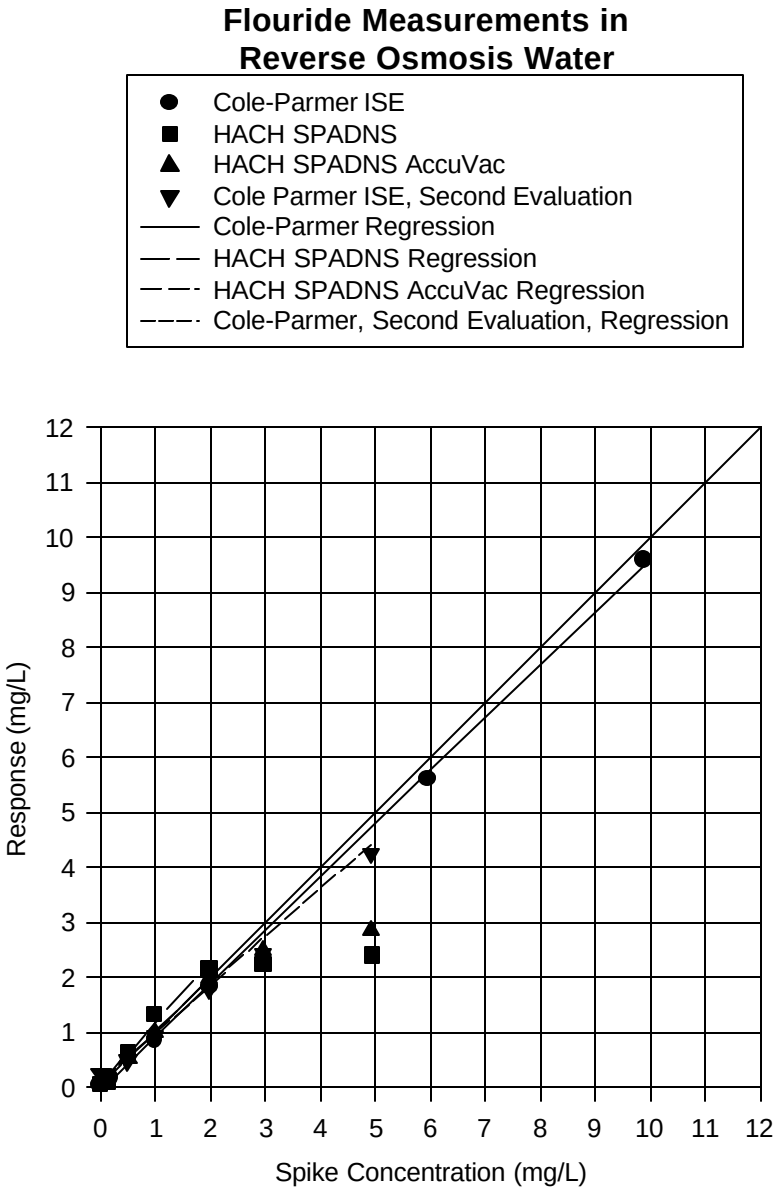

Flouride Measurements in
Reverse Osmosis Water
Cole-Parmer ISE
HACH SPADNS
HACH SPADNS AccuVac
Cole Parmer ISE, Second Evaluation
Cole-Parmer Regression
HACH SPADNS Regression
HACH SPADNS AccuVac Regression
Cole-Parmer, Second Evaluation, Regression
Response (mg/L)
Spike Concentration (mg/L)
0
1
2
3
4
5
6
7
8
9
10
11
12

*Figure 60*

## Flouride Measurements in Runoff Water

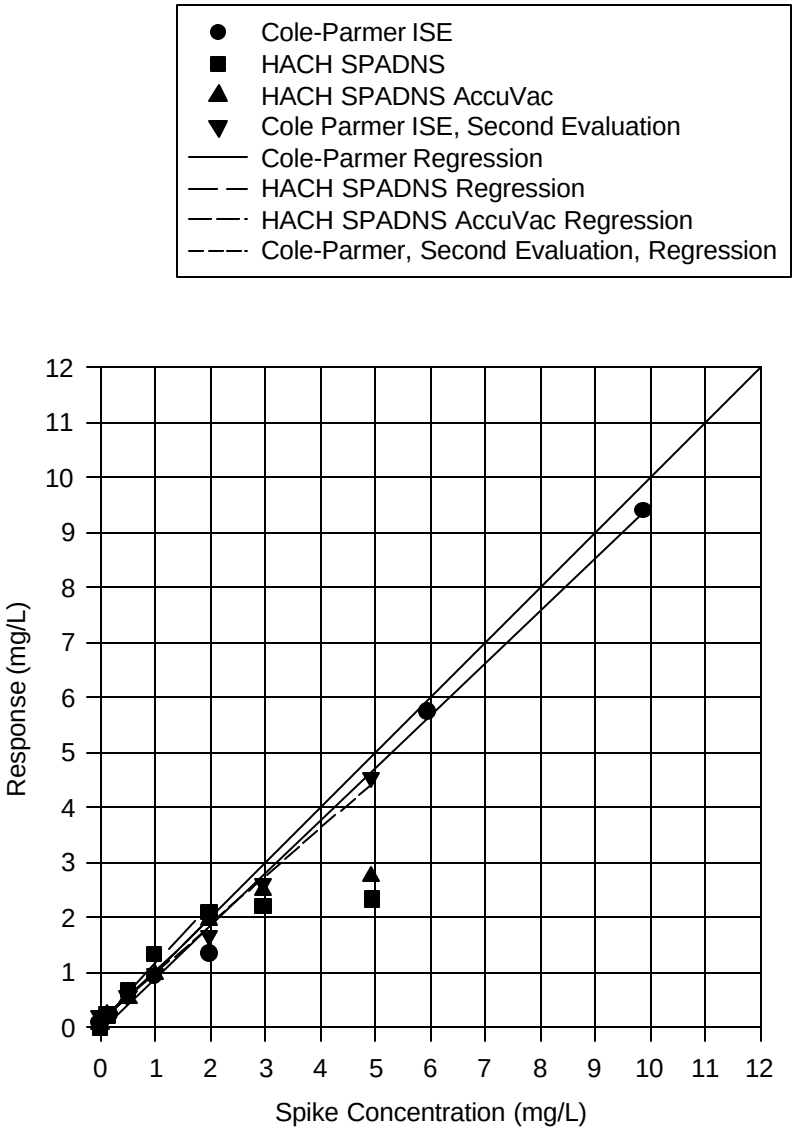



*Figure 61*

## Comparison of HACH AccuVac to Cole-Parmer Fluoride Tester

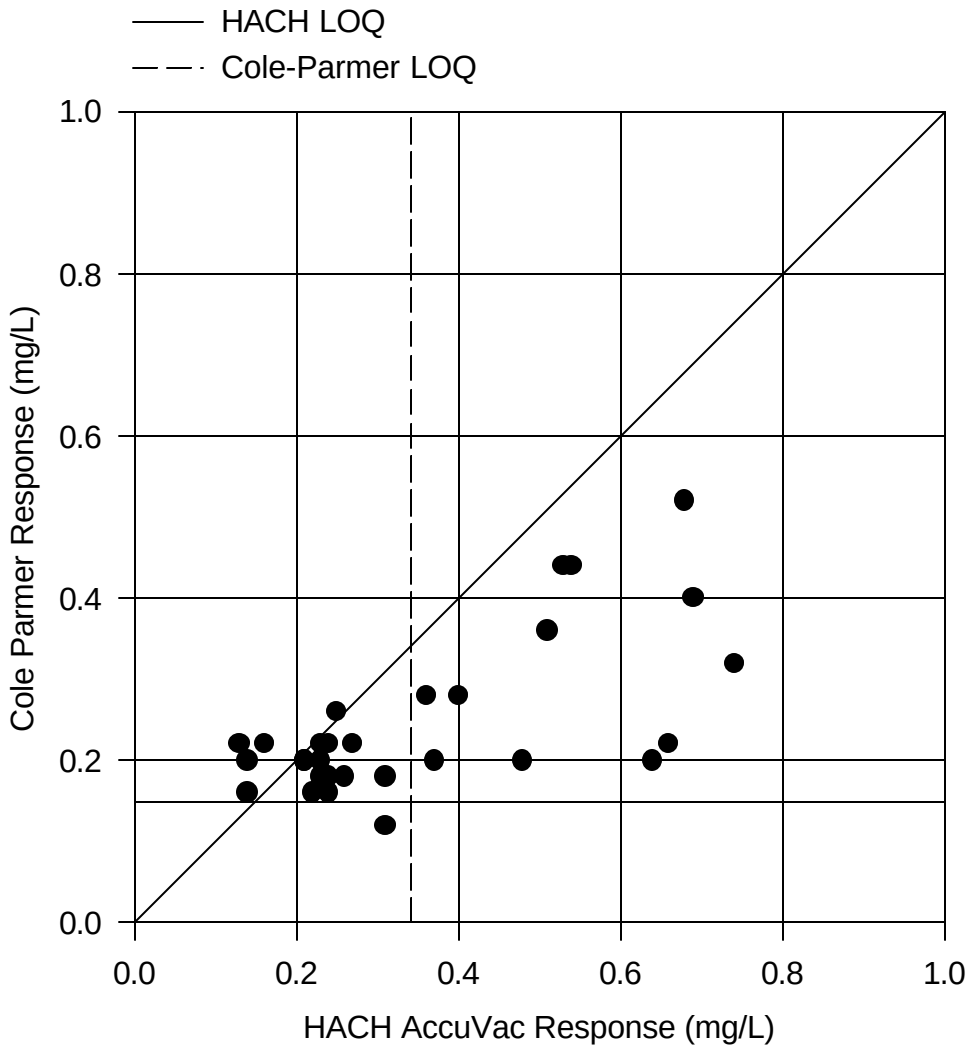



*Figure 62*

*Table 67*

Precision Measurements

| Sample ID | HACH AccuVac | | Corrected Cole-Parmer ISE |
|---|---|---|---|
| JD0001 | 0.51 | 0.16 | 0.32 |
| JD0002 | 0.46 | 0.18 | 0.36 |
| JD0003 | 0.50 | 0.18 | 0.36 |
| JD0004 | 0.45 | 0.10 | 0.20 |
| JD0005 | 0.47 | 0.19 | 0.38 |
| Average | 0.48 | 0.16 | 0.32 |
| Standard Deviation | 0.026 | 0.036 | 0.036 |
| COV | 0.054 | 0.22 | 0.16 |

*Table 68*

| Sample ID | Spike Conc. (mg/l) | Analysis Order | RO Response (mg/L) | Corrected RO Response (mg/L) | RO Percent Recovery | Analysis Order | Runoff Response (mg/L) | Corrected Runoff Response (mg/L) |
|---|---|---|---|---|---|---|---|---|
| F X 0 | 0.0000 | 8 | 0.02 | 0.04 | NA | 7 | 0.04 | 0.08 |
| F X 1 | 0.1998 | 4 | 0.09 | 0.18 | 90 | 1 | 0.12 | 0.24 |
| F X 2 | 0.9981 | 2 | 0.43 | 0.86 | 86 | 9 | 0.46 | 0.92 |
| F X 3 | 1.9942 | 11 | 0.91 | 1.82 | 91 | 5 | 0.67 | 1.34 |
| F X 4 | 5.9588 | 12 | 2.81 | 5.62 | 94 | 10 | 2.87 | 5.74 |

*Table 69*

Reverse Osmosis
First Evaluation

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.999785332 |
| R Square | 0.999570711 |
| Adjusted R Square | 0.999463389 |
| Standard Error | 0.088578314 |
| Observations | 6 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 73.07661553 | 73.07661553 | 9313.729214 | 6.91183E-08 |
| Residual | 4 | 0.031384471 | 0.007846118 | | |
| Total | 5 | 73.108 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | -0.053324879 | 0.048185222 | -1.106664601 | 0.330511107 | -0.187108779 | 0.080459021 | -0.187108779 | 0.080459021 |
| Spike Conc. (mg/l) | 0.968331159 | 0.010033723 | 96.50766402 | 6.91183E-08 | 0.94047302 | 0.996189297 | 0.94047302 | 0.996189297 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Corrected RO Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | -0.053324879 | 0.093324879 | 1.053586088 |
| 2 | 0.140128362 | 0.039871638 | 0.45012866 |
| 3 | 0.913168288 | -0.053168288 | -0.600240463 |
| 4 | 1.877732327 | -0.057732327 | -0.651765933 |
| 5 | 5.716812261 | -0.096812261 | -1.092956692 |
| 6 | 9.525483641 | 0.074516359 | 0.841248339 |

*Table 70*

Runoff
First Evaluation

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.99792859 |
| R Square | 0.995861471 |
| Adjusted R Square | 0.994826838 |
| Standard Error | 0.272328841 |
| Observations | 6 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 71.38388134 | 71.38388134 | 962.5269167 | 6.43167E-06 |
| Residual | 4 | 0.29665199 | 0.074162998 | | |
| Total | 5 | 71.68053333 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | -0.084188009 | 0.148142644 | -0.568290177 | 0.600221648 | -0.495498779 | 0.32712276 | -0.495498779 | 0.32712276 |
| Spike Conc. (mg/l) | 0.957050321 | 0.030848094 | 31.02461791 | 6.43167E-06 | 0.871402104 | 1.042698537 | 0.871402104 | 1.042698537 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Corrected Runoff Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | -0.084188009 | 0.164188009 | 0.602903492 |
| 2 | 0.107011546 | 0.132988454 | 0.488337753 |
| 3 | 0.871045732 | 0.048954268 | 0.179761598 |
| 4 | 1.82437282 | -0.48437282 | -1.778632106 |
| 5 | 5.618728344 | 0.121271656 | 0.445313304 |
| 6 | 9.383029567 | 0.016970433 | 0.062315958 |

*Table 71*

Reverse Osmosis
Second Evaluation

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.998458693 |
| R Square | 0.996919761 |
| Adjusted R Square | 0.996303713 |
| Standard Error | 0.089723862 |
| Observations | 7 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 13.02751957 | 13.02751957 | 1618.250734 | 1.78986E-07 |
| Residual | 5 | 0.040251857 | 0.008050371 | | |
| Total | 6 | 13.06777143 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.143227081 | 0.047579083 | 3.010295084 | 0.029745536 | 0.020921353 | 0.265532808 | 0.020921353 | 0.265532808 |
| Spike Conc. (mg/l) | 0.818744805 | 0.02035287 | 40.2274873 | 1.78986E-07 | 0.766426173 | 0.871063436 | 0.766426173 | 0.871063436 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Corrected RO Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.143227081 | 0.116772919 | 1.301470047 |
| 2 | 0.240590354 | -0.020590354 | -0.22948582 |
| 3 | 0.548753306 | -0.048753306 | -0.543370562 |
| 4 | 0.953874409 | -0.013874409 | -0.154634554 |
| 5 | 1.76290368 | 0.01709632 | 0.19054374 |
| 6 | 2.570319731 | -0.130319731 | -1.452453423 |
| 7 | 4.18033144 | 0.07966856 | 0.887930572 |

*Table 72*

Runoff
Second Evaluation

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.997915264 |
| R Square | 0.995834874 |
| Adjusted R Square | 0.995001849 |
| Standard Error | 0.110856096 |
| Observations | 7 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 14.69089749 | 14.69089749 | 1195.44382 | 3.80712E-07 |
| Residual | 5 | 0.06144537 | 0.012289074 | | |
| Total | 6 | 14.75234286 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.131523931 | 0.058785158 | 2.237366305 | 0.075463712 | -0.019587881 | 0.282635743 | -0.019587881 | 0.282635743 |
| Spike Conc. (mg/l) | 0.86944448 | 0.025146484 | 34.57519081 | 3.80712E-07 | 0.80480349 | 0.934085469 | 0.80480349 | 0.934085469 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Corrected Runoff Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.131523931 | 0.068476069 | 0.617702332 |
| 2 | 0.234916295 | 0.065083705 | 0.587100823 |
| 3 | 0.562161824 | 0.017838176 | 0.1609129 |
| 4 | 0.992369509 | -0.012369509 | -0.11158168 |
| 5 | 1.851496833 | -0.171496833 | -1.547022127 |
| 6 | 2.708911041 | -0.088911041 | -0.802040163 |
| 7 | 4.418620567 | 0.121379433 | 1.094927914 |

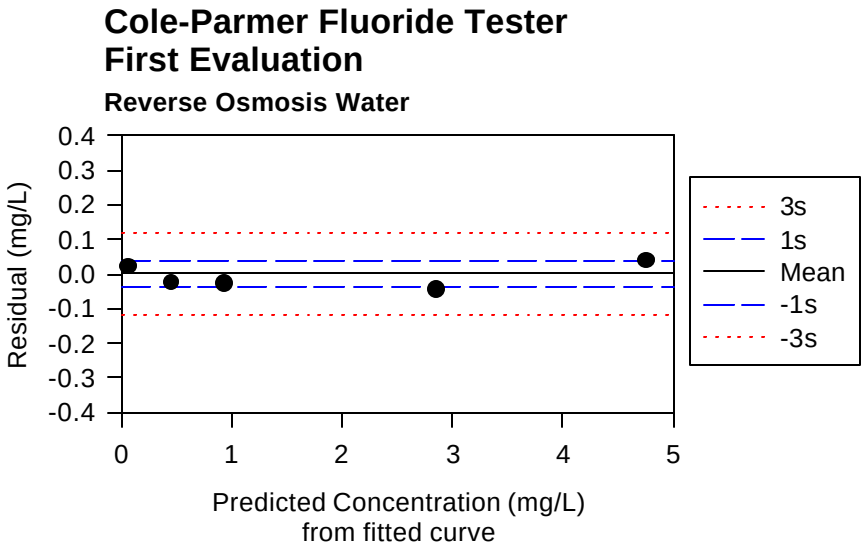



*Figure 63*

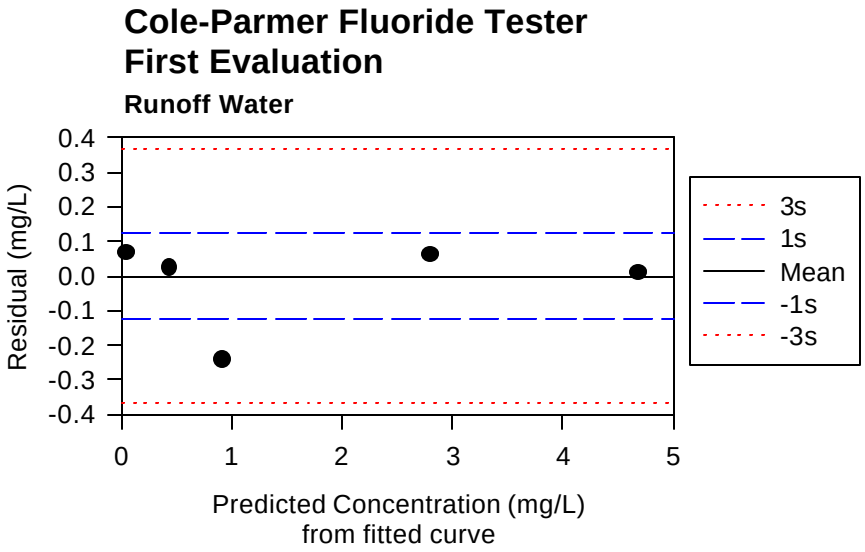



*Figure 64*

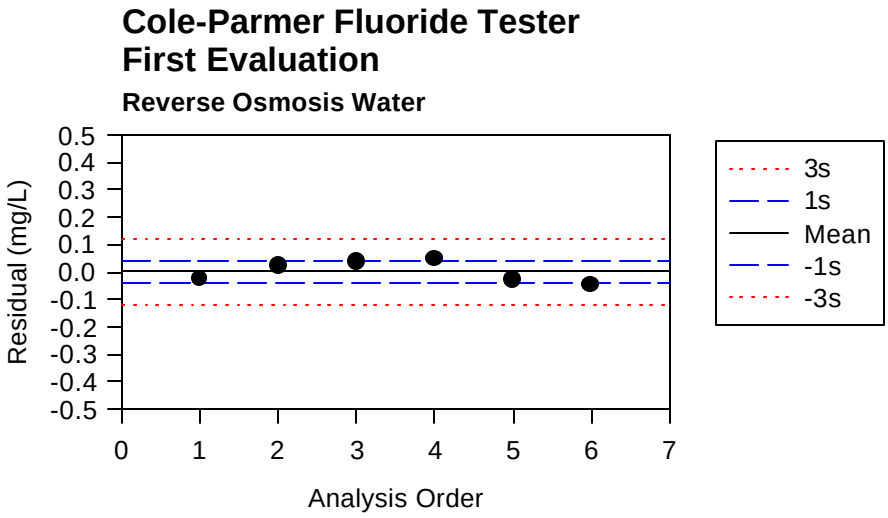



*Figure 65*

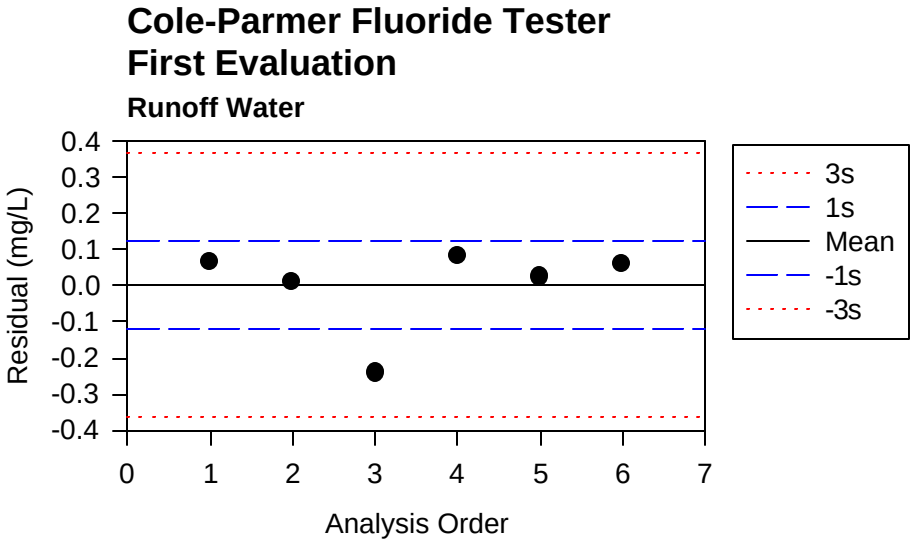



*Figure 66*

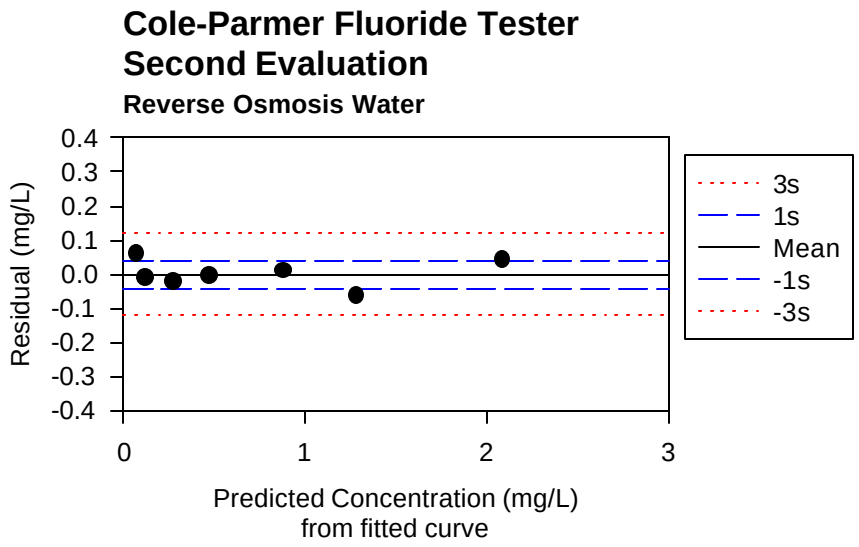



*Figure 67*

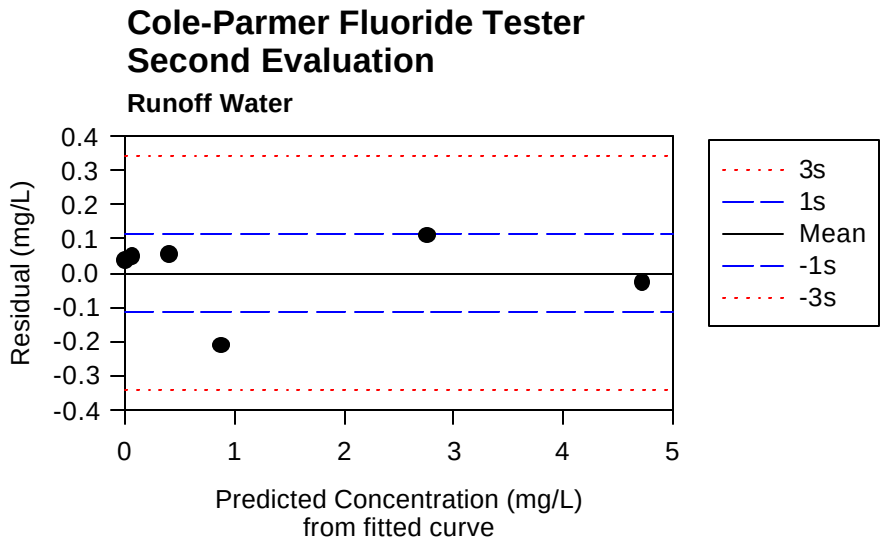



*Figure 68*

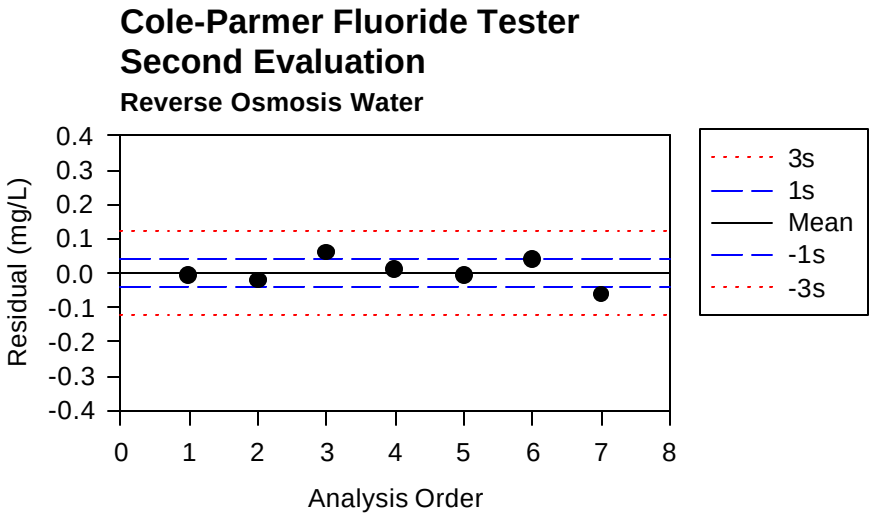



*Figure 69*

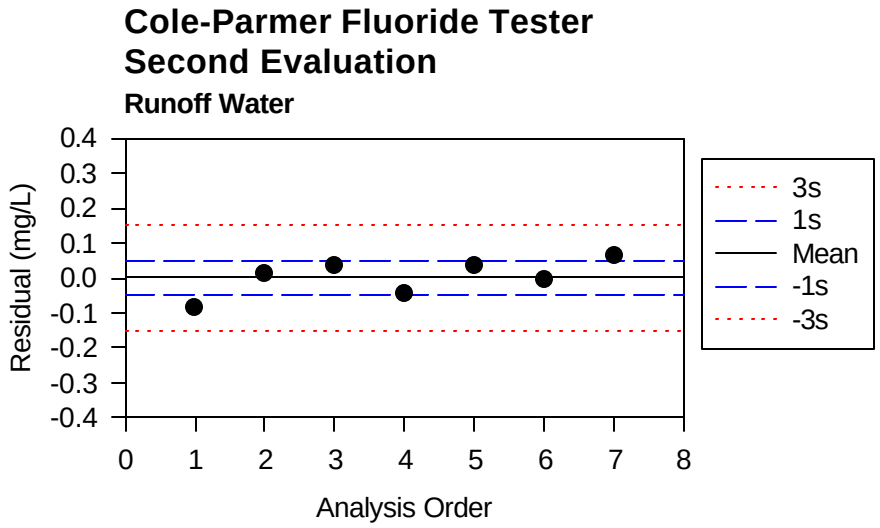



*Figure 70*

# 22 HACH SPADNS Reagent

## 22.1 Method

The HACH SPADNS Reagent method for the determination of fluoride utilizes the HACH DR 2000 spectrophotometer. The user collects a 25 mL sample in a cuvette. A 25 mL sample of de-ionized water is collected in a second cuvette as a reagent blank. The user adds 5 mL of SPADNS reagent to the sample and the reagent blank. These additions must be made as close to simultaneously as possible. The reaction time for the test is one minute. At the conclusion of the reaction time, the DR 2000 is zeroed using the reagent blank, and the sample is immediately read.

The method determines fluoride concentration by measuring the reduction in absorbance of the SPADNS reagent in the sample compared to the reagent blank. SPADNS reagent is a red dye that reacts with fluoride. The product of the reaction is colorless. Therefore, the amount of light absorbed at 400 nm by the sample is reduced from the same light in the reagent blank. A spectrophotometer measures the difference in absorbance between the reagent blank and the sample and calculates the concentration in mg/L from a pre-programmed calibration curve.

The SPADNS reagent method is listed in Standard Methods (4500-$F^-$ D) for fluoride determination. Some common interferents and the level producing a 10% error at a sample concentration of 1.0 mg/L are listed in Table 11 (Standard Methods 1992).

*Table 73*

| | |
|---|---|
| Alkalinity | 5000 mg/L (as $CaCO_3$) |
| $Cl^-$ | 7000 mg/L |
| turbidity | unpredictable |
| hexametaphosphate $[Na(PO_3)]_6$ | 1.0 mg/L |
| sulfate ($SO_4^{2-}$) | 200 mg/L |
| $Al^{3+}$ | 0.1 mg/L |
| $Cl_2$ | remove with arsenite |
| iron | 10 mg/L |

## 22.2 Observations

The efficiency of this method is greatly improved by the use of an automatic pipette. Without an automatic pipette, the time between addition of SPADNS reagent to the blank and sample may be a minute or more. The increased reaction time invalidates the instrument calibration. This makes results less reliable.

Some laboratory equipment is required to complete the test: a graduated cylinder, a pipette (as mentioned before, preferably automatic), KimWipes (or substitute). This test is not sold as field kit, therefore, glassware, cuvettes, and tissue are sold separately. These costs have not been considered in the expendable costs reported in the summary table.

The dye is messy if spilled, plus it contains enough sodium arsenite to be classified as a hazardous waste under the Federal RCRA regulations. A small amount will stain skin and clothing. In our lab analyses, the cuvettes were cleaned using a dilute hydrochloric acid solution (about 5% HCl) between sample runs. The user must thoroughly rinse the cleaning agent from the cuvettes with water before making another reading. If the acid remains in the vials, it will also remove SPADNS reagent during the evaluation. The reported fluoride concentrations if the cuvettes contain the rinse will be increased from the true value. If the cuvettes are not cleaned, and sample is carried over to the next run, the fluoride readings will not reflect the true value.

The data collected for this method clearly indicate that the relationship between fluoride concentration and absorbance becomes non-linear at concentrations greater than 2 mg/L. Unlike most methods, the instrument did not report an error when measuring samples at concentrations significantly higher than 2 mg/L. Therefore, any sample with a reported concentration of 2.0 mg/L should be diluted and re-examined. Standard Methods (1992) does not recommend the determination of samples with concentrations greater than 1.40 mg/L using this method.

*Table 74*

| Sample ID | Spike Conc. (mg/L) | Analysis Order | RO Response (mg/L) | RO Percent Recovery | Analysis Order | Runoff Response (mg/L) |
|---|---|---|---|---|---|---|
| F X 0 | 0.00 | 6 | 0.07 | NA | 5 | 0 |
| F X 1 | 0.12 | 14 | 0.12 | 101 | 1 | 0.2 |
| F X 2 | 0.50 | 4 | 0.63 | 127 | 7 | 0.69 |
| F X 3 | 0.99 | 8 | 1.33 | 134 | 3 | 1.35 |
| F X 4 | 1.98 | 13 | 2.16 | 109 | 11 | 2.11 |
| F X 5 | 2.96 | 9 | 2.25 | 76 | 2 | 2.22 |

Note: F X 5 and F X 6 obviously lie outside the linear response range of the instrument. Therefore, these points were not used in the regression analysis.

*Table 75*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.993089847 |
| R Square | 0.986227445 |
| Adjusted R Square | 0.981636594 |
| Standard Error | 0.119977179 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 3.09229643 | 3.09229643 | 214.8245093 | 0.000688834 |
| Residual | 3 | 0.04318357 | 0.014394523 | | |
| Total | 4 | 3.13548 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.078517661 | 0.075738551 | 1.036693476 | 0.376106208 | -0.162516435 | 0.319551758 | -0.162516435 | 0.319551758 |
| Spike Conc. (mg/L) | 1.093463041 | 0.074604014 | 14.6568929 | 0.000688834 | 0.85603955 | 1.330886532 | 0.85603955 | 1.330886532 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.078517661 | -0.008517661 | -0.070994013 |
| 2 | 0.208549804 | -0.088549804 | -0.738055394 |
| 3 | 0.620112474 | 0.009887526 | 0.082411724 |
| 4 | 1.161166232 | 0.168833768 | 1.407215683 |
| 5 | 2.241653828 | -0.081653828 | -0.680578 |

*Table 76*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.989638128 |
| R Square | 0.979383625 |
| Adjusted R Square | 0.9725115 |
| Standard Error | 0.14373233 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 2.944223052 | 2.944223052 | 142.5153947 | 0.001264198 |
| Residual | 3 | 0.061976948 | 0.020658983 | | |
| Total | 4 | 3.0062 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.105506133 | 0.090734575 | 1.162799658 | 0.329000148 | -0.183252051 | 0.394264317 | -0.183252051 | 0.394264317 |
| Spike Conc. (mg/L) | 1.06696188 | 0.089375403 | 11.93798118 | 0.001264198 | 0.782529192 | 1.351394568 | 0.782529192 | 1.351394568 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.105506133 | -0.105506133 | -0.734045939 |
| 2 | 0.232386817 | -0.032386817 | -0.225327298 |
| 3 | 0.633974858 | 0.056025142 | 0.389788034 |
| 4 | 1.161915642 | 0.188084358 | 1.308573781 |
| 5 | 2.21621655 | -0.10621655 | -0.738988578 |

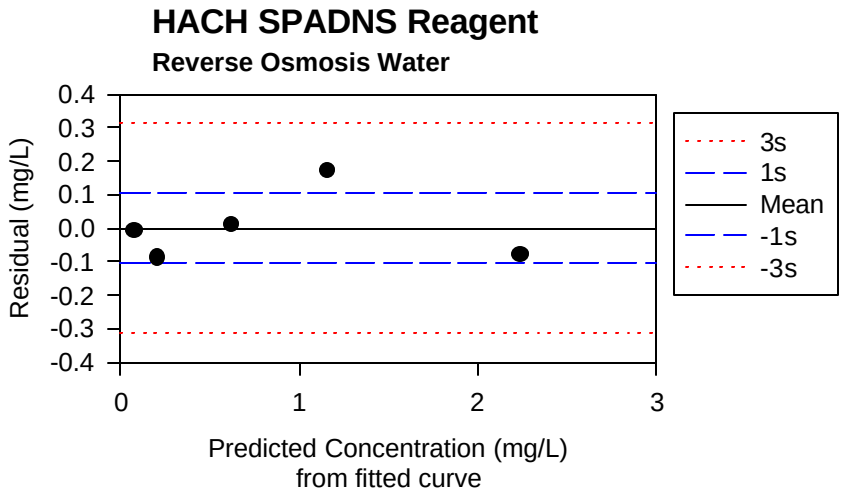

HACH SPADNS Reagent
Reverse Osmosis Water
Residual (mg/L)
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
0
1
2
3
Predicted Concentration (mg/L)
from fitted curve
3s
1s
Mean
-1s
-3s

*Figure 71*

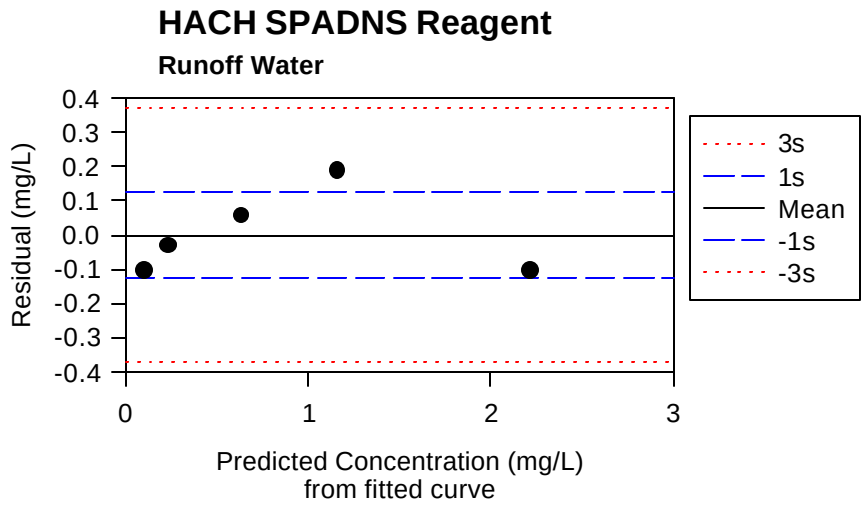

HACH SPADNS Reagent
Runoff Water
Residual (mg/L)
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
0
1
2
3
Predicted Concentration (mg/L)
from fitted curve
3s
1s
Mean
-1s
-3s

*Figure 72*

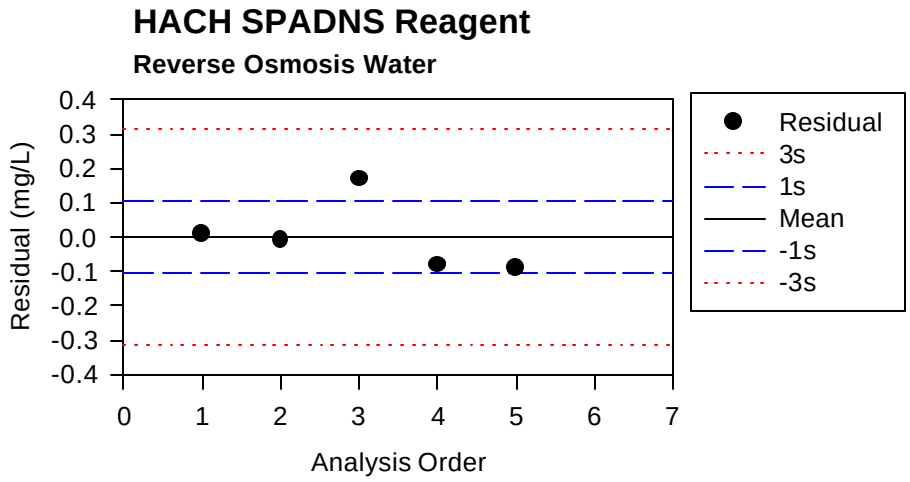



*Figure 73*

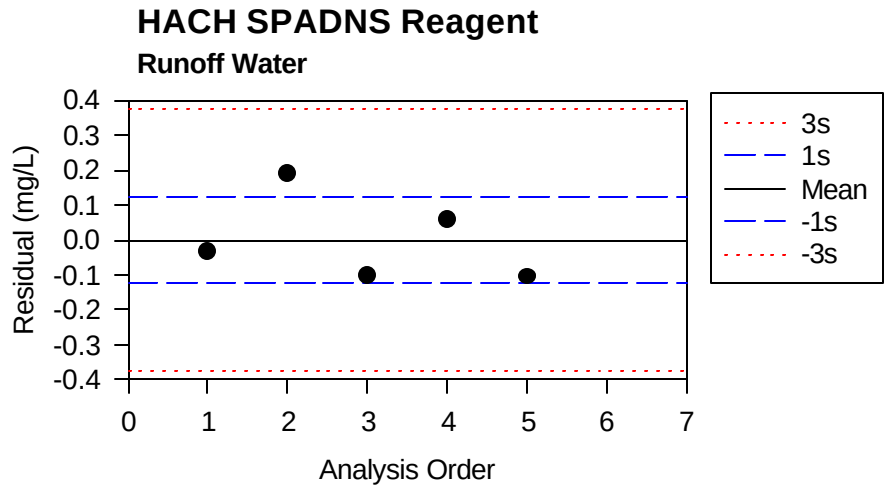



*Figure 74*

# 23 HACH SPADNS Reagent (AccuVac)

## 23.1 Method

The HACH SPADNS Reagent method for the determination of fluoride utilizes the HACH DR 2000 spectrophotometer. The user collects a 25 ml sample in a beaker. A 25 mL sample of de-ionized water is collected in a second beaker as a reagent blank. The user simultaneously breaks SPADNS reagent ampoules tips in each beaker. A one minute reaction time is required. At the conclusion of the reaction time, the DR 2000 is zeroed using the reagent blank, and the sample is immediately read.

The method determines fluoride concentration by measuring the reduction in absorbance of the SPADNS reagent in the sample compared to the reagent blank. SPADNS reagent is a red dye that reacts with fluoride. The product of the reaction is colorless. Therefore, the amount of light absorbed at 400 nm by the sample is reduced from the same light in the reagent blank. The DR 2000 measures the difference in absorbance between the reagent blank and the sample and calculates the concentration in mg/L from a pre-programmed calibration curve.

SPADNS reagent is listed in Standard Methods (4500 $F^-$ D) as an appropriate method for fluoride determination. Some common interferents from Standard Methods (1992) are listed in Table 15.

*Table 77*

| | |
|---|---|
| alkalinity | 5000 mg/L (as $CaCO_3$) |
| chloride | 7000 mg/L |
| turbidity | |
| hexametaphosphate $[Na(PO_3)]_6$ | 1.0 mg/L |
| sulfate ($SO_4^{2-}$) | 200 mg/L |
| $Al^{3+}$ | 0.1 mg/L |
| $Cl_2$ | remove with arsenite |
| iron | 10 mg/L |

## 23.2 Observations

This method overcomes the handling limitations of the other examined SPADNS method by providing prepackaged aliquots of SPADNS reagent in the ampoules. The ampoules remove the need to measure the sample, blank or reagent accurately. Therefore, the only glassware required are beakers (or plastic cups) to hold the sample while breaking the ampoules. The ampoules also eliminate the need for an acid wash between determinations. The amount of reagent entering the sample cup is very small. This small amount of SPADNS can be removed with a thorough water rinse. However, the reagent and the waste is still classified as a hazardous waste under the Federal RCRA regulations because of the sodium arsenite that is used to remove some of the interferences.

The added convenience of this method over the other HACH method is reflected in the increased expendable costs. Plus, the used ampoules represent a “sharps” hazard.

The data collected for this method clearly indicate that the relationship between fluoride concentration and absorbance becomes non-linear at concentrations greater than 2 mg/L. Unlike most methods, the instrument did not report an error when measuring samples at concentrations significantly higher than 2 mg/L. Therefore, any sample with a reported concentration of 2.0 mg/L should be diluted and re-examined. Standard Methods (1992) does not recommend the measurement of samples with concentrations greater than 1.40 mg/L with this method.

*Table 78*

| Sample ID | Spike Conc. (mg/L) | Analysis Order | RO Response (mg/L) | RO Percent Recovery | Analysis Order | Runoff Response (mg/L) |
|---|---|---|---|---|---|---|
| F X 0 | 0.00 | 10 | 0.09 | NA | 12 | 0.08 |
| F X 1 | 0.12 | 1 | 0.13 | 109 | 14 | 0.23 |
| F X 2 | 0.50 | 5 | 0.53 | 107 | 13 | 0.53 |
| F X 3 | 0.99 | 11 | 1.00 | 101 | 3 | 0.96 |
| F X 4 | 1.98 | 2 | 1.98 | 100 | 8 | 1.97 |
| F X 5 | 2.96 | 9 | 2.49 | 84 | 4 | 2.50 |
| F X 6 | 4.93 | 6 | 2.85 | 58 | 7 | 2.76 |

Note: F X 5 and F X 6 obviously lie outside the linear response range of the instrument. Therefore, these points were not used in the regression analysis.

*Table 79*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.999371406 |
| R Square | 0.998743208 |
| Adjusted R Square | 0.998324277 |
| Standard Error | 0.031996087 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 2.440648751 | 2.440648751 | 2384.029058 | 1.89168E-05 |
| Residual | 3 | 0.003071249 | 0.00102375 | | |
| Total | 4 | 2.44372 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.04994863 | 0.020198318 | 2.472910336 | 0.089832314 | -0.014331494 | 0.114228754 | -0.014331494 | 0.114228754 |
| Spike Conc. (mg/L) | 0.971440465 | 0.019895755 | 48.82652003 | 1.89168E-05 | 0.908123234 | 1.034757695 | 0.908123234 | 1.034757695 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.04994863 | 0.04005137 | 1.251758371 |
| 2 | 0.165470125 | -0.035470125 | -1.108576968 |
| 3 | 0.531105374 | -0.001105374 | -0.034547171 |
| 4 | 1.011781442 | -0.011781442 | -0.368215095 |
| 5 | 1.971694428 | 0.008305572 | 0.259580863 |

*Table 80*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.998871138 |
| R Square | 0.99774355 |
| Adjusted R Square | 0.9969914 |
| Standard Error | 0.041593694 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 2.294929894 | 2.294929894 | 1326.521931 | 4.5522E-05 |
| Residual | 3 | 0.005190106 | 0.001730035 | | |
| Total | 4 | 2.30012 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.079047263 | 0.026257044 | 3.010516389 | 0.05718825 | -0.00451445 | 0.162608975 | -0.00451445 | 0.162608975 |
| Spike Conc. (mg/L) | 0.941994269 | 0.025863723 | 36.42144877 | 4.5522E-05 | 0.859684281 | 1.024304256 | 0.859684281 | 1.024304256 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.079047263 | 0.000952737 | 0.022905812 |
| 2 | 0.191067083 | 0.038932917 | 0.936029322 |
| 3 | 0.545619236 | -0.015619236 | -0.375519337 |
| 4 | 1.011725104 | -0.051725104 | -1.243580438 |
| 5 | 1.942541314 | 0.027458686 | 0.660164641 |

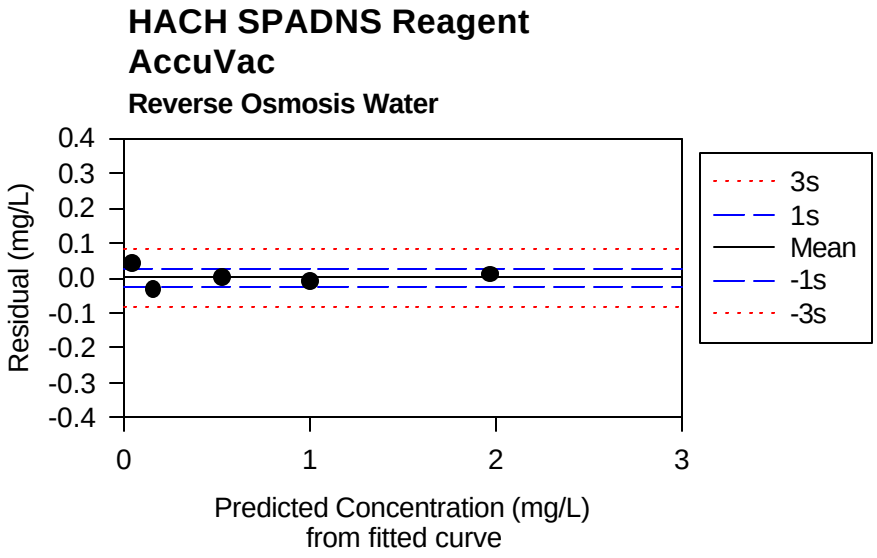

HACH SPADNS Reagent
AccuVac
Reverse Osmosis Water
Residual (mg/L)
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
0
1
2
3
Predicted Concentration (mg/L)
from fitted curve
3s
1s
Mean
-1s
-3s

*Figure 75*

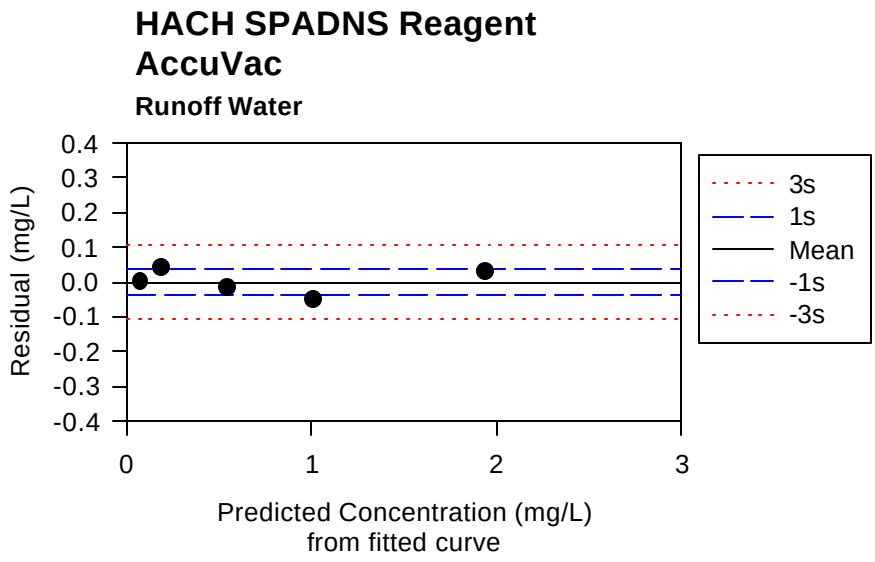

HACH SPADNS Reagent
AccuVac
Runoff Water
Residual (mg/L)
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
0
1
2
3
Predicted Concentration (mg/L)
from fitted curve
3s
1s
Mean
-1s
-3s

*Figure 76*

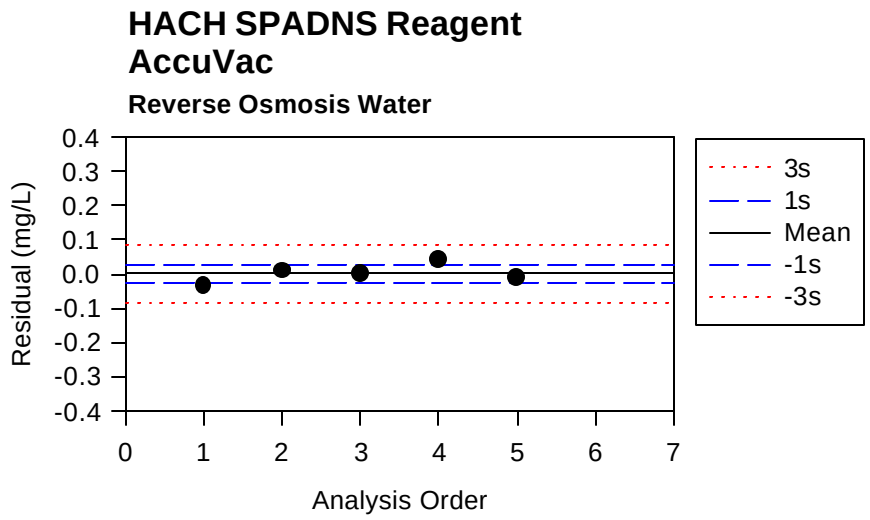



*Figure 77*

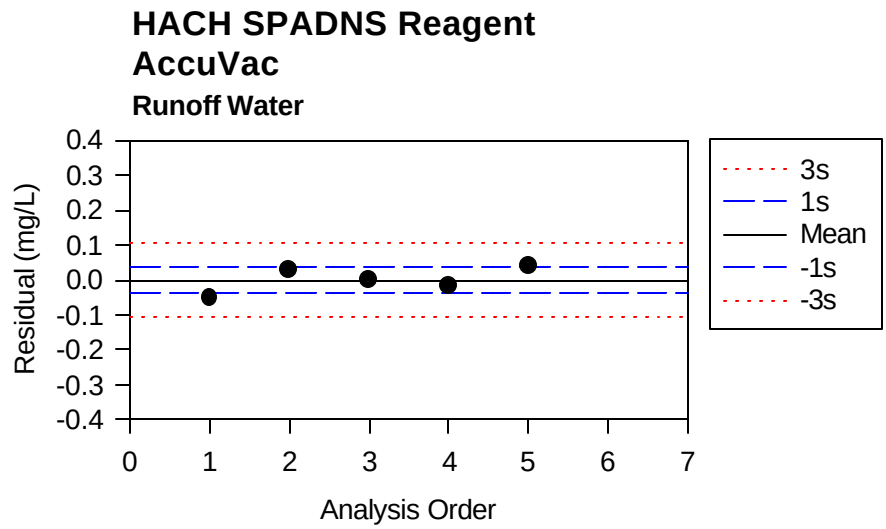



*Figure 78*

# 24 Hardness Summary

# 25 Hardness

The HACH digital titrator is our standard lab procedure for total hardness determinations and it also is our recommended field method for hardness. It is simple, effective and reliable. A comparison to the two kits tested is shown below. The HACH titrator, although larger, outperformed the CHEMetrics method in every aspect of the evaluation.

*Table 81*

| Kit Name | Method | Capital Cost | Expendable Cost (per sample) | Time Required (min) | Sample Vol. (mL) | Expertise Required |
|---|---|---|---|---|---|---|
| CHEMetrics Total Hardness | EDTA Titration | $0.00 | $2.25 | 5-10 | 25 | some |
| HACH Total Hardness | EDTA Titration | $94.00 | varies with concentration | varies with concentration | varies with concentration (100 mL max) | some |

*Table 82*

| Kit Name | Precision | Shelf Life | Regular Maintenance | Safety Hazards | Upper Limit of Useful Range (mg/L) |
|---|---|---|---|---|---|
| CHEMetrics Total Hardness | .01442 | not indicated | none | sharps | 200 |
| HACH Total Hardness | not evaluated | not indicated | none | NA | 160 |

## 25.1 Spiked Samples

The HACH Total Hardness Method is clearly superior to the CHEMetrics Titration Cells. In addition to its superior analytical capability, the HACH digital titrator is easier to use than the CHEMetrics method. The analyses are based solely on data from reverse osmosis samples.

*Table 83*

| Kit Name | Adjusted $R^2$ | Standard Error | Intercept | p-Value | Slope | p-Value | Detection Limit (mg/L) | Limit of Quantification (mg/L) |
|---|---|---|---|---|---|---|---|---|
| CHEMetrics | 0.0289 | 27.4542 | 0.0000 | NA | 0.7974 | 2.296E-2 | 46.2328 | 92.4656 |
| HACH | 0.9741 | 8.5019 | 4.4854 | 0.4460 | 0.6610 | 1.1564E-3 | 18.8026 | 33.1199 |

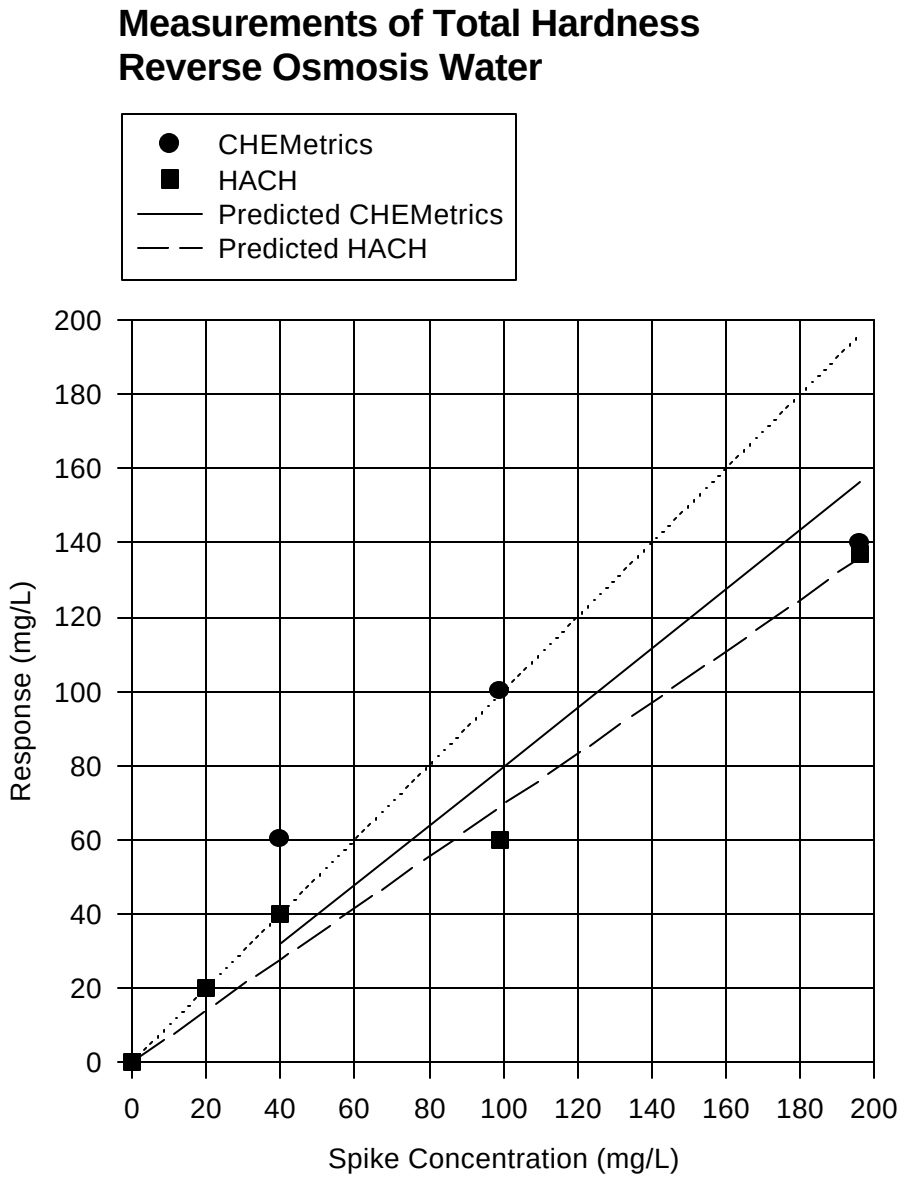

Measurements of Total Hardness
Reverse Osmosis Water
CHEMetrics
HACH
Predicted CHEMetrics
Predicted HACH
Response (mg/L)
Spike Concentration (mg/L)
0
20
40
60
80
100
120
140
160
180
200

*Figure 79*

## 25.2 Parallel Analyses

The correlation of data may not be as poor as the fit first appears. The upper limits of the test methods (200 mg/L for CHEMetrics and 160 mg/L for HACH) are quite limiting. The HACH method is easier to adjust for more concentrated solutions. However, many of the CHEMetrics results simply are reported as “over-range.”

| Sample ID | HACH (mg/L as $CaCO_3$) | CHEMetrics (mg/L as $CaCO_3$) |
|---|---|---|
| 2464 | 166 | 200 |
| 2473 | 283 | >200 |
| 2491 | 120 | 140 |
| 2501 | 460 | >200 |
| 2530 | 156 | 100 |
| 2539 | 143 | 140 |
| 2638 | 220 | 200 |
| 2695 | 297 | >200 |
| 2722 | 291 | >200 |
| 2731 | 155 | 200 |
| 2774 | 215 | 80 |

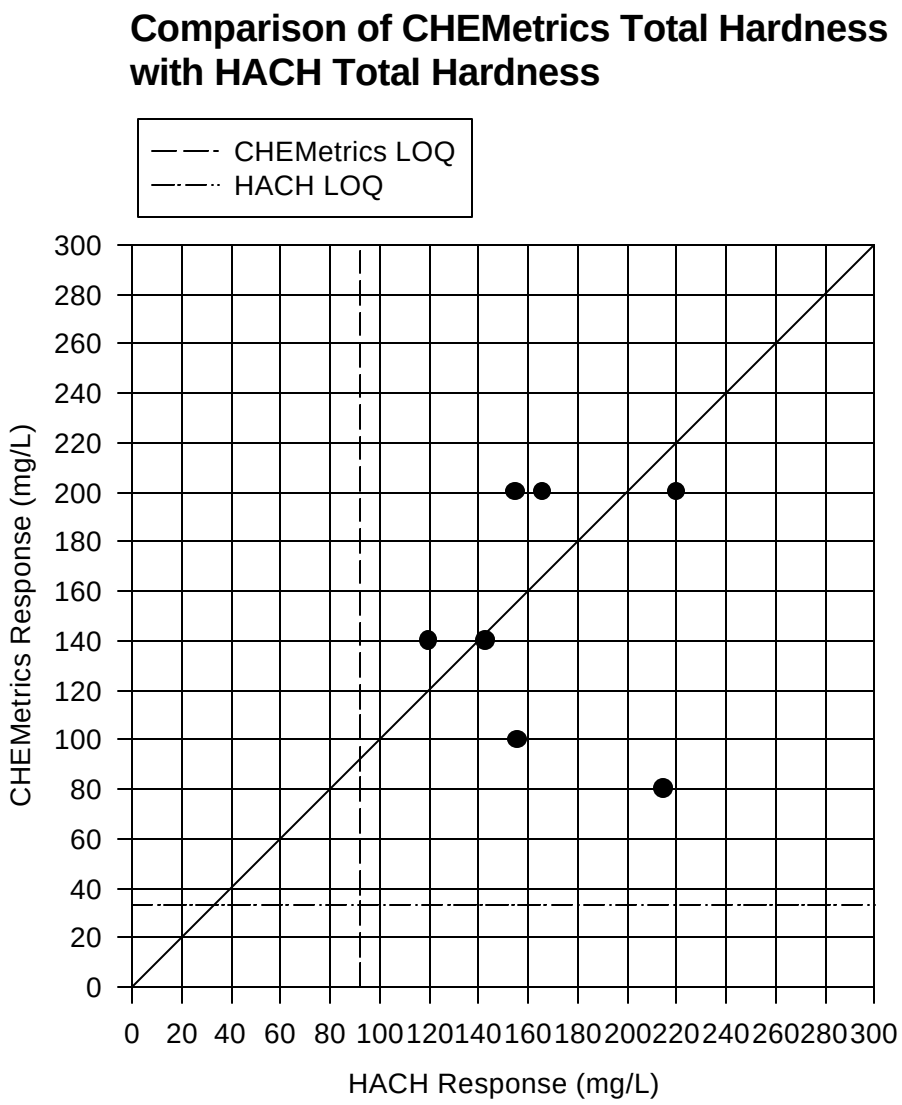



*Figure 80*

## 25.3 CHEMetrics

### *25.3.1 Method*

The CHEMetrics Total Hardness Titration Cells are devices that back titrate samples to determine the total hardness of the solution. The method is based on EDTA titration with calmagite (1-(10hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulfonic acid) indicator. This method is an adaptation of Standard Methods 2340 C (1994).

The method requires a little manual dexterity, but is actually quite simple. The user collects 25 mL of sample. A titration cell is placed in the specially designed holder. The tip of the ampoule is then immersed in the sample, and the tip is broken. The cell holder keeps the tube to the ampoule closed when held. The user releases the holder to allow a small amount of sample to enter the titration cell. Small amounts of sample are drawn into the cell until the desired color change (blue to pink) is achieved. If the endpoint is not reached, the hardness concentration is less than 20 mg/L. If the endpoint is reached immediately, the hardness exceeds 200 mg/L. Other concentrations are read directly from the printed scale on the side of the ampoule.

### *25.3.2 Observations*

The printed scale is not linear. As the hardness concentration increases, the scale loses resolution. In addition, the ampoule must be inverted to read the scale properly; the scale is printed upside down. The ampoule may be ejected from the holder if too much pressure is applied, therefore, the user should take care to prevent injury from flying, broken glass. Due to the limited data available, the intercept of the regression for the spike samples was forced through zero.

*Table 84*

| Sample ID | Spike Conc. (mg/L) | Order | Response | Recovery (%) |
|---|---|---|---|---|
| HAR RO 0 | 0.000 | 2 | <20 | NA |
| HAR RO 1 | 19.960 | 3 | <20 | NA |
| HAR RO 2 | 39.841 | 4 | 60 | 151 |
| HAR RO 3 | 99.010 | 1 | 100 | 101 |
| HAR RO 4 | 196.078 | 5 | 140 | 71 |

*Table 85*

SUMMARY OUTPUT

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.727267368 |
| R Square | 0.528917825 |
| Adjusted R Square | 0.028917825 |
| Standard Error | 27.45417054 |
| Observations | 3 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 1692.537039 | 1692.537039 | 2.245543783 | 0.374625393 |
| Residual | 2 | 1507.462961 | 753.7314803 | | |
| Total | 3 | 3200 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0 | #N/A | #N/A | #N/A | #N/A | #N/A | #N/A | #N/A |
| X Variable 1 | 0.797449399 | 0.122979567 | 6.484405659 | 0.022966485 | 0.268310662 | 1.326588136 | 0.268310662 | 1.326588136 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Y* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 31.7711815 | 28.2288185 | 1.028216039 |
| 2 | 78.95546498 | 21.04453502 | 0.766533266 |
| 3 | 156.3622832 | -16.36228323 | -0.595985342 |

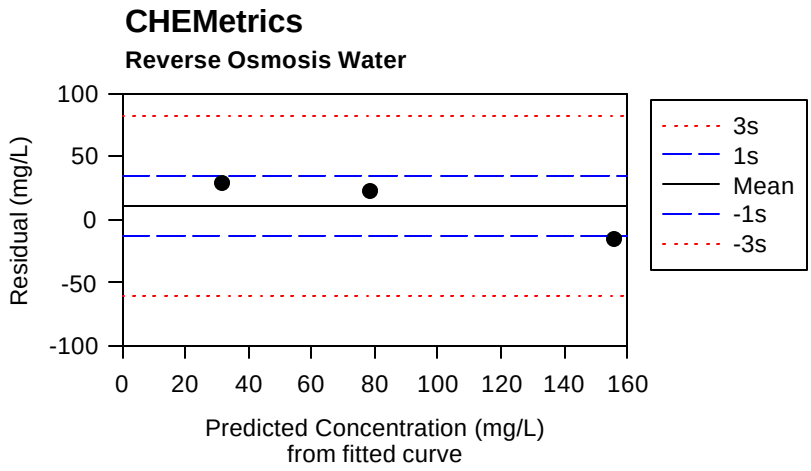



*Figure 81*

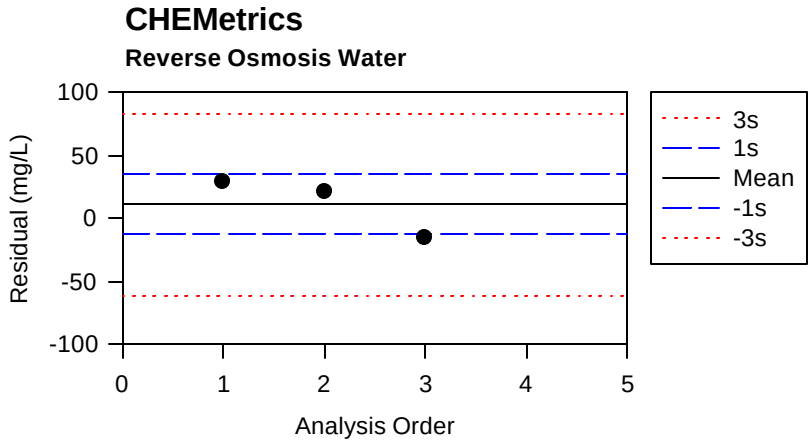



*Figure 82*

## 25.4 HACH Total Hardness

### *25.4.1 Method*

The HACH digital titrator is used to perform an EDTA titration of the sample for a quick and accurate measurement of the total hardness of the sample. The indicator used is calmagite (1-(10hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulfonic acid). The method is an adaptation of Standard Methods 2340-C (1994).

The procedure is very simple, but like all titrations, the method involves some guesswork. A sample of water is taken, but the required sample volume is dependent on the hardness of the water. Table 6 provides some guidance for selecting sample volumes and titration cartridges based on expected hardness concentrations.

*Table 86*

| Expected Range (mg/L as $CaCO_3$) | Sample Volume (mL) | Titration Cartridge | Digit Multiplier |
|---|---|---|---|
| 10-40 | 100 | 0.0800 | 0.1 |
| 40-160 | 25 | 0.0800 | 0.4 |
| 100-400 | 100 | 0.800 | 1.0 |
| 200-800 | 50 | 0.800 | 2.0 |
| 500-2000 | 20 | 0.800 | 5.0 |
| 1000-4000 | 10 | 0.800 | 10.0 |

To analyze a sample, choose the appropriate volume and titration cartridge. Load the cartridge into the digital titrator. Place the sample in an Erlenmeyer Flask and add 1.0 mL of Hardness 1 Buffer Solution. Then, add the contents of 1 ManVer 2 Powder Pillow (calmagite). Set the titrator to read zero digits. Titrate the sample by slowly turning the titrator knob until the endpoint is reached. The endpoint is marked by a red to blue color change in the solution. Use the digit multiplier based on the selected volume and titration cartridge to calculate the hardness of the solution in mg/L as $CaCO_3$. The procedure is made simple by the use of a magnetic stirrer and titration stand.

The measurement of total hardness by this method will include all divalent cations in the sample. However, some polyvalent cations may interfere (charge greater than 2). Transition metals and heavy metals will alter the endpoint. Iron concentrations below 15 mg/L will not interfere. Iron concentrations of 15-30 mg/L will alter the appearance of the endpoint. The solution will change from red to green, not blue. Iron concentrations in excess of 30 mg/L make the test unusable. If iron concentrations of greater than 30 mg/L are present, a CDTA titration cartridge can be substituted for the EDTA titration cartridge. Manganese in excess of the 20 mg/L must be masked using 0.1 g of hydroxylamine hydrochloride. Copper interferes at 0.10 mg/L. Aluminum interferes at 0.20 mg/L. Any cobalt or nickel in the sample must be masked. A 0.5 g addition of potassium cyanide will remove the interference of these metals (Cu, Al, Zn, Co and Ni) up to 100 mg/L each. High salt concentrations will also mask the endpoint.

### *25.4.2 Observations*

If the user has no idea of the expected concentration, the 100-400 mg/L range is a good first attempt. The EM Science total hardness test strips may also be used to provide a first approximation of the hardness concentration. Alternatively, the user may elect to titrate the sample quickly using large additions of titrant to determine the approximate endpoint, then titrate the sample with more care to accurately determine the concentration.

This analysis is our standard laboratory technique. With its rugged design we are confident recommending the HACH digital titrator for field use.

*Table 87*

| Sample ID | Spike Concentration (mg/L) | Order | Response (mg/L) | Recovery (%) |
|---|---|---|---|---|
| HAR RO 0 | 0 | 5 | 0 | NA |
| HAR RO 1 | 19.9 | 3 | 20 | 100 |
| HAR RO 2 | 39.8 | 2 | 40 | 100 |
| HAR RO 3 | 99.0 | 4 | 60 | 61 |
| HAR RO 4 | 196 | 1 | 137 | 70 |

*Table 88*

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.987964285 |
| R Square | 0.976073428 |
| Adjusted R Square | 0.726073428 |
| Standard Error | 8.170088759 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 10892.1986 | 10892.1986 | 163.1781488 | 0.001035091 |
| Residual | 4 | 267.0014013 | 66.75035034 | | |
| Total | 5 | 11159.2 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0 | #N/A | #N/A | #N/A | #N/A | #N/A | #N/A | #N/A |
| Spike Concentration (mg/L) | 0.692663275 | 0.036452088 | 19.00201925 | 4.51831E-05 | 0.591455845 | 0.793870706 | 0.591455845 | 0.793870706 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0 | 0 | 0 |
| 2 | 13.82555897 | 6.174441027 | 0.755737325 |
| 3 | 27.59639755 | 12.40360245 | 1.518172301 |
| 4 | 68.58059088 | -8.580590875 | -1.050244511 |
| 5 | 135.8160297 | 1.18397033 | 0.144915235 |

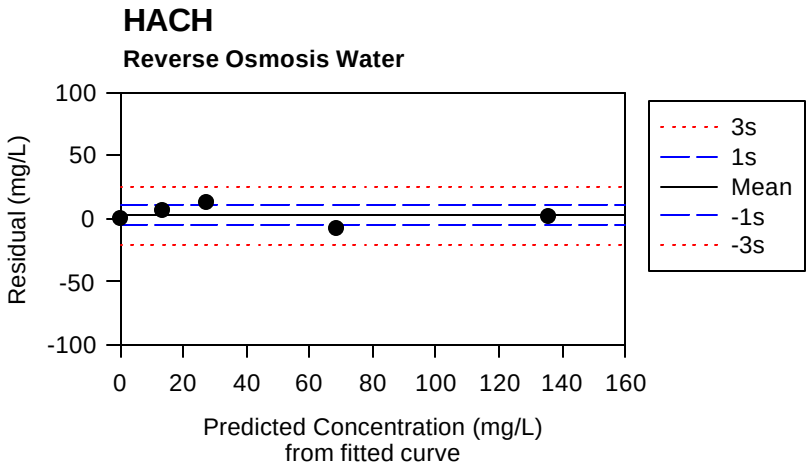



*Figure 83*

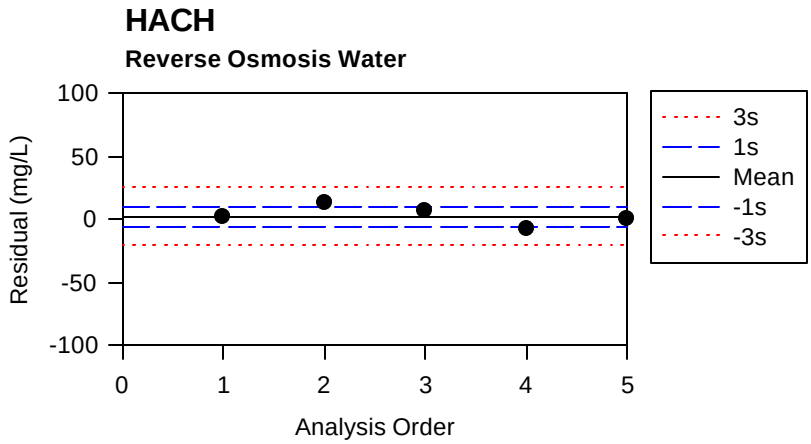



*Figure 84*

# 26 Hydrocarbon Summary

# 27 Hydrocarbons

These tests are summarized together since many of the selected methods do not readily distinguish between these types of compounds. These kits measure different overlapping groups of organic compounds. Therefore, the response factors will vary in magnitude, but the measurements indicate similar general trends in concentration. Several of these kits are quite expensive and were therefore only reviewed in a preliminary manner. Therefore, a full and complete comparison is not available for all of the instruments. The information about each method is summarized in this section.

## 27.1 Dtech BTEX Test Kit

### *27.1.1 Method*

The Dtech BTEX method uses immunoassay technology to determine the concentration of benzene, toluene, ethylbenzene and xylene (BTEX). The developers of the test have developed antibodies specific to these compounds. The antibodies are attached to a latex matrix. The BTEX compounds compete for reaction sites (the antibodies) on the latex particles. A color development solution is added to quantitate the amount of BTEX compounds in the sample. The user may use a color card for visual comparisons or the Dtechtor (a small spectrophotometer) to quantitate the results of the test. A soil extraction pack is available separately to perform BTEX analyses on soil samples.

### *27.1.2 Soil Samples*

A plunger is provided with the kit to measure a known volume of soil. The plunger is filled with sediment. In our analyses, the sediment was not consistent enough to draw the soil into the plunger. The soils simply ran back out of the plunger. However, spooning the sediment into an upside down plunger was sufficient. If this is necessary for other users, take care to fill the plunger with sediment, not water.

The sediment is expunged from the sample into a methanol extraction bottle with metal bearings to help break up clumps of soil. The material is then filtered and the extract used to conduct the water analysis. The sediment samples may take up to an hour to settle and separate in fine soils. A cloudy sample will skew the results of the analysis. After separation, the extract is treated as a water sample.

### *27.1.3 Water Samples*

The user takes 1.0 mL of extract or water sample and fills Bottle A. A snap-on filtration tip is then placed on the bottle to remove particulates from the solution. Bottle A is used to place approximately 14 drops of solution into a reagent vial. The vial has calibration lines to measure the amount of sample needed. Immediately after adding sample to the BTEX vial, add Reagent C to the reference vial in the same manner. Wait 5 minutes. Pour the sample into the side of the sample cup marked T (test). Pour the reference vial into the side of the cup marked R (reference). Allow both sides to drain completely.

Use 5 drops of reagent D to rinse each side of the sample cup. Allow both sides to drain completely. Use 5 drops of reagent E to rinse both sides of the sample cup. Allow both sides to drain completely. The test is completed when the color of the reference side of the cup matches the reference color on the color card. The user may determine the concentration by matching the color to the color card or using the Dtechtor.

If the Dtechtor is used, the user must first zero the instrument. A zero cup assembly is provided with the instrument. Select program #1. Insert the cup and read. The answer is displayed in percent. There is a conversion chart included in the directions for the kit.

When working with immunoassays, interference by similar compounds is refereed to as cross reactivity. The interference occurs when the antibody for the target molecule mistakes a structurally similar molecule for the target. All target and cross reactive compounds are listed in Table 1.

*Table 89*

| Compound | Concentration causing positive test (ppm) | Compound | Concentration causing positive test (ppm) |
|---|---|---|---|
| benzene | 1.2 | nitrobenzene | 6.0 |
| toluene | 0.6 | 2-nitrophenol | 7.0 |
| ethylbenzene | 0.6 | methylcyclohexane | 100 |
| xylenes | 0.6 | cis-1,3-dichloropropene | 200 |
| o-cresol | 1.5 | iso-octane | N/A |
| chlorobenzene | 1.8 | benzoic acid | N/A |
| 1,2-dichlorobenzene | 6.0 | hexane | N/A |

(Dtech BTEX 1993)

### *27.1.4 Observations*

This test is difficult to use, but the manufacturer has made every effort to make these tests as simple as possible. The reagent bottles are color coded. The reagent sets are packaged so that everything you need for an analysis is located in a logical fashion. The kit is one of the few that addresses waste disposal. The kit is designed to package the waste products at the completion of a test.

There are several major problems with the widespread application of this test method: short shelf-life, long analysis time, well-trained operator, and expense. The expendable cost for this method is $25.00/sample. The kit has a shelf-life of about one month and must be refrigerated. These problems would make widespread field use difficult. In addition, the test takes about 30 minutes to run and it is relatively complex, with errors common for inexperienced users. If the sample is sediment, the test can take over an hour for fine particles. Expired kits produce no usable data.

## 27.2 Dexsil PetroFlag

The Dexsil PetroFlag is a field method for the determination of hydrocarbon content in soil. The kit uses a proprietary solvent extraction system to remove hydrocarbons from soil samples. The extract is filtered to remove particulate interference. A color developing solution is added to the extract for hydrocarbon determination. The user may choose a general response factor for a total hydrocarbon reading or select a response factor for a particular contaminant of interest (if known).

The kit costs about $700 with expendable costs of $10 to $15 per sample. The manufacturer reports that a single operator may analyze up to 25 samples per hour. The test method appears simple. However, the identity of the hydrocarbons are unknown.

## 27.3 PetroSense PHA-100*Plus* Portable Hydrocarbon Analyzer

### *27.3.1 Method*

The PetroSense PHA-100*Plus* Portable Hydrocarbon Analyzer is sensitive to all hydrocarbons containing at least 6 carbon atoms. The manufacturer indicates increased sensitivity to aromatic compounds. Therefore, this device should be sensitive to both BTEX and PAH compounds. The device will measure these compounds dissolved in water or as vapor in head space. The probe has a coated membrane that "traps" hydrocarbons from its surroundings. A fiber optic cable allows the instrument to measure the amount of hydrocarbons attached to the membrane using a light beam. The probe is rinsed between measurements to prevent carry over.

The instrument must be calibrated prior to initial use. The user may select a single point verification and blank or a two-point calibration and a blank for internal calibration. The calibration procedure will take at least 30 minutes to complete, but is infrequently required. However, the probe should be pre-conditioned in a hydrocarbon containing water solution before measurements are made. Best results will be obtained if the pre-conditioning solution has a similar composition and concentration as the samples to be tested.

The actual measurements are quite simple. The probe is immersed in the desired matrix, water in this case, and allowed to equilibrate with its surroundings. After equilibration, the device reports the concentration of hydrocarbons as the compound used for calibration. There are two modes available for making the measurement, single sample and continuos reading. The single sample mode allows the probe to equilibrate for a pre-determined amount of time (the default is 5 minutes) and takes a 30 s reading. The continuo mode displays the readings as a running average of the last 5 readings taken at 30 s intervals. The meter will display an S beside the response when the readings seem to settle down. However, the equilibrated answer in this mode will continue to change with time, especially during the first few minutes. We recommend using the sample mode to make measurements. The sample mode should increase the repeatability of the analyses by not requiring the operator to determine when the test is finished.

### *27.3.2 Observations*

The PetroSense is a rugged instrument. The probe is housed in a steel frame to protect the sensor from damage. The instrument is designed for *in situ* measurements, but it is also easily used in the laboratory. The meter has an internal data logger that may be very useful for extended field surveys. The keypad on the meter allows the user to enter sample IDs and automatically records the date, time and temperature when the sample is taken. The device has an RS-232 port for downloading the data to a computer via a serial port for further analysis. Table 3 summarizes the composition of the standard stock standard solution used for testing.

*Table 90*

| Sample ID | Order | Total Spike Concentration (µg/L) | Total Spike Concentration (mg/L) | Response (mg/L) as xylene |
|---|---|---|---|---|
| L0 | | 0 | 0.000 | 0.00 |
| L1 | 1 | 2053 | 2.053 | 14.6 |
| L2 | 6 | 1027 | 1.027 | 7.30 |
| L3 | 8 | 513 | 0.513 | 6.90 |
| L4 | 7 | 257 | 0.257 | 4.90 |

*Table 91*

| Spike Contents | | | |
|---|---|---|---|
| Compound | Certified Concentration (µg/L) for 1L dilution | Spike Concentration (µg/L) | Spike Concentration (mg/L) |
| anthracene | 54.3 | 108.6 | 0.1086 |
| benzo(g,h,i)perylene | 42.6 | 85.2 | 0.0852 |
| benzo(a)pyrene | 23.1 | 46.2 | 0.0462 |
| 2-chloronaphthalene | 81.0 | 162 | 0.162 |
| 2,2'-oxybis(1-chloropropane) | 121 | 242 | 0.242 |
| chrysene | 28.0 | 56 | 0.056 |
| dibenzofuran | 74.2 | 148.4 | 0.1484 |
| 1,2-dichlorobenzene | 55.3 | 110.6 | 0.1106 |
| 1,4-dichlorobenzene | 170 | 340 | 0.34 |
| 2,4-dichlorobenzene | 91.9 | 183.8 | 0.1838 |
| bis(2-ethylhexyl)phthalate | 36.1 | 72.2 | 0.0722 |
| naphthalene | 72.0 | 144 | 0.144 |
| nitrobenzene | 36.4 | 72.8 | 0.0728 |
| N-nitroso-di-N-propylamide | 44.9 | 89.8 | 0.0898 |
| pyrene | 52 | 104 | 0.104 |
| 1,2,4-trichlorobenzene | 43.9 | 87.8 | 0.0878 |
| Total | 1026.7 | 2053.4 | 2.0534 |

*Table 92*

SUMMARY OUTPUT

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.954769855 |
| R Square | 0.911585476 |
| Adjusted R Square | 0.882113968 |
| Standard Error | 1.808129789 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 101.124 | 101.124 | 30.93107667 | 0.011468516 |
| Residual | 3 | 9.808 | 3.269333333 | | |
| Total | 4 | 110.932 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 1.97 | 1.178756407 | 1.671252846 | 0.193264835 | -1.781332491 | 5.721332491 | -1.781332491 | 5.721332491 |
| Total Spike Concentration (mg/L) | 0.006194604 | 0.001113823 | 5.561571421 | 0.011468516 | 0.00264992 | 0.009739288 | 0.00264992 | 0.009739288 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Response (mg/L) as xylene* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 1.97 | -1.97 | -1.089523558 |
| 2 | 14.69 | -0.09 | -0.049775188 |
| 3 | 8.33 | -1.03 | -0.569649373 |
| 4 | 5.15 | 1.75 | 0.967850876 |
| 5 | 3.56 | 1.34 | 0.741097242 |

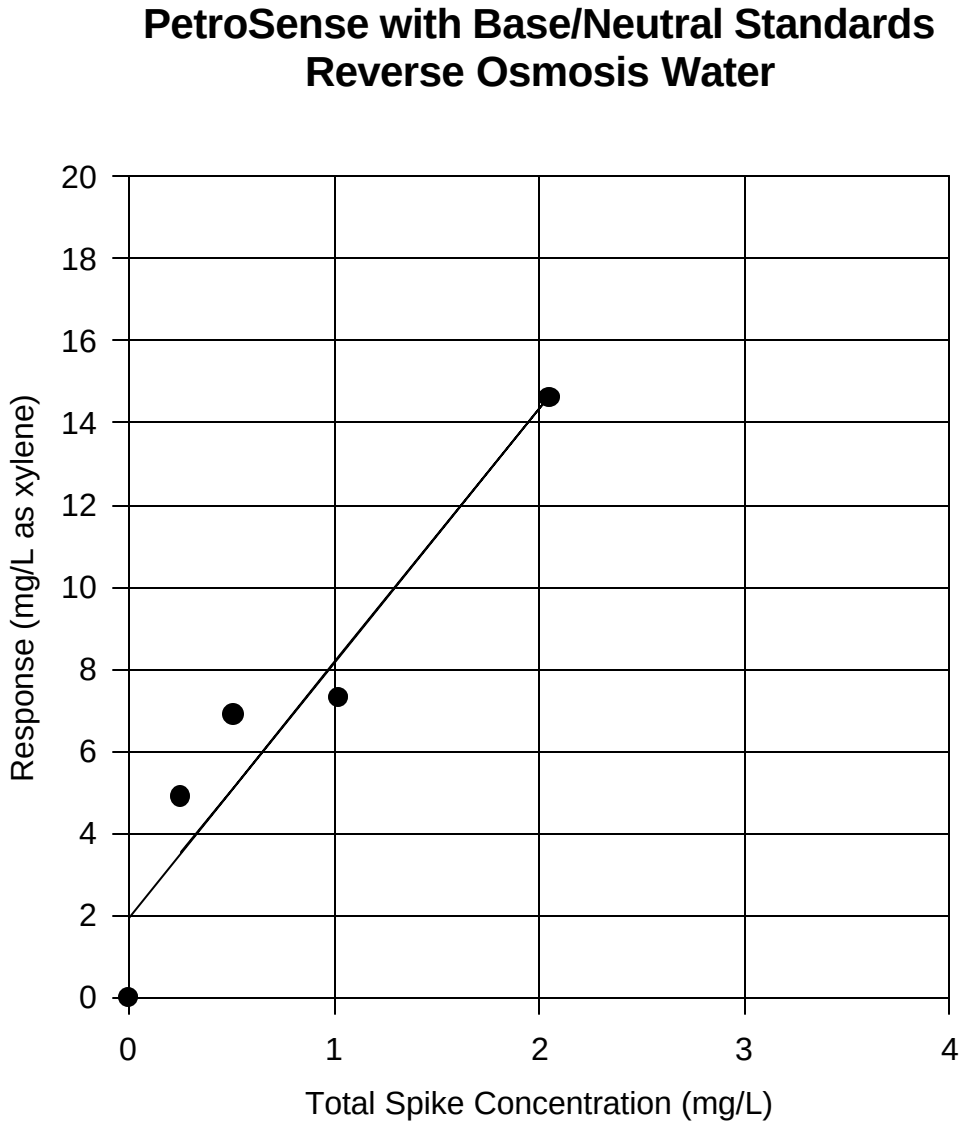

PetroSense with Base/Neutral Standards
Reverse Osmosis Water
Response (mg/L as xylene)
20
18
16
14
12
10
8
6
4
2
0
0
1
2
3
4
Total Spike Concentration (mg/L)

*Figure 85*

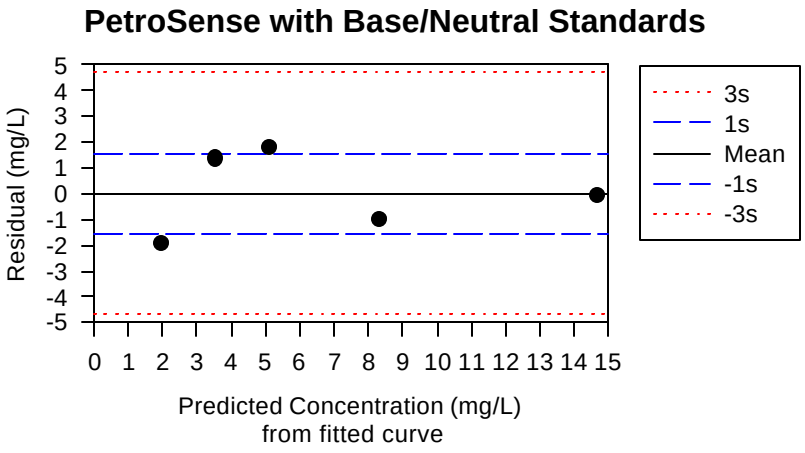



*Figure 86*

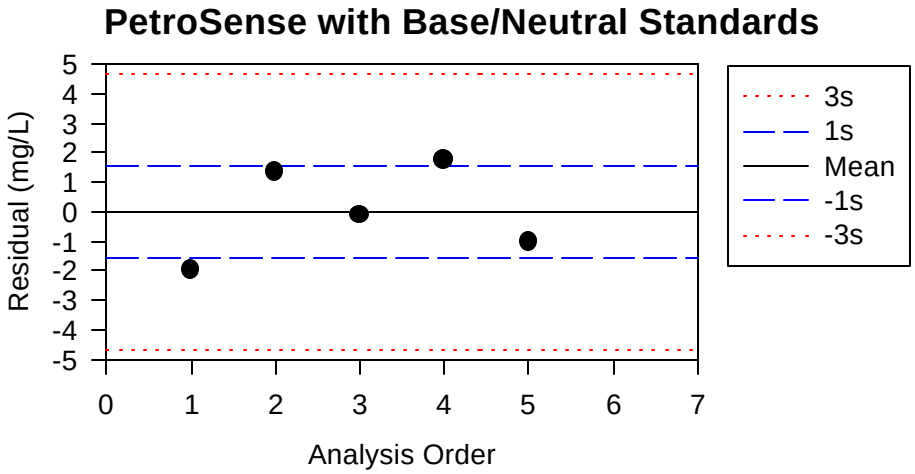



*Figure 87*

## 27.4 Precision Analyses

*Table 93*

| Sample ID | Response (mg/L) |
|---|---|
| L1 | 14.6 |
| L1 | 17.0 |
| L1 | 17.2 |
| L1 | 17.8 |
| L1 | 18.2 |
| Average | 17.0 |
| Standard Deviation | 1.41 |
| COV | 0.0830 |

## 27.5 Wilkes Infracal Oil in Water Analyzer

The Wilkes Infracal is a simple filter infrared (IR) spectrometer. The device quantitates hydrocarbons by measuring the IR absorbance of C-H bonds present in all hydrocarbons. This requires the sample to be extracted from water, as water greatly interferes with this test. Traditionally, a Freon extraction is used to remove hydrocarbons from the water for analysis. This would be unacceptable for field use due to the expense and potential hazards associated with Freon. However, the manufacturer has designed the instrument to use 3M disposable IR cards that do not require Freon extraction. Instead the oils and greases are extracted using hexane. Hexane poses a reduced health and environmental threat compared to Freon. However, hexane also contains C-H bonds and would interfere with the test. The new method only requires 10 µL of extract. The residual hexane is easily evaporated from this small sample size allowing quick interference free measurement.

The kit has a capital cost of about $5000. The expendable costs are unknown at this time, but would include the disposal IR cards and hexane.

## 27.6 Forestry Supply Oil in Water Test Kit

This method has a very high detection limit, designed to detect free-floating hydrocarbons on water. If this method was usable, it would be the cheapest test kit to use in this group. The test stains floating hydrocarbons on sample water. It is not suitable for detecting “dissolved” hydrocarbons.

## 27.7 Dtech PAH Test Kit

### *27.7.1 Method*

The Dtech PAH Test Kit is virtually identical to the Dtech BTEX Test kit. It also uses immunoassay technology for measurement. However, the antibodies and enzymes utilized for this kit are selective for polyaromatic hydrocarbons (PAHs). A separate PAH Soil Extraction kit is available for the determination of PAH in soil.

### *27.7.2 Soil*

The volume of sediment is measure using the syringe provided with the Soil Extraction Pack. The soil is then placed in a mixing bottle containing isopropanol to extract PAHs from the slurry. The mixture of soil and isopropanol is shaken for 3 minutes. The mixing bottle contains metal balls to break up clumps of soil sample. The sample is then allowed to settle until a clear liquid layer appears over the sediment. This may take 30 minutes or more depending on particle size. The user removes 1 mL of the clear layer in the water procedure to determine PAH concentrations in the soil sample. The clear extract may be treated as a water sample for the remainder of the analysis.

### *27.7.3 Water*

The water sample (or soil extract) is added to a mixing bottle fitted with a filter tip. After mixing, enough sample is introduced to the test vial to bring the liquid layer between the two calibration marks. Immediately thereafter, the reference vial must be filled in the same way with Reagent C. Both vials are allowed to set undisturbed for 5 minutes. At the conclusion of the reaction time, the vials are emptied into the appropriate sides of the sample cup (as marked). The contents must drain completely through the filter before proceeding. Ten drops of Reagent D are added to each side of the cup. After draining again, 5 drops of reagent D are added to each cup. The user must now wait until the reference side of the cup develops a blue color that matches the reference color chart included with the kit. The color development time is temperature dependent. Cold samples will take longer to develop than warm samples. At 70°F, the development time is about 10 minutes. After full development, the color may be fixed by adding 8 drops of Reagent F if the concentrations are to be measured later. Concentrations may be determined using the color card included with the kit or with the Dtech Dtechtor for lower detection and better precision. If the Dtechtor is used, the user must first zero the instrument. A zero cup assembly is provided with the instrument. Select program #2. Insert the cup and read. The answer is displayed in percent. There is a conversion chart included in the directions for the kit.

When working with immunoassays, interference by similar compounds is referred to as cross reactivity. The interference occurs when the antibody for the target molecule mistakes a structurally similar molecule for the target. All target compounds listed in Table 6 will produce a positive response at the listed concentration.

*Table 94*

| Compound | Concentration causing a positive test (ppb) | Compound | Concentration causing a positive test (ppb) |
|---|---|---|---|
| naphthalene | 1766 | benzo(a)anthracene | 42 |
| acenaphthalene | 311 | chrysene | 8 |
| acenaphthene | 311 | benzo(b)fluoranthrene | 53 |
| fluorene | 106 | benzo(a)pyrene | 10 |
| phenanthrene | 421 | dibenz(a,h)anthracene | 1060 |
| anthracene | 10 | benzo(g,h,i)perylene | 42 |
| fluoranthrene | 5 | indeno(123-cd)pyrene | 8 |
| pyrene | 10 | | |

(Dtech PAH 1994)

### *27.7.4 Observations*

Dtech has tried to make a very complex task simple with only partial success. The packaging of the test is excellent. Reagents are clearly marked by color code and letters. However, the contents of the reagents are not disclosed. Despite the effort, the test is difficult, time consuming and expensive. The major problem with the procedure is determining the "end of test." This is a subjective measurement that depends on the individuals color perception. The shades of blue used as an indicator may make this very problematic. It is also difficult to decide if the reference filter had developed to the required color in all tests. Although other individuals may have better color perception, the differences among individuals will decrease the repeatability of the test. Finally, the results are reported as total PAH concentration without an adequate description of this term. The directions state, "The PAH mixture consists of individual PAHs blended together at ratios similar to those found at sites of both petrogenic and pyrolitic contamination (Dtech1994)." However, this mixture is not disclosed in the instruction packet.

The test is the most sensitive field screening tool for PAH compounds we have tested. The manufacturer acknowledges the limitations of the test. The documentation of performance and recommended uses for this test and the similar Dtech BTEX kit are probably the best of any of the evaluated methods for all the parameters.

The method does not directly read PAH concentration. The color card only gives broad total PAH concentration ranges. The meter output is in percent. This value must be transformed into a total PAH concentration. The Dtech instruction manual and the color card both include a table to make this transformation. The table outlines different linear regions of the working range of the instrument. Linear interpretation of the percent response can be used to determine total PAH concentration. The results are summarized below. The figure shows the instrument response (µg/L as total PAH) versus the total concentration of the spike standard. The total concentration of the spike standard is the sum of the

individual constituents. The standard used was designed for QA/QC applications with base/neutral extractions for GC/MS chromatography. Therefore, the antibodies in the assay may not be sensitive to all compounds present.

*Table 95*

| Sample ID | Order | Total Spike Concentration (µg/L) | PAH Spike Concentration (µg/L) | Response (%) | Response (µg/L) |
|---|---|---|---|---|---|
| L0 | | 0 | 0 | not tested | not tested |
| L1 | 1 | 2053.4 | 1088.0 | 16 | 53 |
| L2 | 6 | 1026.7 | 544.0 | 8 | 21 |
| L3 | 8 | 513.4 | 272.0 | 1 | 8 |
| L4 | 7 | 256.7 | 136.0 | LO | <8.0 |

*Table 96*

SUMMARY OUTPUT

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.998349705 |
| R Square | 0.996702133 |
| Adjusted R Square | 0.993404267 |
| Standard Error | 1.870828693 |
| Observations | 3 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 1057.792181 | 1057.792181 | 302.2263374 | 0.036579323 |
| Residual | 1 | 3.5 | 3.5 | | |
| Total | 2 | 1061.292181 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | -8.055555556 | 2.291287847 | -3.515732676 | 0.17641829 | -37.16900333 | 21.05789222 | -37.16900333 | 21.05789222 |
| X Variable 1 | 0.058656104 | 0.003374015 | 17.38465811 | 0.036579323 | 0.015785357 | 0.101526851 | 0.015785357 | 0.101526851 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Y* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 52.16666667 | 0.5 | 0.267261242 |
| 2 | 22.05555556 | -1.5 | -0.801783726 |
| 3 | 7 | 1 | 0.534522484 |

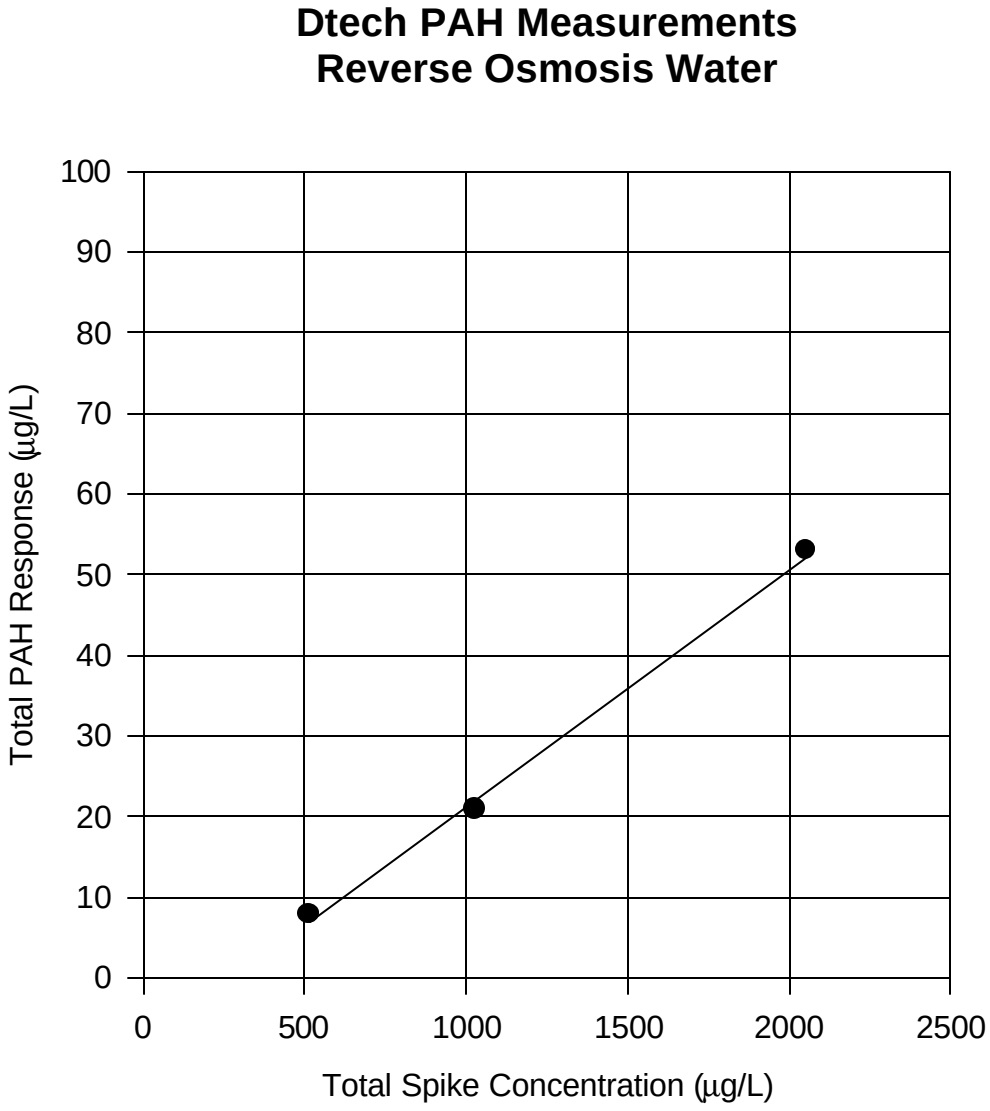

Dtech PAH Measurements
Reverse Osmosis Water
Total PAH Response (µg/L)
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
Total Spike Concentration (µg/L)

*Figure 88*

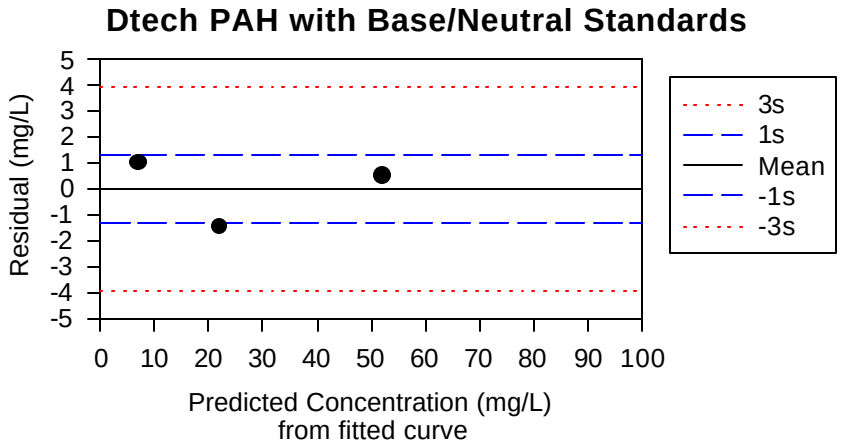



*Figure 89*

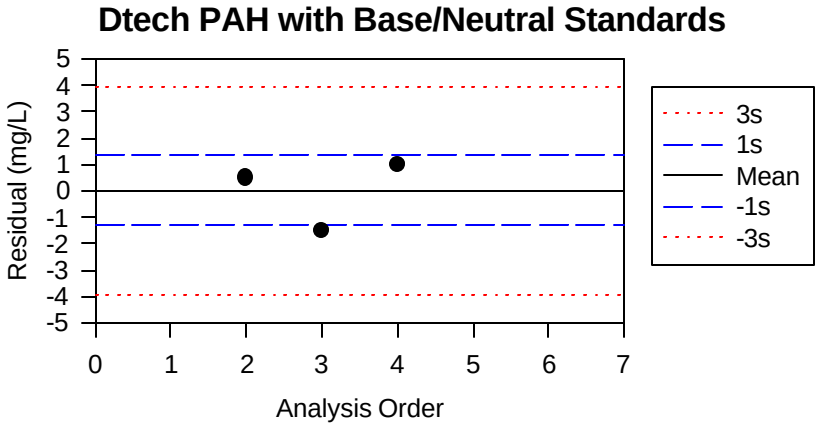



*Figure 90*

### *27.7.5 Precision Analyses*

*Table 97*

| Sample ID | Response (%) |
|---|---|
| L1 | 16 |
| L1 | 22 |
| L1 | 29 |
| L1 | 32 |
| Average | 25 |
| Standard Deviation | 7.2 |
| COV | 0.29 |

## 27.8 Turner Model 10-AU

### *27.8.1 Method*

The Turner Model 10-AU is a multi-purpose fluorometer. All PAHs naturally fluoresce, therefore the instrument can be used to determine PAH concentrations. The instrument is capable of single sample analysis or continuos flow-through monitoring.

Before the first use in a particular application. The span of the instrument must be manually set. A solution representing about 20% of full scale concentration is measured and the adjustment knob is turned until the instrument reads the sample as 80-100% of full scale with the high aperture. This should not be changed unless the lamp, filters or cuvette size is changed.

The instrument may be internally calibrated with a single standard representing 85% of the maximum concentration to be measured. A blank is measured and subtracted from the 85% concentration. The user may enter the concentration of the 85% standard so that output will be in desired units. The user may opt to have output in raw form from the detector. Once the instrument is setup correctly, actual measurements are quite simple. Fill the cuvette and read.

### *27.8.2 Observations*

The method has been compared to the PetroSense. The results look promising. There is evidence of a trend existing in higher concentrations. The reported detection limits of each are shown for reference.

*Table 98*

| Sample ID | Turner Response (mg/L) | PetroSense Response (mg/L) |
|---|---|---|
| 2464 | 10.9 | 0.0 |
| 2473 | OVER | 0.2 |
| 2491 | OVER | 0.0 |
| 2501 | 34.6 | 0.0 |
| 2511 | 34.6 | 0.0 |
| 2530 | 61.3 | 0.0 |
| 2539 | 61.9 | 0.0 |
| 2548 | 59.5 | 0.0 |
| 2566 | OVER | 1.4 |
| 2573 | 53.4 | 1.2 |
| 2585 | 21.2 | 0.0 |
| 2595 | 25.2 | 0.0 |
| 2613 | 31.3 | 0.0 |
| 2620 | 37.3 | 0.5 |
| 2629 | OVER | 0.0 |
| 2638 | 16.5 | 0.0 |
| 2647 | 32.4 | 0.6 |
| 2656 | 59.1 | 0.0 |
| 2666 | 23.7 | 0.0 |
| 2674 | 24.8 | 0.2 |
| 2695 | 29.7 | 0.3 |
| 2704 | 40.7 | 1.1 |
| 2713 | 35.7 | 0.6 |
| 2722 | 35.8 | 1.4 |
| 2731 | 3.5 | 0.2 |
| 2740 | 11.2 | 0.3 |
| 2749 | 30.7 | 0.0 |
| 2765 | 41.3 | 1.1 |
| 2774 | 56.6 | 0.0 |
| 2783 | OVER | 0.3 |
| 2783 | OVER | 0.3 |
| 2792 | 62.8 | 2.0 |
| 2792 | 62.8 | 2.0 |
| 2801 | 30.9 | 0.3 |
| | | |
| JD001 | 56.4 | 0.3 |
| JD002 | 56.1 | 1.4 |
| JD003 | 58.4 | 0.9 |
| JD004 | 48.7 | |
| JD005 | 52.2 | 0.8 |
| Average | 54.4 | 0.9 |
| Standard Deviation | 3.9 | 0.5 |
| COV | 0.1 | 0.5 |

## Comparison of Turner Flurometer and PetroSense PHA-100

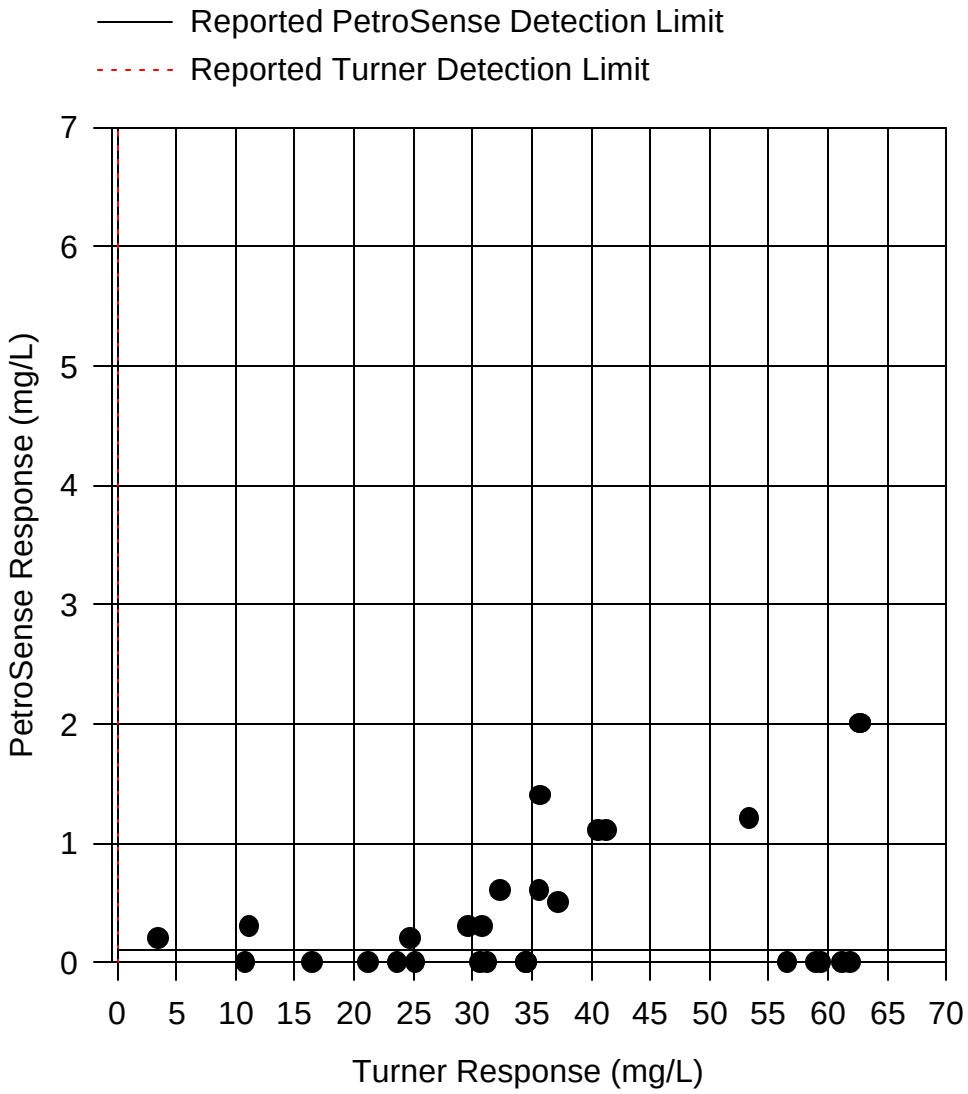



*Figure 91*

## 27.9 Hydrocarbon Test (as supplied in GDS's AquaVat kit)

This test procedure utilizes an organic extraction of a 500 mL water sample in a separatory funnel. After the water sample is placed in the funnel, the organic solvent is poured into the funnel. The cap is placed on the funnel and it is vigorously shaken for two minutes. The cap is slowly unscrewed to release pressure and placed on a ring stand supplied in the test kit. The funnel sits on the stand until the solvent sinks to the bottom of the funnel, with a distinct phase separation (several minutes). The solvent extract is then drained from the bottom stopcock into a small screw-top glass vial, taking care not to allow any of the water to enter the vial. A small vial of "colorizing" reagent (aluminum chloride, a corrosive, harmful solid chemical that violently reacts with water) is then added to the larger vial containing the solvent extract. The color of the resulting mixture is then compared to color photographs in the supplied book to estimate the material and concentration. Care needs to be taken to examine the color of the sediment (the "colorizing reagent"), and not of the overlying extract solution, or of any white precipitate clinging to the glass vial. After the test is completed, the solvent extract is poured into the waste jar, the empty color reagent vial is placed back into the plastic jar, and the broken solvent ampoule can be placed into the screw-top glass vial for shipping back to GDS for proper disposal (along with expended reagents from the other tests). The following table summarizes the hydrocarbons included in the photo booklet:

**Table 11**

| **Hydrocarbon** | **Maximum concentration level shown** |
|---|---|
| Red coloration (all indistinguishable in booklet) | |
| Regular gasoline | <20 ppm |
| Unleaded gasoline | <20 ppm |
| Super unleaded gasoline | <20 ppm |
| Kerosene | <20 ppm |
| | |
| Orange coloration (all indistinguishable in booklet) | |
| Toluene | <10 ppm |
| Xylene | <10 ppm |
| Benzene | <10 ppm |
| | |
| Pale yellow | |
| PCBs | <0.2 ppm |
| | |
| Dark purple | |
| Naphthalene | <2.5 ppm |
| | |
| Black | |
| Diesel | <20 ppm |

Many of the compounds are not possible to distinguish, but the test can identify grossly contaminated water (having greater than several ppm hydrocarbons). A series of tests were conducted to attempt to distinguish typical hydrocarbons that may be found in the water from telecommunication manholes (Table 12).

Table 12

| Sample | Observation | Kit Conclusion |
|---|---|---|
| Blank (extract solvent only) | White | blank |
| Blank (tap water) | White/cream | blank |
| Motor oil (1 drop in 500 mL, or about 100 ppm) | Light brown | Not like anything in photo book |
| Motor oil (5 drops in 500 mL, or about 500 ppm) | Dark/dirty brown | Not like anything in photo book |
| Kerosene (1 drop in 500 mL, or about 100 ppm) | White | blank |
| Kerosene (5 drops in 500 mL, or about 500 ppm) | Purple | 20 ppm kerosene |
| Gasoline (1 drop in 500 mL, about 100 ppm) | Purplish-brown | 5 ppm gasoline |
| Gasoline (5 drops in 500 mL, or about 500 ppm) | Brown | 20 ppm gasoline |
| Canola oil (5 drops in 500 mL, or about 500 ppm) | Yellow | 1 ppm benzene |
| “Super Oil” Household oil (5 drops in 500 mL, or about 500 ppm) | Brown | Not like anything in photo book |

The test conclusions were generally correct for identifying the sample hydrocarbons that were represented in the book, but at greatly reduced sensitivity. However, motor oil, the most likely hydrocarbon that may be found in telecommunication manholes from stormwater and other urban sources, is not included in the book and is not like anything represented. In addition, canola oil, another possible contaminant in urban areas near fast food restaurants, was identified as benzene! However, this kit may be useful to identify any significant hydrocarbon contamination in water at levels of several hundred ppm.

# 28 Lead Summary

# 29 Lead

There are three major types of lead tests discussed in this section. The first two methods are much more involved, but can detect very low lead concentrations. These kits were designed for testing domestic water supplies for lead contamination. The second set of kits are very simple qualitative or semi-quantitative kits designed to detect lead at much higher concentrations. These kits are designed for a broader consumer market interested in problems such as lead paint contamination. The third type of kits are electrochemical methods adopted for field use. The Palintest SA-100 Scanning Analyzer uses anodic stripping voltametry to determine both lead and copper concentrations in water. The Metalyzer 3000 uses potenitometric methods to determine both lead and copper in the sample as well. Both methods are extremely sensitive, but they are also expensive ($2300 and $4200, respectively) and have therefore not been thoroughly tested.

Choosing the best lead kit is very difficult. The La Motte kit may have been the best compromise between complexity and analytic capability. However, the kit is no longer available. The HACH LeadTrak System is the only kit evaluated capable of making quantitative measurements at a reasonable

*Table 99*

| Kit Name | Method | Capital cost | Expendable Cost (per sample) | Time Required (min) | Sample Vol. (ml) | Expertise Required |
|---|---|---|---|---|---|---|
| La Motte Lead in Water Kit | chloroform extraction, visual comparator | $74.85 for kit | $1.57 | 20 | 10 | extensive |
| HACH LeadTrak system | solid phase extraction, colorimeter | $395 for kit w/ DR 100. $1495 for DR 2000 | $4.61 | 45 | 100 | extensive |
| CHEMetrics Lead C6350 Comparator Kit | extraction and visual comparator | Supplied as part of GDS's Aqua Vats test kit | na | 10 | 100 | moderate |
| Innovative Synthesis Corporation The Lead Detective | Sulfide Staining | $0.00 | Varies | 5 | surface test | little |
| Carolina Environment Company KnowLead | colorimetric (positive or negative) | $0.00 | $3.75 | 5 | surface test | little |
| HybriVet Lead Check Swabs | colorimetric (positive or negative) | $0.00 | $2.25 | 5 | surface test | little |
| EM Science Lead | test strips | $500.25 for ReflectoQuant Meter | $1.11 | 10 | drops | little |
| Palintest SA-1000 Scanning Analyzer | anodic stripping voltametry | $2295 | $5.55 for both Cu and Pb | 3 | 5 | little |
| Environmental Technologies Metalyzer 3000 | potentiometry | $4200 | $15 for both Cu and Pb | 3 | 25 | little |

cost. The other methods are all about equally useful for determining high lead concentrations.

*Table 100*

| Kit Name | Precision | Shelf Life | Regular Maintenance | Safety Hazards | Upper Limit of Useful Range (mg/L) |
|---|---|---|---|---|---|
| La Motte Lead in Water Kit | not evaluated | not indicated | none | Chloroform extraction | 1.5 |
| HACH LeadTrak system | not evaluated | not indicated | none | Great deal of reagents that are inadequately labeled. | 0.15 |
| CHEMetrics Lead C6350 Comparator Kit | not evaluated | not indicated | none | Hazardous extraction chemical (carbon tetrachloride) and potassium cyanide | 0.05 |
| Innovative Synthesis Corporation The Lead Detective | not evaluated | 6 weeks after mixing | none | none | NA |
| HybriVet Lead Check Swabs | not evaluated | not indicated | none | none | NA |
| EM Science Lead | Not evaluated | not indicated | Clean reflectoquant optics | none | 500 |
| Carolina Environment Company KnowLead | NA | not indicated | none | none | NA |
| Palintest SA-1000 Scanning Analyzer | not directly tested | about 1 year | none | none | NA |
| Environmental Technologies Metalyzer 3000 | not directly tested | about 1 year | none | none | NA |

## 29.1 Spiked Samples

The spiked analyses were conducted on the La Motte and HACH LeadTrak Kits only. The detection limit of the simple tests are so much greater that the test are only applicable for positive detection of lead. If one of the simpler test does detect lead, there is a serious lead contamination problem.

At the moment, the only lower priced test kit that can be used to quantify results is the HACH LeadTrak System. This is unfortunate, since the LeadTrak system is also the most complicated of all the kits evaluated. The qualitative tests are not included in this part of the evaluation.

*Table 101*

Reverse Osmosis

| Kit Name | Adjusted $R^2$ | Standard Error | Intercept | p-Value | Slope | p-Value | Detection Limit ($\alpha$=0.05) (mg/L) | Limit of Quantification ($\alpha$=0.05) (mg/L) |
|---|---|---|---|---|---|---|---|---|
| La Motte Lead in Water Kit | 0.9493 | 0.1221 | 0.0670 | 0.2602 | 0.9586 | 2.6100E-05 | 0.2726 | 0.4783 |
| EM Science Lead | NA | NA | NA | NA | NA | NA | NA | NA |
| HACH LeadTrak system | 0.9873 | 0.0041 | -0.0020 | 0.4580 | 0.8427 | 3.9523E-04 | 0.0049 | 0.0118 |

*Table 102*

Runoff

| Kit Name | Adjusted $R^2$ | Standard Error | Intercept | p-Value | Slope | p-Value | Detection Limit ($\alpha$=0.05) (mg/L) | Limit of Quantification ($\alpha$=0.05) (mg/L) |
|---|---|---|---|---|---|---|---|---|
| EM Science Lead | NA | NA | NA | NA | NA | NA | NA | NA |
| La Motte Lead in Water Kit | 0.9987 | 0.0203 | 0.0051 | 0.5638 | 1.0218 | 4.2534E-10 | 0.0393 | 0.0736 |
| HACH LeadTrak system | 0.9889 | 0.0040 | 0.0009 | 0.7324 | 0.8675 | 3.2487E-04 | 0.0075 | 0.0142 |

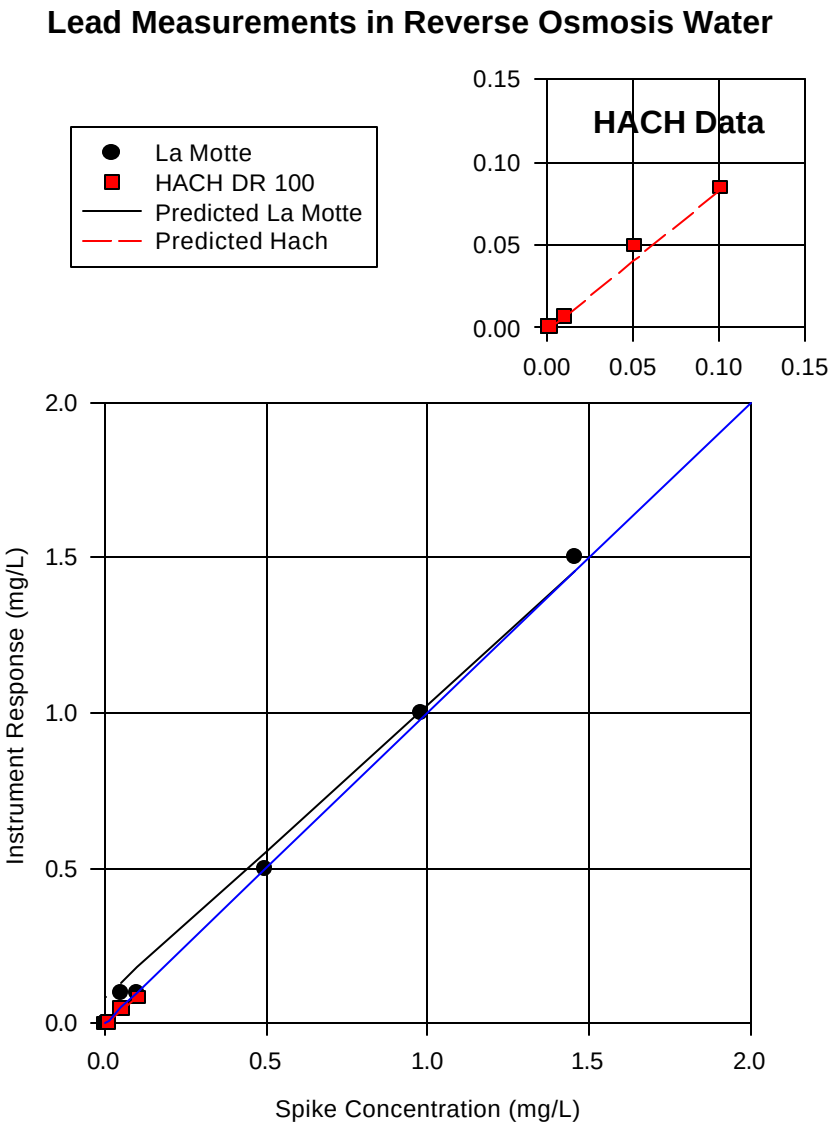

Lead Measurements in Reverse Osmosis Water
La Motte
HACH DR 100
Predicted La Motte
Predicted Hach
HACH Data
0.15
0.10
0.05
0.00
0.00
0.05
0.10
0.15
2.0
1.5
1.0
0.5
0.0
Instrument Response (mg/L)
0.0
0.5
1.0
1.5
2.0
Spike Concentration (mg/L)

*Figure 92*

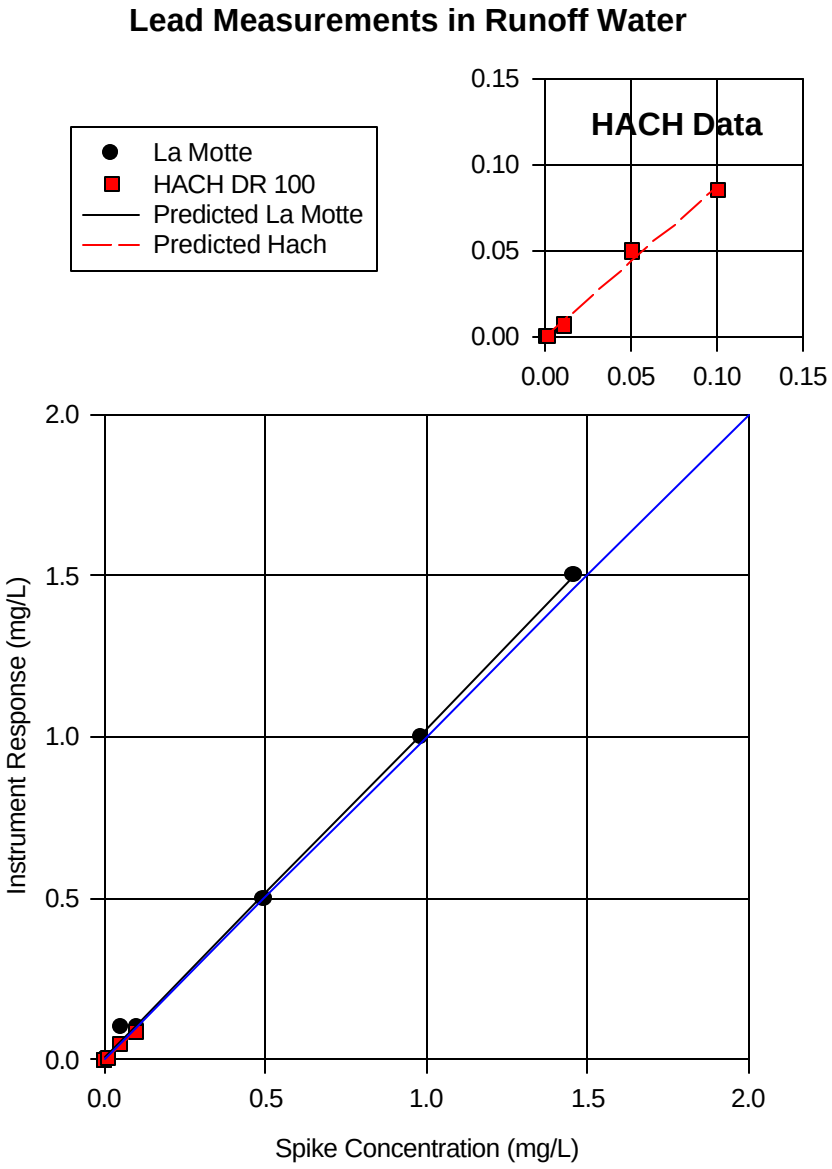



*Figure 93*

## 29.2 La Motte Lead in Water Kit

### *29.2.1 Method*

The La Motte Lead in Water Kit extracts lead from water samples using chloroform. The resulting extract is reacted with dithizone. A positive test is indicated by the formation of pink in the extract. The depth of color is visually compared to standards to determine the approximate lead concentration.

The procedure for lead determination first requires pH adjustment of the sample to pH 9-11. The instructions do not indicate the volume of sample required initially. In our evaluation, we only used 10 mL of sample. The adjusted sample must be analyzed immediately after pH adjustment. Use a pipette to withdraw Lead Dithizone Reagent (dithizone dissolved in chloroform) from the bottom layer of liquid (green) in the reagent bottle. The top layer is a barrier to prevent exposure of the reagent. Place the dithizone reagent in a clean test tube. Add 5 drops of Lead Reagent #2 (aqueous sodium cyanide) to the solution. Cap, mix for 15 s and vent. Be careful. The vapor pressure of chloroform can pop a cap off the vial. Allow the solutions to separate. The upper layer will be orange; the lower layer will be green. Add pH adjusted sample water to bring the total volume of the test tube to 10 mL. Cap, mix for 30 s and vent. Allow the layers to separate. Compare the color in the bottom layer to the standards in the comparator.

This method uses some hazardous reagents. Chloroform is a known carcinogen. Sodium cyanide will produce hydrogen cyanide gas under acidic conditions. Therefore, the method should always be performed with caution. The principal intereferents of the dithizone reaction are other heavy metals. The pH adjustment step should remove most common interferences except copper and iron. Copper at concentrations greater than 0.5 mg/L and iron at concentrations greater than 2.0 mg/L will interfere.

### *29.2.2 Observations*

The method is unpleasant, but so are all the lead tests. However, the kit is well packaged to protect the user from the reagents; although exposure is still a concern. The quantitative capabilities of the test are not as strong as some other tests. Like all visual comparators, the measurement depends on the color perception of the user. The test did positively identify a lead concentration of 1 µg/L. Therefore, the test could be used for qualitative analysis. The test is much simpler than the HACH test.

Unfortunately, the La Motte corporation has removed this kit from its product line. Through telephone conversations, we also learned that La Motte currently has no plans to replace this method with another. However, we have enough information to duplicate this method, if warranted.

The residual analyses indicate improved performance in natural waters (runoff) in comparison to reverse osmosis water. This is probably due to the buffering capacity of the natural water as reverse osmosis water has no buffering capacity.

*Table 103*

| Sample ID | Spike Conc. (mg/L) | Order | RO Response (mg/L) | RO Percent Recovery | Order | Runoff Response (mg/L) |
|---|---|---|---|---|---|---|
| Pb X 0 | 0.000 | 5 | 0.0 | NA | 3 | 0 |
| Pb X 1 | 0.001 | 13 | 0.0 | 0 | n.t. | 0 |
| Pb X 2 | 0.010 | 12 | 0.0 | 0 | 4 | 0 |
| Pb X 3 | 0.050 | 9 | 0.3 | 600 | 10 | 0.1 |
| Pb X 4 | 0.100 | 7 | 0.3 | 300 | 11 | 0.1 |
| Pb X 5 | 0.495 | 12 | 0.4 | 81 | 1 | 0.5 |
| Pb X 6 | 0.980 | 2 | 1.0 | 102 | 8 | 1 |
| Pb X 7 | 1.456 | 8 | 1.5 | 103 | 6 | 1.5 |

*Table 104*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.978025395 |
| R Square | 0.956533674 |
| Adjusted R Square | 0.949289286 |
| Standard Error | 0.122124458 |
| Observations | 8 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 1.969263701 | 1.969263701 | 132.0378916 | 2.60926E-05 |
| Residual | 6 | 0.089486299 | 0.014914383 | | |
| Total | 7 | 2.05875 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* |
|---|---|---|---|---|---|---|---|
| Intercept | 0.066989877 | 0.053888611 | 1.243117524 | 0.260196666 | -0.064870901 | 0.198850654 | -0.064870901 |
| Spike Conc. (mg/L) | 0.958629038 | 0.083425975 | 11.49077419 | 2.60926E-05 | 0.754492882 | 1.162765194 | 0.754492882 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.066989877 | -0.066989877 | -0.548537764 |
| 2 | 0.067948506 | -0.067948506 | -0.556387371 |
| 3 | 0.076576167 | -0.076576167 | -0.627033837 |
| 4 | 0.114921329 | 0.185078671 | 1.51549227 |
| 5 | 0.162852781 | 0.137147219 | 1.123011903 |
| 6 | 0.541511251 | -0.141511251 | -1.158746196 |
| 7 | 1.006446334 | -0.006446334 | -0.052784955 |
| 8 | 1.462753756 | 0.037246244 | 0.304985952 |

*Table 105*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.99944581 |
| R Square | 0.998891926 |
| Adjusted R Square | 0.998707247 |
| Standard Error | 0.020339146 |
| Observations | 8 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 2.237517915 | 2.237517915 | 5408.802347 | 4.2534E-10 |
| Residual | 6 | 0.002482085 | 0.000413681 | | |
| Total | 7 | 2.24 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* |
|---|---|---|---|---|---|---|---|
| Intercept | 0.005059746 | 0.008974847 | 0.563769621 | 0.593340694 | -0.016900929 | 0.027020421 | -0.016900929 |
| Spike Conc. (mg/L) | 1.021837656 | 0.01389413 | 73.54456028 | 4.2534E-10 | 0.98783992 | 1.055835391 | 0.98783992 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.005059746 | -0.005059746 | -0.248768858 |
| 2 | 0.006081584 | -0.006081584 | -0.299008808 |
| 3 | 0.015278123 | -0.015278123 | -0.751168358 |
| 4 | 0.056151629 | 0.043848371 | 2.155861022 |
| 5 | 0.107243512 | -0.007243512 | -0.356136475 |
| 6 | 0.510869386 | -0.010869386 | -0.534407191 |
| 7 | 1.006460649 | -0.006460649 | -0.317646024 |
| 8 | 1.492855373 | 0.007144627 | 0.351274692 |

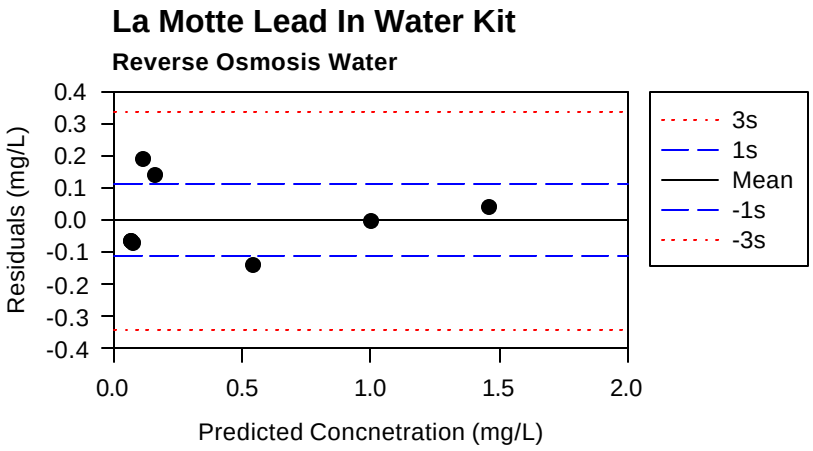



*Figure 94*

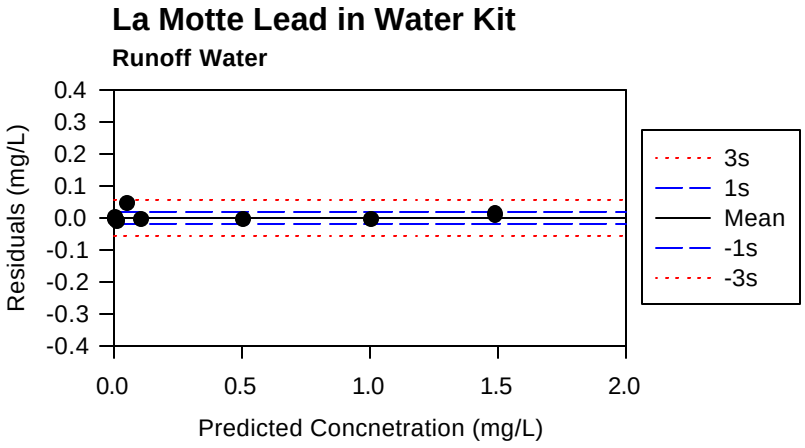



*Figure 95*

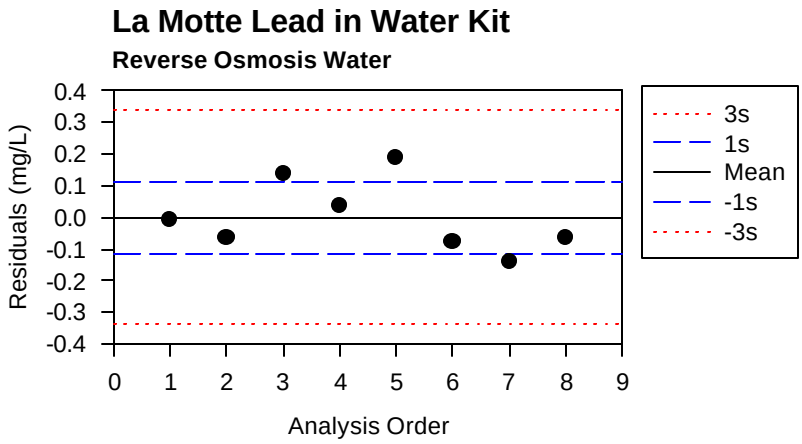



*Figure 96*

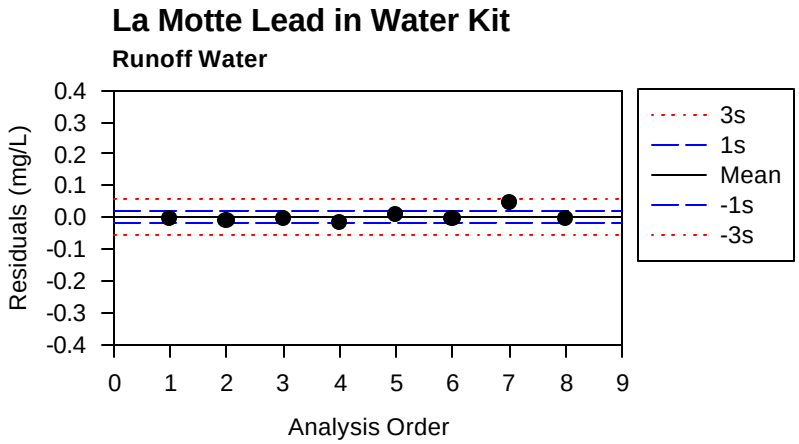



*Figure 97*

## 29.3 HACH LeadTrak System

### *29.3.1 Method*

The LeadTrak system determines lead concentrations through colorimetric determination of a lead complex extracted from the sample. The test procedure is quite complicated, requires a great deal of space compared to the other tests, and uses hazardous chemicals. However, it does produce good results.

The HACH LeadTrak System is nothing short of a portable laboratory. The method uses a solid phase extraction step to remove lead from the sample water. The extract is then reacted with dithizone to form a colored complex. The sample concentration is quantified with a spectrophotometer. The user may use the DR 2000 or a dedicated spectrophotometer included with the LeadTrak kit.

A 100 mL sample is treated with an acid preservative, a nitric acid solution buffered with potassium nitrate. The solution is then treated with a solution of tris-hydroxymethylaminomethane, potassium nitrate, succinic acid, and imidazole. The prepared sample is then filtered through a solid phase extractor (basically a syringe with a cloth plug). The lead in solution is held by the filter in the extractor. The lead is then removed from the plug with the eluant solution, another nitric acid solution. The eluant is allowed to pass over the plug until it stops flowing. The remaining eluant is forced through with the syringe plunger. This produces approximately 30 mL of extracted lead. The extract is neutralized with a solution of tris-hydroxyaminomethane, tartaric acid, and sodium hydroxide. One powder pillow, containing potassium chloride and meso-tetra(-4-N-methylpryidyl)-porphine tetratosylate is added to the elutant. Two 10 ml portions are taken. A decolorizing solution is added to 1 portion; this portion is now the blank. Please note the blank does not turn clear after adding the decolorizer. In fact, no perceptible color change between the two 10 mL samples is normal.

### *29.3.2 Observations*

The test is very sensitive. It detected spike concentrations of 1 ppb. However, the procedure is quite complicated. As a result, mistakes are easy to make. There is a misprint in the directions for the DR 100 procedure, step 5. The directions should read, "…discard the contents of the 125 mL sample bottle." However, procedural errors produce colors that alert an experienced user that the test results will be flawed. A single test will take at least 15-30 minutes, for an experienced individual. The test requires at least 3 $ft^2$ and uses several hazardous chemicals.

*Table 106*

| Sample ID | Spike Conc. (mg/L) | Order | RO Response (mg/L) | Order | Runoff Response (mg/L) |
|---|---|---|---|---|---|
| Pb X 0 | 0 | 11 | 0.0005 | 10 | 0.001 |
| Pb X 1 | 0.001 | 12 | 0.001 | 7 | 0.001 |
| Pb X 2 | 0.01 | 8 | 0.004 | 2 | 0.007 |
| Pb X 3 | 0.05 | 4 | 0.035 | 6 | 0.05 |
| Pb X 4 | 0.1 | 13 | 0.085 | 3 | 0.085 |
| Pb X 5 | 0.495 | nt | >0.150 | 5 | >0.150 |
| Pb X 6 | 0.98 | 9 | >0.150 | nt | >0.150 |
| Pb X 7 | 1.456 | 1 | >0.150 | nt | >0.150 |

*Table 107*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.995229605 |
| R Square | 0.990481967 |
| Adjusted R Square | 0.987309289 |
| Standard Error | 0.004107282 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 0.005266591 | 0.005266591 | 312.1911707 | 0.000395234 |
| Residual | 3 | 5.06093E-05 | 1.68698E-05 | | |
| Total | 4 | 0.0053172 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* |
|---|---|---|---|---|---|---|---|
| Intercept | -0.00203391 | 0.002394218 | -0.849508893 | 0.458014685 | -0.009653387 | 0.005585568 | -0.009653387 |
| Spike Conc. (mg/L) | 0.842667997 | 0.047692072 | 17.66893236 | 0.000395234 | 0.690890396 | 0.994445598 | 0.690890396 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | -0.00203391 | 0.00253391 | 0.616931043 |
| 2 | -0.001191242 | 0.002191242 | 0.533501653 |
| 3 | 0.00639277 | -0.00239277 | -0.582567917 |
| 4 | 0.04009949 | -0.00509949 | -1.241573109 |
| 5 | 0.08223289 | 0.00276711 | 0.673708329 |

*Table 108*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.995814311 |
| R Square | 0.991646143 |
| Adjusted R Square | 0.988861523 |
| Standard Error | 0.003959048 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 0.005581778 | 0.005581778 | 356.1155362 | 0.000324871 |
| Residual | 3 | 4.70222E-05 | 1.56741E-05 | | |
| Total | 4 | 0.0056288 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* |
|---|---|---|---|---|---|---|---|
| Intercept | 0.000865953 | 0.00230781 | 0.375227168 | 0.732449795 | -0.006478535 | 0.008210441 | -0.006478535 |
| Spike Conc. (mg/L) | 0.867516988 | 0.045970849 | 18.87102372 | 0.000324871 | 0.721217092 | 1.013816885 | 0.721217092 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.000865953 | 0.000134047 | 0.033858396 |
| 2 | 0.00173347 | -0.00073347 | -0.185264206 |
| 3 | 0.009541123 | -0.002541123 | -0.641851929 |
| 4 | 0.044241802 | 0.005758198 | 1.454439808 |
| 5 | 0.087617652 | -0.002617652 | -0.661182069 |

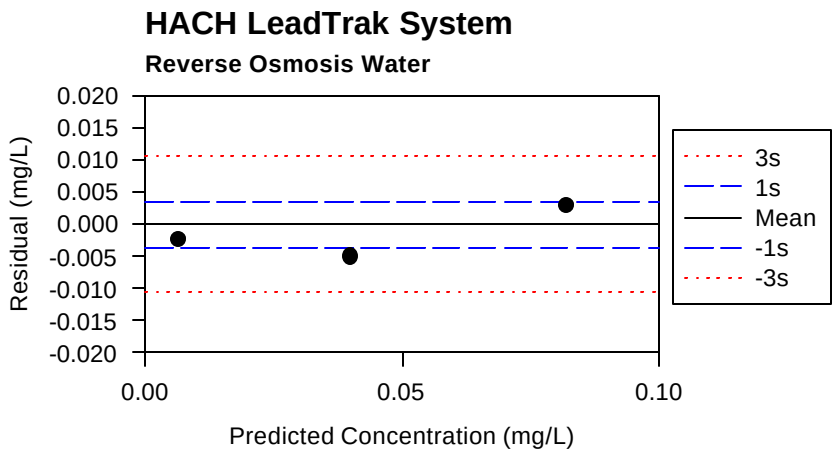



*Figure 98*

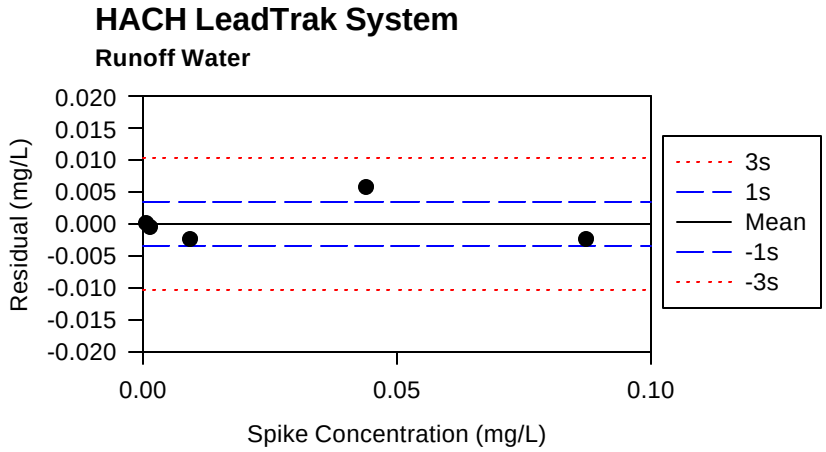



*Figure 99*

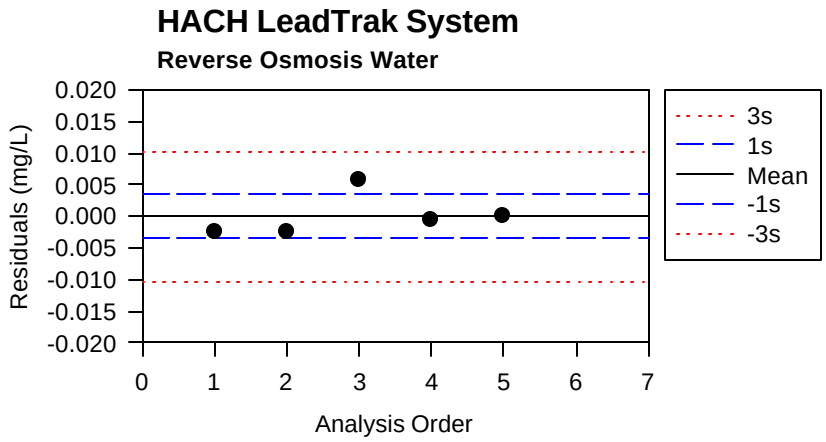



*Figure 100*

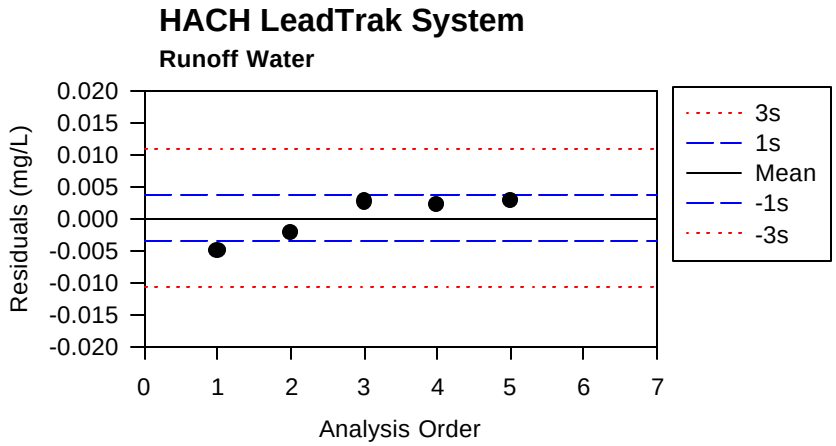



*Figure 101*

## 29.4 EM Science Quant Lead Strips

### *29.4.1 Method*

The EM Science Lead strips are simple test strips that also take advantage of the lead dithizone reaction.

The test is very simple. The lead strips are immersed in the sample for 2 s. The strip is allowed to dry for 1 minute. At the end of the 1 minute reaction time, the test strip may be compared to scale on the reagent bottle or measured using the RQFlex Reflectometer.

If the Reflectometer is used, it must be set up for lead testing prior to analysis. The meter is a simple spectrophotometer that reads reflected light off the test strip, rather than transmitted light like a conventional spectrophotometer or scattered light like a nephlometer. The instrument is designed to store the calibration information for up to 5 parameters. EM Science ships clear plastic strips with the calibration information with every set of reagents. The calibration must be updated whenever the reagent lots are changed. The information is entered into the meter using a bar code reader installed in the instrument.

### *29.4.2 Observations*

The test is very simple and quick. However, it lacks sensitivity. The reported detection limit is 20 ppm. This test will quickly identify only extremely gross levels of contamination, but will not identify lower levels of contamination that are still problematic. The high detection limit prevented the anlysis of the test strips with the spiked standards.

## 29.5 The Lead Detective

The Lead Detective by Innovative Synthesis Corporation is designed to detect lead on surfaces. The method uses the reaction of lead with sodium sulfide to indicate the presence of lead. When mixed, lead and sodium sulfide form lead sulfide, a black compound. The major interferents for the test are other heavy metals and transition metals. The manufacturer reported detection limit for the test is 1% lead content.

To test a surface, sodium sulfide is mixed with water to form the test solution. The solution is applied to the surface of interest. The formation of a black color indicates the presence of lead. The test includes a contaminated paint chip for comparison. The sodium sulfide solution has a shelf life of about 6 weeks. Sodium sulfide in solid form is extremely hygroscopic. To extend the shelf life, the test should be stored in a cool, dry place.

## 29.6 LeadCheck Swabs

The LeadCheck Swabs from HybriVet are a simple swab procedure for the presence of lead in high concentrations (1%). A positive test is indicated by a pink color change. The procedure is simple. Each swab has two glass ampoules encased in cardboard. The user breaks both ampoules, mixes the

solutions and waits for the yellow fluid to soak into the swab. The swab is then rubbed on the surface for about 10 s. Lead contaminated swatches are included for comparison.

### 29.7 KnowLead

The Know Lead test by Carolina Environment is another quick test for the presence of lead. The pink color change suggests the test takes advantage of the dithizone reaction of lead. The reported detection limit of the test is reported to be 0.6%.

The test procedure is simple. Wet the non-abrasive swab with water. Rub the moistened swab on the surface for 10 seconds. If a red or pink color develops within 2 minutes, lead is present. This test also includes a lead standard for comparison.

### 29.8 CHEMetrics C-6350 Lead Test (as supplied in GDS's AquaVat test kit)

This is a very sensitive test, with a reported range of 5 to 50 µg/L lead. Unfortunately, the test uses hazardous chemicals (30.2% carbon tetrachloride, a highly toxic nervous system depressant). Carbon tetrachloride is quite volatile and the vapors can be toxic or corrosive. Other chemicals in the kit are listed as being an irritant. The ampoules must have the ends snapped off by a special device included in the kit. During the evaluation, reagents splashed out of the ampoules onto the gloved hands of the operator.

The test procedure is somewhat complex, requiring an extraction of the lead with carbon tetrachloride, drawing off the extract and reacting the extract with a reagent in a vacuole to develop color. The vacuole is placed in the color comparator and the lead concentration is estimated based on the color intensity (more than the color itself). The design of the kit minimizes exposure of the operator to the chemicals and the kit is designed to use relatively small amounts of chemicals. However, a strong chemical odor is always present when working with the kit and the analyses should always be conducted in an extremely well-ventilated area. Work in a chemical fume hood is recommended, and careful operator protection with gloves and safety glasses is a must with this lead procedure.

The small number of reagents supplied with this test limited a complete evaluation. Three samples (with previously determined lead levels from using a standard TJA graphite furnace atomic absorption spectrophotometer), along with a 25 µg/L standard solution and a de-ionized water blank (18 megohm water) were selected for evaluation. Table 11 shows the results of these tests. The test results were not readable because of different and dark colors developed for all of the samples, including the blank which should have been pale.

29.8.1.1 Table 11

| | | Previously Measured Values | |
|---|---|---|---|
| | CHEMetrics C-6350 results | (µg/L) | (mg/L) |
| 6458 | not readable* | 312.9 | 0.313 |
| 6290 | not readable | 20.3 | 0.02 |
| 6237 | not readable | 7.78 | 0.008 |
| 25 µg/L | not readable | | |
| De-ionized water | not readable | | |

* the colors (and especially their intensities) in the reaction tube were different than in the comparison tubes and the values were therefore not readable

This lead analysis method is not recommended for the determination of lead in water. The kit failed to accurately reproduce the known lead concentrations in the previously evaluated samples and to determine the standard concentration and the blank, possibly due to confusion associated with different colors in the test samples and the color comparator. A more serious problem is the required use of highly toxic carbon tetrachloride in this method.

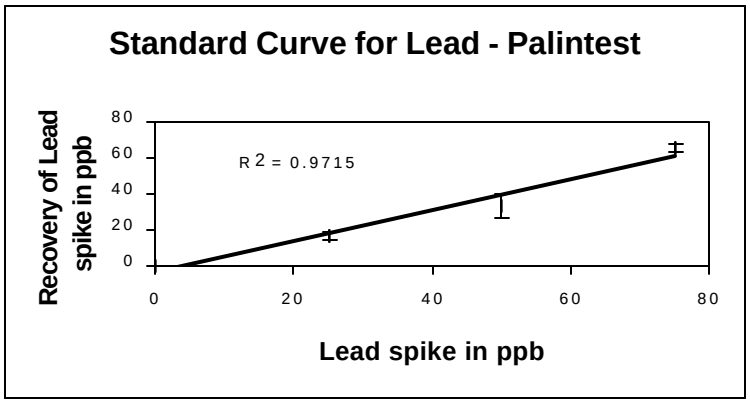
# 30 Field-Adapted Stripping Voltametry Methods

Due to the cost of these instruments and supplies for analyses, complete evaluations were not conducted. Comparisons with four standard solutions and with two previously evaluated samples (using a graphite furnace atomic absorption spectrophotometer) were made. We have also used the Palintest instrument for numerous field measurements (with few detectable results) and in laboratory treatability analyses (frequently in the range of detection). These are the only field measurement methods evaluated that provided consistent low-level analyses of lead in a relatively rapid manner. The reported detection limits for both of these instruments is 5 µg/L for lead. They also simultaneously evaluate copper using the same sample and supplies.

## 30.1 Palintest

The test supplies for the Palintest are relatively expensive, at about $5 per analysis (simultaneous with copper). The only reagent is a buffer pill that must be crushed in the bottom of the sample vial. The metals in the sample are electroplated on to an expendable electrode, which must be carefully inserted into the test tube holder. Touching the electrode, bending it, or prematurely inserting it into the sample will ruin the electrode. This makes the test a little difficult and expensive to do (new users probably ruin about half of the electrodes, while more experienced users may still ruin up to about one-fourth of the electrodes). The instrument automatically begins the analysis, taking about 5 minutes to return the results. The lowest reported value is 5 µg/L, while the highest value that can be reported is 100 µg/L.

Figure 11 and Table 12 shows the results of analyzing known standard lead concentrations with the Palintest. The test had a low recovery (around 66% for concentrations of 25 and 50 µg/L, while the recovery was 87% for the 75 µg/L standard). The precision is quite good, with an $R^2$ value of 0.9715.




30.1.1.1 Figure 11

30.1.1.2 Table 12

| standard (µg/L) | Lead test1 | test2 | test3 | average | st dev | recovery (avg/std) |
|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 | na |
| 25 | 14 | 19 | 17 | 16.66667 | 2.516611 | 0.666667 |
| 50 | 40 | 27 | 34 | 33.66667 | 6.506407 | 0.673333 |
| 75 | 64 | 68 | 64 | 65.33333 | 2.309401 | 0.871111 |

Table 13 shows the results of analyzing previously evaluated water samples collected from telecommunication manholes. The Palintest results were about 3 µg/L low for the 8 and 20 µg/L samples, and reported 119 µg/L (over the reported upper limit of the instrument of 100 µg/L) for the sample that had a lead concentration of about 310 µg/L. It reported >100 µg/L for the other samples larger than the upper limit.

30.1.1.3 Table 13

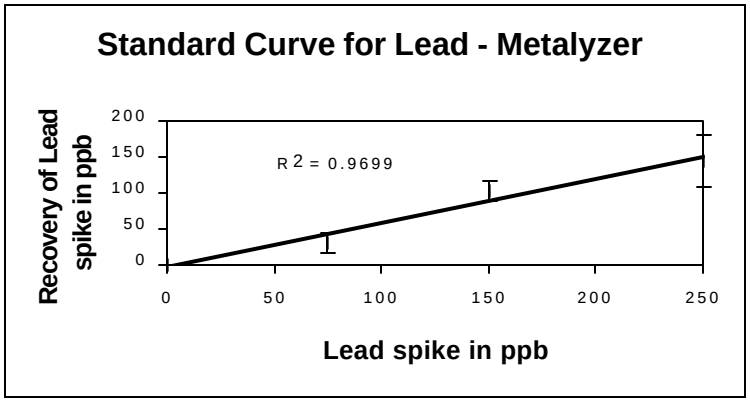
| Sample | Palintest results | Previously measured values by graphite furnace AAS (µg/L) |
|---|---|---|
| 6458 | 119 | 312.9 |
| 6290 | 17 | 20.3 |
| 6237 | 5 | 7.78 |
| 6304 | >100 | 277.4 |
| 6327 | >100 | 666.4 |

## 30.2 Metalyzer

The test supplies for the Metalyzer are also expensive (about $15 per test for both copper and lead), plus the instrument is expensive to purchase (over $4,000). Because of these high costs, a full evaluation was not conducted with the Metalyzer. The detection limit of the Metalyzer was reported to be 5 to 300µg/L for lead.

The reagent package contains a glass vial and disposal electrode enclosed in a plastic capsule. The glass shards and reagents are completely enclosed in the plastic capsule, minimizing any potential safety problems. The vial is inserted into the machine for use, and no contact is made with the reagents. The reagent vials are well packed in foam for shipment.

Figure 12 shows the results of analyzing known standard lead concentrations with the Metalyzer. The test had a low recovery (around 40% for the lead concentrations of 75 µg/L, while the recovery was about 60 to 70% for the 150 to 250 µg/L standards). The precision is quite good, with an $R^2$ value of 0.9699. However, the replicate analyses indicated some results that were quite different from the others.




30.2.1.1 Figure 12

Table 14 shows the reported concentrations of previously analyzed water samples collected from telecommunication manholes, compared to Metalyzer results. The high value is quite close (reported the upper limit of the instrument), but the low value over-predicted the concentration by about double.

30.2.1.2 Table 14

| | 6458 | 6290 |
|---|---|---|
| AA | 312.9 | 20.3 |
| Metalyzer | 300 | 40 |

# 31 Nitrate Summary

# 32 Nitrate

Six methods were evaluated to determine nitrate concentrations: La Motte, Horiba Cardy, HACH Nitrate LR, HACH Nitrate MR, EM Quant Test Strips and CHEMetrics Nitrate. The Horiba Cardy is an ion selective electrode for nitrate. The other tests determine nitrate by cadmium reduction and subsequent diazotization, likely causing the wastes to be classified as a hazardous waste by Federal RCRA regulations.

*Table 109*

| Kit Name | Method | Capital cost | Expendable Cost (per sample) | Time Required (min) | Sample Vol. (ml) | Expertise Required |
|---|---|---|---|---|---|---|
| La Motte Nitrate | Spectrophotometric | $895 for Smart Colorimeter | $1.22 | 20 | 10 | little |
| Horiba CARDY | ISE | $235 for kit | $60.00/ electrode | N/A | drops | little |
| EM Science Nitrate Quant Test Strips | test strips | $500.25 for Reflecto-Quant Meter | $0.49 | 2 | drops | none |
| HACH Nitrate, LR | Spectrophotometric | $1495 for DR 2000 | | | | |
| HACH Nitrate, MR | Spectrophotometric | $1495 for DR 2000 | $0.56 | 7 | 25 | none |
| CHEMetrics Nitrate (Nitrogen) | colorimeter | $47.5 for 1st 30 tests and standards | $0.73 | 30 | 25 | little |

*Table 110*

| Kit Name | Precision | Shelf Life | Regular Maintenance | Safety Hazards | Upper Limit of Useful Range (mg/L) |
|---|---|---|---|---|---|
| La Motte Nitrate | not evaluated | not indicated | Charge batteries. | Cd in wastes | 3*, our test extended this range |
| Horiba CARDY | 0.9700 | none | One point calibration daily. Two point calibration monthly. | None | not detected |
| EM Science Nitrate Quant Test Strips | All replicates below detection. | must be refrigerated | Clean ReflectoQuant optics. | Cd in wastes | 500* |
| HACH Nitrate, LR | | not indicated | | Sharps and Cd in wastes | |
| HACH Nitrate, MR | not available | not indicated | Charge batteries. | Sharps and Cd in wastes | 16* |
| CHEMetrics Nitrate (Nitrogen) | not evaluated | not indicated | Change batteries. | Sharps and Cd in wastes | 22* |

## 32.1 Spiked Samples

The comparison of spiked samples showed the tests operating at about the same level of performance, with the exception of the Horiba Cardy. However, the Horiba Cardy results are greatly influenced by a single error. Therefore, we chose three methods for further study: EM Science Quant Strips, HACH Nitrate MR and the Horiba Cardy. The best kit based on these analyses was the HACH Nitrate MR. The EM Science Quant Strips were also very good in runoff samples and performed well in the parallel analyses. The strips were selected as the easiest test. The Horiba is also so simple and inexpensive to operate that we tested it further with the parallel samples.

*Table 111 Revere Osmosis*

| Kit Name | Adjusted $R^2$ | Standard Error | Intercept | p-Value | Slope | p-Value | Detection Limit ($\alpha$=0.05) (mg/L) | Limit of Quantification ($\alpha$=0.05) (mg/L) |
|---|---|---|---|---|---|---|---|---|
| La Motte Nitrate | 0.9326 | 0.3391 | 0.2184 | 0.4671 | 0.8084 | 4.8944E-03 | 0.7894 | 1.3605 |
| Horiba CARDY | 0.3102 | 1.7020 | 1.9970 | 0.2273 | 0.9041 | 1.9290E-01 | 4.8632 | 7.7293 |
| EM Science Nitrate Quant Test Strips | 0.8567 | 0.6335 | 0.5984 | 0.3101 | 1.0038 | 1.5472E-02 | 1.6652 | 2.7321 |
| HACH Nitrate, LR | NA | NA | NA | NA | NA | NA | NA | NA |
| HACH Nitrate, MR | 0.9790 | 0.2132 | 2.4622 | 0.0001 | 0.9277 | 8.4052E-04 | 2.8212 | 3.1803 |
| CHEMetrics Nitrate (Nitrogen) | 0.9640 | 0.3213 | -0.0901 | 0.7415 | 1.0602 | 1.9014E-03 | 0.4510 | 0.9922 |

*Table 112 Runoff*

| Kit Name | Adjusted $R^2$ | Standard Error | Intercept | p-Value | Slope | p-Value | Detection Limit ($\alpha$=0.05) (mg/L) | Limit of Quantification ($\alpha$=0.05) (mg/L) |
|---|---|---|---|---|---|---|---|---|
| La Motte Nitrate | 0.9089 | 0.5199 | 1.6792 | 0.0252 | 1.0556 | 7.7451E-03 | 2.5547 | 3.4302 |
| Horiba CARDY | 0.9227 | 0.3170 | 3.9988 | 5.05E-04 | 0.7027 | 6.0291E-03 | 4.5326 | 5.0664 |
| EM Science Nitrate Quant Test Strips | 0.9795 | 0.3652 | 1.7968 | 7.91E-03 | 1.6064 | 8.1376E-04 | 2.4117 | 3.0267 |
| HACH Nitrate, LR | NA | NA | NA | NA | NA | NA | NA | NA |
| HACH Nitrate, MR | 0.9056 | 0.5323 | 4.0457 | 2.25E-03 | 1.0633 | 8.1743E-03 | 4.9421 | 5.8384 |
| CHEMetrics Nitrate (Nitrogen) | 0.9090 | 0.5002 | 1.6255 | 2.47E-02 | 1.0163 | 7.7294E-03 | 2.4679 | 3.3102 |

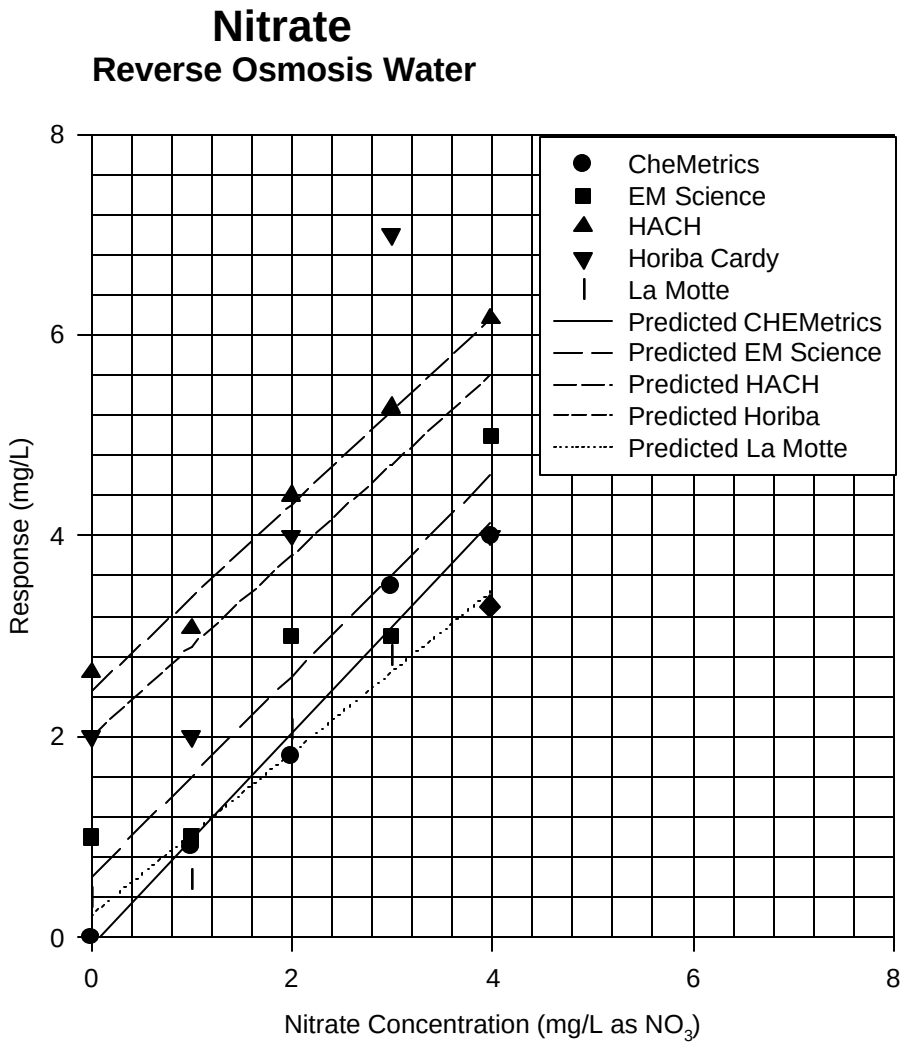

Nitrate
Reverse Osmosis Water
CheMetrics
EM Science
HACH
Horiba Cardy
La Motte
Predicted CHEMetrics
Predicted EM Science
Predicted HACH
Predicted Horiba
Predicted La Motte
Response (mg/L)
Nitrate Concentration (mg/L as NO3)
0
2
4
6
8

*Figure 102*

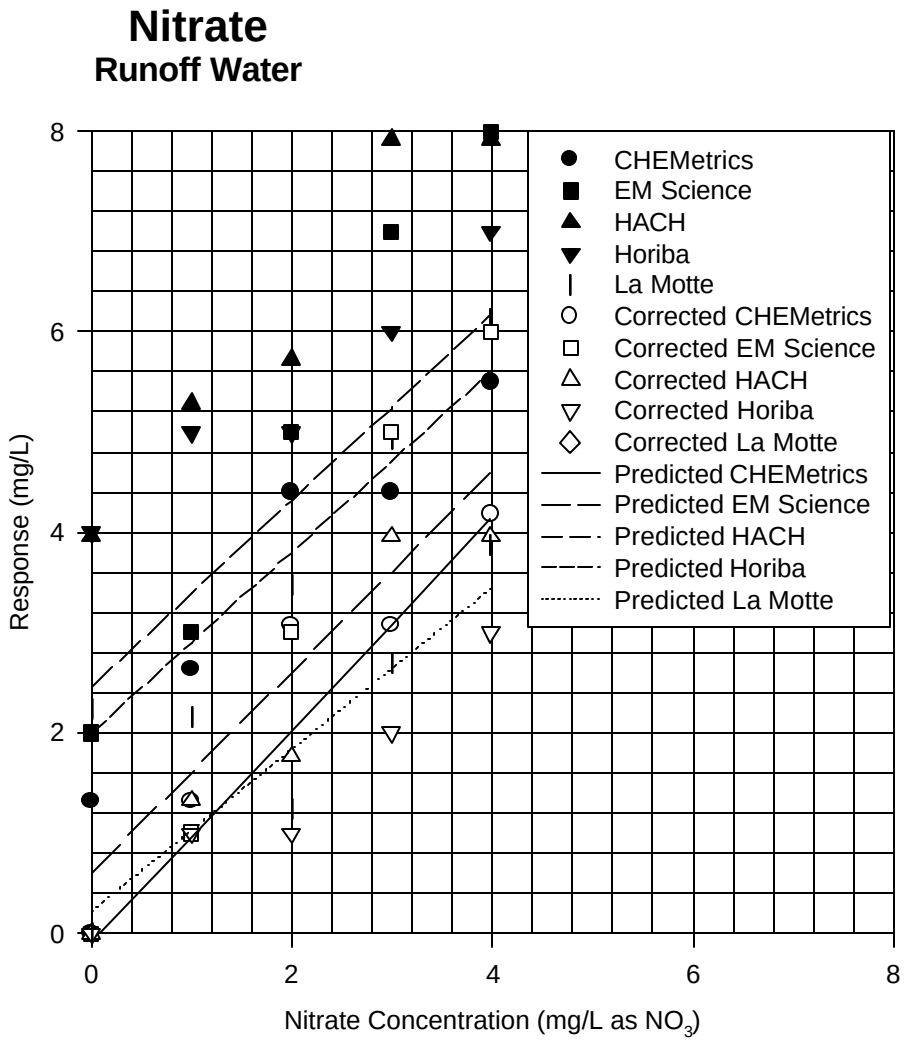



*Figure 103*

## 32.2 Parallel Analyses

The parallel analyses confirmed the poorer performance of the Horiba Cardy for the concentrations found in manhole waters, compared to the other test methods. The EM Quant and HACH MR test kits tracked each other reasonably well when used above their respective detection limits.

*Table 113*

| Sample ID | HACH MR Nitrate Response (mg/L as N) | HACH MR Nitrate Response (mg/L as NO3) | EM Nitrate (mg/L as NO3) | Horiba Nitrate (mg/L as NO3) |
|---|---|---|---|---|
| 2464 | 2.2 | 9.7 | 11 | 20 |
| 2473 | 1.2 | 5.3 | 1 | 14 |
| 2491 | 1.0 | 4.4 | 5 | 29 |
| 2501 | 1.8 | 7.9 | 10 | 25 |
| 2511 | 1.0 | 4.4 | 5 | 7 |
| 2530 | over-range | over-range | 4 | 2 |
| 2539 | 0.9 | 4.0 | 4 | 17 |
| 2548 | 0.6 | 2.6 | 1 | 24 |
| 2585 | 0.9 | 4.0 | NA | 9 |
| 2595 | 1.2 | 5.3 | 6 | NA |
| 2613 | 2.7 | 11.9 | 13 | 18 |
| 2629 | 0.7 | 3.1 | 0 | 30 |
| 2638 | 0.7 | 3.1 | 2 | 15 |
| 2656 | 0.8 | 3.5 | 7 | 11 |
| 2666 | 1.3 | 5.7 | 6 | 6 |
| 2674 | 1.2 | 5.3 | 6 | 5 |
| 2695 | 1.8 | 7.9 | 12 | 37 |
| 2722 | 1.2 | 5.3 | 2 | 41 |
| 2731 | 0.8 | 3.5 | 5 | 4 |
| 2740 | 3.1 | 13.6 | 17 | 18 |
| 2749 | 2.5 | 11.0 | 13 | 7 |
| 2774 | 0.5 | 2.2 | 1 | 0 |
| 2785 | 1.0 | 4.4 | 3 | 9 |
| 2801 | 0.7 | 3.1 | 1 | 4 |
| 2810 | 1.0 | 4.4 | 3 | 0 |

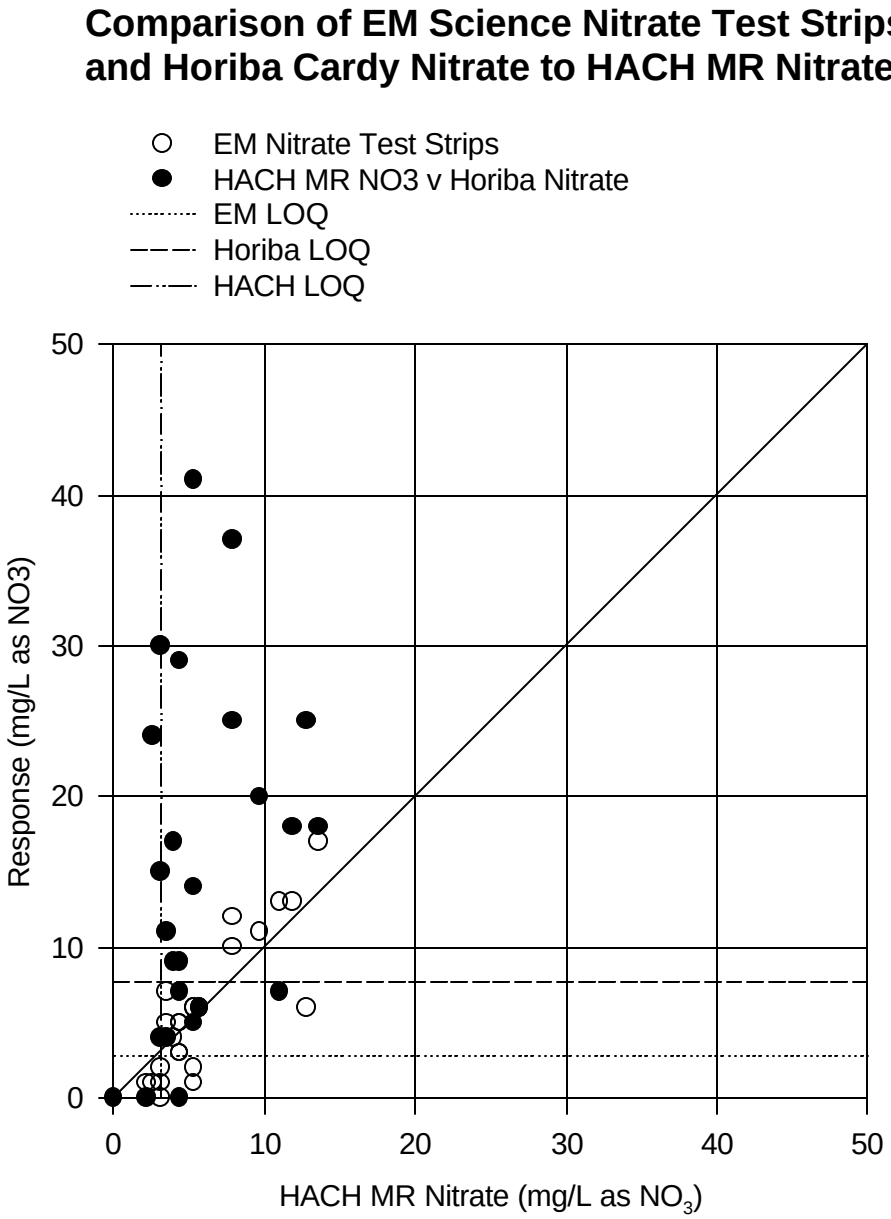



*Figure 104*

## 32.3 La Motte Nitrate

### *32.3.1 Method*

The La Motte Nitrate method determines the amount of nitrate in a sample by cadmium reduction of all nitrate ($NO_3^-$) to nitrite ($NO_2^-$). The nitrite then forms a diazonium salt with sulfanimide. The diazonium salt is coupled with N-(1-naphthyl)-ethylenediamine dihydrochloride. The result is a highly colored compound in direct proportion to the original concentration of nitrate and nitrite in the sample.

To measure the nitrate concentration, collect 10 mL of sample in a cuvette. Use the Scan Blank function to zero the spectrophotometer. Pour off 5 mL of the blank and discard. Add 5 mL of Mixed Acid Reagent to the remaining sample. Mix and wait 2 minutes. Add 0.2 g of Nitrate Reducing Agent (Cd powder) to the sample. Shake vigorously for 4 minutes. Allow the sample to set undisturbed for an additional 10 minutes. Use the Scan Sample function to determine the concentration which is reported as N.

The major interferent with this test is that the test measures nitrite plus nitrate. The test reduces all nitrate to nitrite; any nitrite in the original sample will also be detected. Strong oxidizers and reducers will interfere with the dye formation and interfere in an unpredictable manner. Samples with high iron or copper concentrations will produce results decreased from the true value.

### *32.3.2 Observations*

This test does not include a graduated cylinder or pipette for splitting the sample after scanning the blank. The user must use a 10 mL sample to zero the instrument. If only 5 mL are used, the light beam from the spectrophotometer will pass over the sample measuring air instead. No graduated cylinder or pipette is included with the kit for splitting the sample. The user is instructed to pour off 5 mL of sample into a graduated cylinder and discard the sample remaining in the cuvette. It is recommend that a 5mL volumetric pipette is used to remove the excess 5 mL of sample and continue the reaction in the cuvette.

This test, like many other nitrogen containing analyses, reports the answer as elemental nitrogen (N). To convert the answers to $NO_3^-$, multiply the results by 4.4.

*Table 114*

| Sample ID | Standard Conc. (mg/L) as NO3 | Order | RO (mg/L) as N | RO (mg/L) as NO3 | Recovery (%) | Order | Runoff (mg/L) as N | Runoff (mg/L) as NO3 | Runoff minus blank (mg/L) as NO3 |
|---|---|---|---|---|---|---|---|---|---|
| NO3 X 0 | 0 | 5 | 0.09 | 0.40 | NA | 1 | 0.51 | 2.24 | 0.00 |
| NO3 X 1 | 0.999 | 7 | 0.13 | 0.57 | 57 | 9 | 0.49 | 2.16 | -0.08 |
| NO3 X 2 | 1.996 | 3 | 0.47 | 2.07 | 104 | 8 | 0.79 | 3.48 | 1.24 |
| NO3 X 3 | 2.991 | 2 | 0.64 | 2.82 | 94 | 6 | 1.12 | 4.93 | 2.69 |
| NO3 X 4 | 3.984 | 10 | 0.75 | 3.30 | 83 | 4 | 1.39 | 6.12 | 3.88 |

*Table 115*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.974412594 |
| R Square | 0.949479903 |
| Adjusted R Square | 0.932639871 |
| Standard Error | 0.339108892 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 6.483674678 | 6.483674678 | 56.38230934 | 0.004894399 |
| Residual | 3 | 0.344984522 | 0.114994841 | | |
| Total | 4 | 6.8286592 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.218358875 | 0.262848342 | 0.830740925 | 0.467056258 | -0.618142646 | 1.054860395 | -0.618142646 | 1.054860395 |
| Standard Conc. (mg/L) as NO3 | 0.8084459 | 0.107666237 | 7.508815442 | 0.004894399 | 0.465803562 | 1.151088239 | 0.465803562 | 1.151088239 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L) as NO3* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.218358875 | 0.177641125 | 0.523846851 |
| 2 | 1.025996329 | -0.453996329 | -1.33879217 |
| 3 | 1.832016892 | 0.235983108 | 0.695891832 |
| 4 | 2.636420563 | 0.179579437 | 0.52956275 |
| 5 | 3.439207341 | -0.139207341 | -0.410509263 |

*Table 116*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.965221332 |
| R Square | 0.931652221 |
| Adjusted R Square | 0.908869627 |
| Standard Error | 0.519892595 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 11.05294307 | 11.05294307 | 40.89315976 | 0.007745056 |
| Residual | 3 | 0.810864932 | 0.270288311 | | |
| Total | 4 | 11.863808 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 1.679230821 | 0.402976478 | 4.167069082 | 0.025150425 | 0.396778615 | 2.961683026 | 0.396778615 | 2.961683026 |
| Standard Conc. (mg/L) as NO3 | 1.055551243 | 0.165064616 | 6.394775974 | 0.007745056 | 0.530241472 | 1.580861015 | 0.530241472 | 1.580861015 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L) as NO3* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 1.679230821 | 0.564769179 | 1.086318952 |
| 2 | 2.733726513 | -0.577726513 | -1.111242049 |
| 3 | 3.786111102 | -0.310111102 | -0.596490708 |
| 4 | 4.83638459 | 0.09161541 | 0.176219879 |
| 5 | 5.884546974 | 0.231453026 | 0.445193926 |

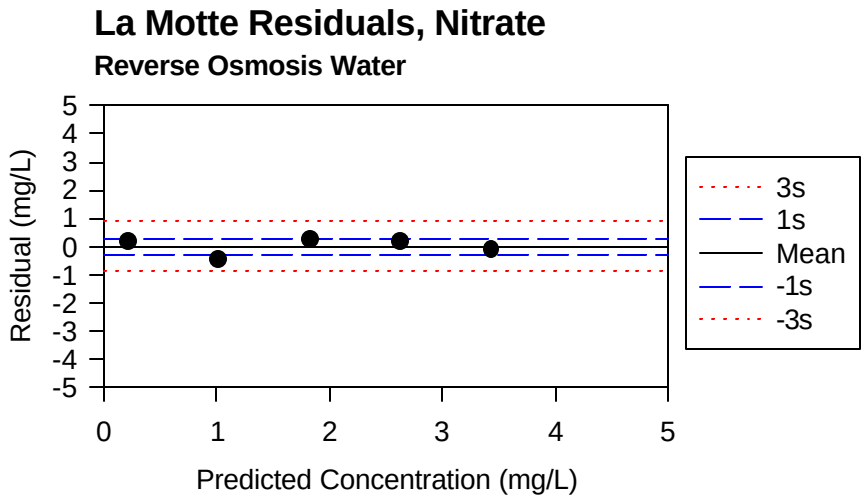



*Figure 105*

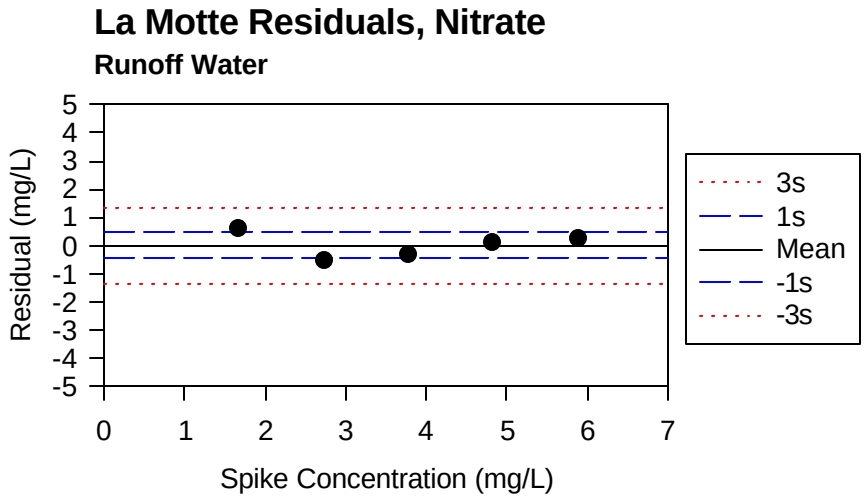



*Figure 106*

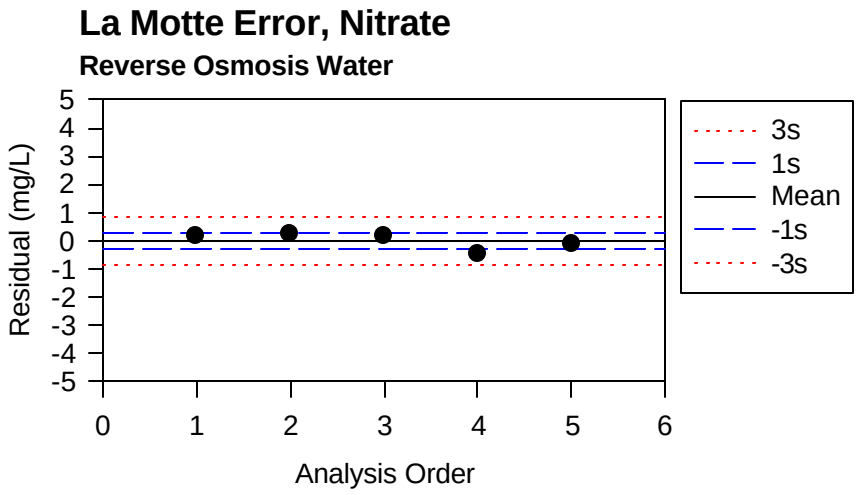

La Motte Error, Nitrate
Reverse Osmosis Water
Residual (mg/L)
5
4
3
2
1
0
-1
-2
-3
-4
-5
0
1
2
3
4
5
6
Analysis Order
3s
1s
Mean
-1s
-3s

*Figure 107*

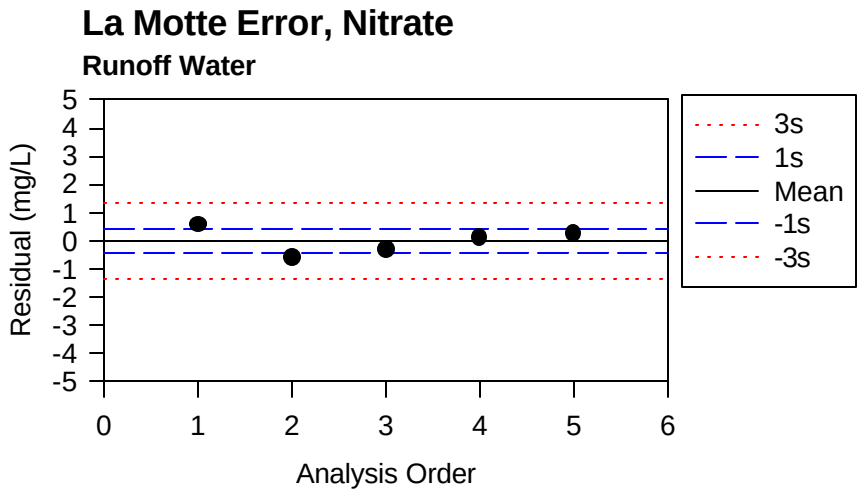



*Figure 108*

## 32.4 Horiba Cardy, Nitrate

### *32.4.1 Method*

The Horiba Cardy uses an ion selective electrode to determine the nitrate concentration in the sample. The procedure is simple. Place a swatch of sample paper over the electrode. Place 1-2 drops of sample solution on the sample paper. Record the displayed concentration.

Before use, the Horiba Cardy must be calibrated. There are two calibration procedures included with the kit, a single point verification and a two point calibration. Horiba recommends a two point calibration once per month and a single point verification once per day. To perform the two point calibration, measure the response for the first calibration solution and adjust the dial on the top of the meter until the instrument reads the correct concentration. Rinse the electrode. Measure the second calibration solution and adjust the slope set screw (located under a rubber plug on the face of the meter) until it reads the correct value. Rinse the electrode and measure the first calibration solution again. If the meter, does not read the correct value within 2 mg/L, repeat the entire procedure. To perform a single point verification. Measure the first mg/L standard solution and adjust the top knob. The instrument may be calibrated to display ppm N or ppm $NO_3^-$.

### *32.4.2 Observations*

This procedure may be the simplest method of all the nitrate test kits, but it had poor sensitivity. There is almost no opportunity for user error once the instrument is calibrated. The directions indicate that the

use of the paper swatches over the electrode is optional. However, we found that the instrument response was much more stable using the swatch than placing sample directly on the electrode.

The unfortunate problem with this method for this application is its designed range. The designed range extends far beyond the values that typically indicate a problem. Thus, this application will usually operate within a very narrow region on the extreme low end of the instruments designed range. This results in a large error for most measurements.

*Table 117*

| Sample ID | Standard Conc. (mg/L) as NO3 | Order | RO (mg/L) as NO3 | Recovery (%) | Order | Runoff (mg/L) as NO3 | Runoff minus Blank (mg/L) as NO3 |
|---|---|---|---|---|---|---|---|
| NO3 X 0 | 0 | 5 | 2 | NA | 1 | 4 | 0 |
| NO3 X 1 | 0.999 | 7 | 2 | 200 | 9 | 5 | 1 |
| NO3 X 2 | 1.996 | 3 | 4 | 200 | 8 | 5 | 1 |
| NO3 X 3 | 2.991 | 2 | 7 | 234 | 6 | 6 | 2 |
| NO3 X 4 | 3.984 | 10 | 4 | 100 | 4 | 7 | 3 |

*Table 118*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.694751892 |
| R Square | 0.482680192 |
| Adjusted R Square | 0.310240256 |
| Standard Error | 1.702054913 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 8.109027221 | 8.109027221 | 2.799120683 | 0.19290948 |
| Residual | 3 | 8.690972779 | 2.896990926 | | |
| Total | 4 | 16.8 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 1.997190291 | 1.31928806 | 1.513839435 | 0.227288068 | -2.20137706 | 6.195757643 | -2.20137706 | 6.195757643 |
| Standard Conc. (mg/L) as NO3 | 0.904117206 | 0.540398236 | 1.673057286 | 0.19290948 | -0.815672777 | 2.623907189 | -0.815672777 | 2.623907189 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L) as NO3* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 1.997190291 | 0.002809709 | 0.001650774 |
| 2 | 2.90040338 | -0.90040338 | -0.529009595 |
| 3 | 3.801808234 | 0.198191766 | 0.116442639 |
| 4 | 4.701404854 | 2.298595146 | 1.350482366 |
| 5 | 5.59919324 | -1.59919324 | -0.939566184 |

*Table 119*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.970585427 |
| R Square | 0.94203607 |
| Adjusted R Square | 0.92271476 |
| Standard Error | 0.31697131 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 4.898587565 | 4.898587565 | 48.7563252 | 0.006029096 |
| Residual | 3 | 0.301412435 | 0.100470812 | | |
| Total | 4 | 5.2 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 3.99879736 | 0.245689174 | 16.27583869 | 0.000504626 | 3.216904023 | 4.780690697 | 3.216904023 | 4.780690697 |
| Standard Conc. (mg/L) as NO3 | 0.702709448 | 0.100637609 | 6.982572964 | 0.006029096 | 0.382435361 | 1.022983536 | 0.382435361 | 1.022983536 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L) as NO3* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 3.99879736 | 0.00120264 | 0.003794161 |
| 2 | 4.700804099 | 0.299195901 | 0.943921079 |
| 3 | 5.401405419 | -0.401405419 | -1.266377763 |
| 4 | 6.10060132 | -0.10060132 | -0.317383046 |
| 5 | 6.798391802 | 0.201608198 | 0.636045569 |

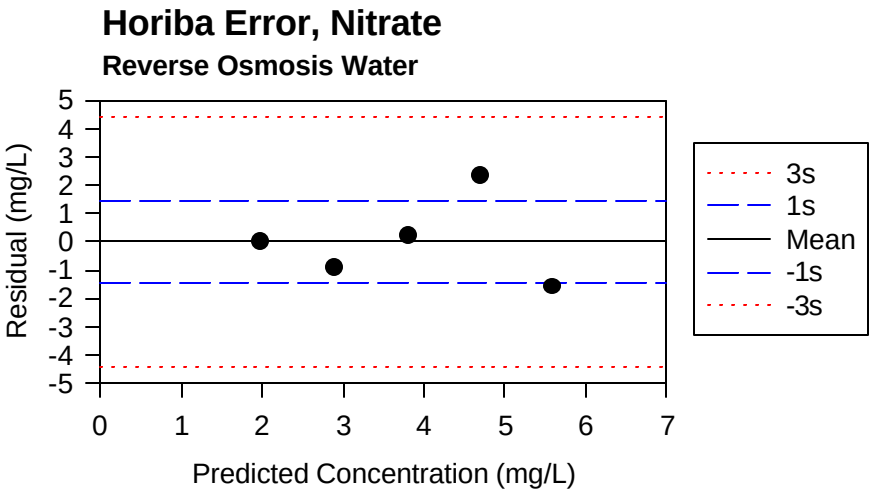

Horiba Error, Nitrate
Reverse Osmosis Water
Residual (mg/L)
5
4
3
2
1
0
-1
-2
-3
-4
-5
0
1
2
3
4
5
6
7
Predicted Concentration (mg/L)
3s
1s
Mean
-1s
-3s

*Figure 109*

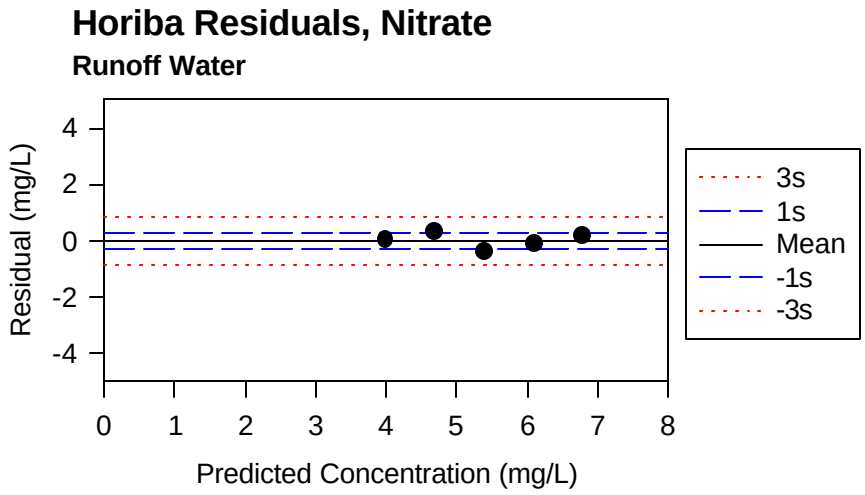



*Figure 110*

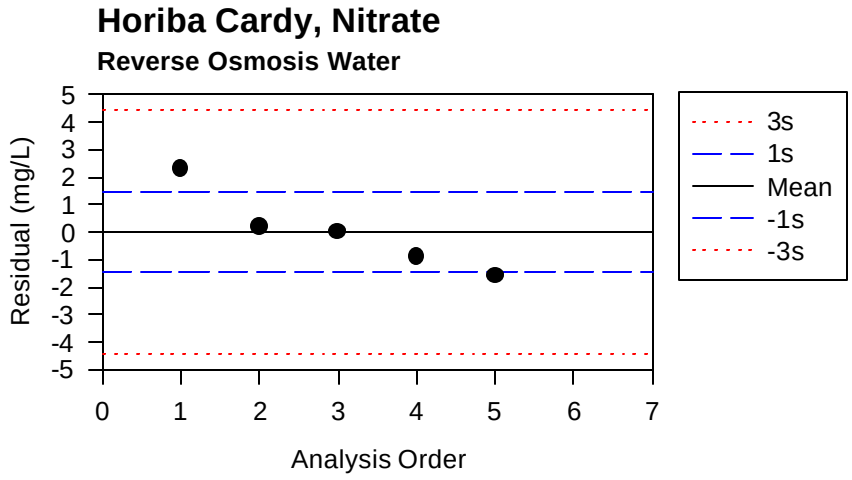



*Figure 111*

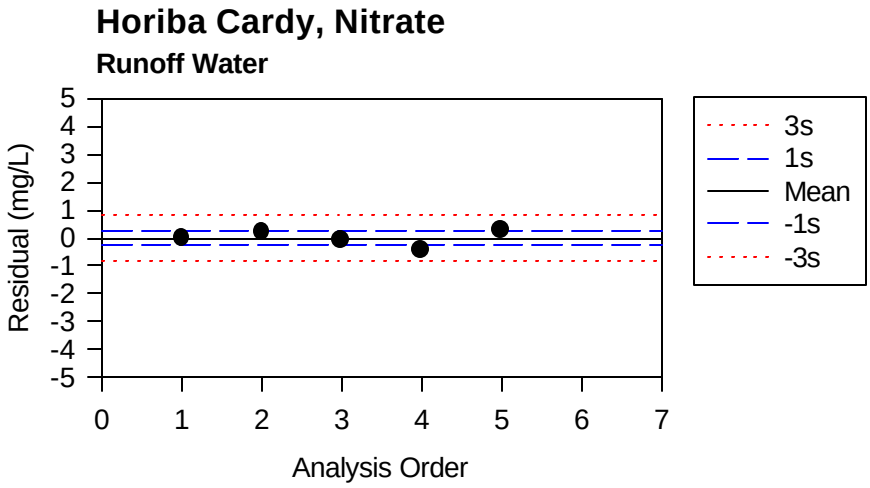



*Figure 112*

## 32.5 EM Science Quant Strips, Nitrate

### *32.5.1 Method*

The Quant Strips by EM Science are a very simple test for determining moderate to high nitrate concentrations. The chemical reaction is identical to the La Motte Method. However, the entire reaction takes place in about one minute on the surface of the test strip. Nitrate is reduce to nitrite. The resulting nitrite is reacted with an aromatic amine to form a diazonium salt. The diazonium salt reacts with N-(1-naphthyl)ethylenediamine hydrochloride to produce a red colored dye. The concentration of the dye is measure using the ReflectoQuant reflectometer.

To measure nitrate concentration with the Quant Test strips, the user dips the strip into the sample for 2 s. The color is allowed to develop for 1 minute. The measurements are made immediately with the scale printed on the reagent bottle of the EM Science Reflectometer.

If the Reflectometer is used, it must be set up for nitrate testing prior to analysis. The meter is a simple spectrophotometer that reads reflected light, rather than transmitted light like a conventional spectrophotometer or scattered light like a nephlometer. The instrument is designed to store the calibration information for up to 5 parameters. EM Science ships clear plastic strips with the calibration

information with every set of reagents. The calibration must be updated whenever the reagent lots are changed. The information is entered into the meter using a bar code reader installed in the instrument.

There are several reported interferents with this test, as listed in Table 12.

*Table 120*

| Compound | Level of Interference (mg/L) | Compound | Level of Interference (mg/L) |
|---|---|---|---|
| $Al^{3+}$ | 1,000 | $Mg^{2+}$ | 1,000 |
| ascorbate | 1,000 | $Mn^{2+}$ | 1,000 |
| $BO_3^-$ | 1,000 | $NO_2^-$ | 0.5 |
| $Ca^{2+}$ | 1,000 | oxalate | 1,000 |
| citrate | 1,000 | $PO_4^{3-}$ | 1,000 |
| $Cl^-$ | 500 | $SO_3^{2-}$ | 10 |
| $CO_3^{2-}$ | 1,000 | tartrate | 1,000 |
| $Cr^{3+}$ | 100 | EDTA | 1,000 |
| $CrO_4^-$ | 10 | anionic surfactants | 10 |
| $Cu^{2+}$ | 1 | cationic surfactants | 10 |

(EM Science undated)

### *32.5.2 Observations*

The test is quite simple to use, but timing is critical. The strips must be read at exactly 1 minute. Otherwise, the method gives erroneous results. We found it difficult to load the strip correctly in the 5 seconds allocated.

*Table 121*

| Sample ID | Standard Conc. (mg/L) as NO3 | Order | RO (mg/L) as NO3 | Recovery (%) | Order | Runoff (mg/L) as NO3 | Runoff minus Blank (mg/L) as NO3 |
|---|---|---|---|---|---|---|---|
| NO3 X 0 | 0 | 5 | 1 | NA | 2 | 2 | 0 |
| NO3 X 1 | 0.999 | 14 | 1 | 100 | 11 | 3 | 1 |
| NO3 X 2 | 1.996 | 12 | 3 | 150 | 15 | 5 | 3 |
| NO3 X 3 | 2.991 | 8 | 3 | 100 | 1 | 7 | 5 |

*Table 122*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.944720775 |
| R Square | 0.892497342 |
| Adjusted R Square | 0.856663123 |
| Standard Error | 0.633516579 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 9.995970232 | 9.995970232 | 24.90628678 | 0.01547186 |
| Residual | 3 | 1.204029768 | 0.401343256 | | |
| Total | 4 | 11.2 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.598396802 | 0.491048116 | 1.218611339 | 0.310078618 | -0.964338927 | 2.161132532 | -0.964338927 | 2.161132532 |
| Standard Conc. (mg/L) as NO3 | 1.003813038 | 0.201139951 | 4.990619879 | 0.01547186 | 0.363695344 | 1.643930732 | 0.363695344 | 1.643930732 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L) as NO3* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.598396802 | 0.401603198 | 0.633926895 |
| 2 | 1.601206027 | -0.601206027 | -0.948998096 |
| 3 | 2.602007626 | 0.397992374 | 0.628227243 |
| 4 | 3.600801599 | -0.600801599 | -0.948359709 |
| 5 | 4.597587946 | 0.402412054 | 0.635203667 |

*Table 123*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.992277177 |
| R Square | 0.984613995 |
| Adjusted R Square | 0.979485327 |
| Standard Error | 0.365164862 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 25.59996387 | 25.59996387 | 191.982389 | 0.000813756 |
| Residual | 3 | 0.400036128 | 0.133345376 | | |
| Total | 4 | 26 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 1.796791669 | 0.283044712 | 6.348084228 | 0.007907601 | 0.896016228 | 2.697567111 | 0.896016228 | 2.697567111 |
| Standard Conc. (mg/L) as NO3 | 1.606423436 | 0.115938943 | 13.85577096 | 0.000813756 | 1.23745363 | 1.975393242 | 1.23745363 | 1.975393242 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L) as NO3* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 1.796791669 | 0.203208331 | 0.556483803 |
| 2 | 3.401608681 | -0.401608681 | -1.099801004 |
| 3 | 5.003212847 | -0.003212847 | -0.008798346 |
| 4 | 6.601604165 | 0.398395835 | 1.091002658 |
| 5 | 8.196782637 | -0.196782637 | -0.53888711 |

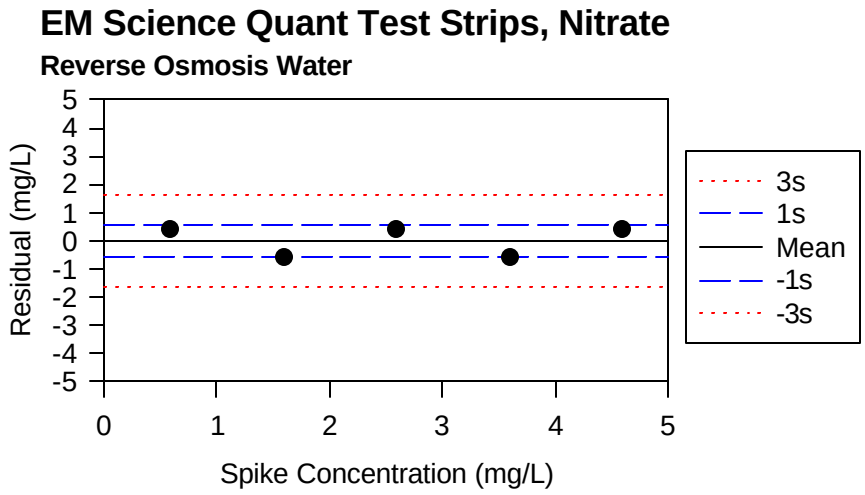

EM Science Quant Test Strips, Nitrate
Reverse Osmosis Water
Residual (mg/L)
5
4
3
2
1
0
-1
-2
-3
-4
-5
0
1
2
3
4
5
Spike Concentration (mg/L)
3s
1s
Mean
-1s
-3s

*Figure 113*

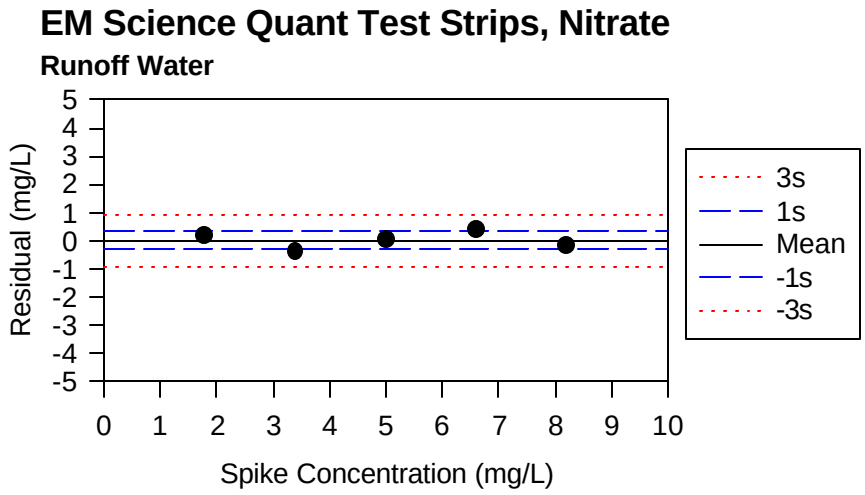



*Figure 114*

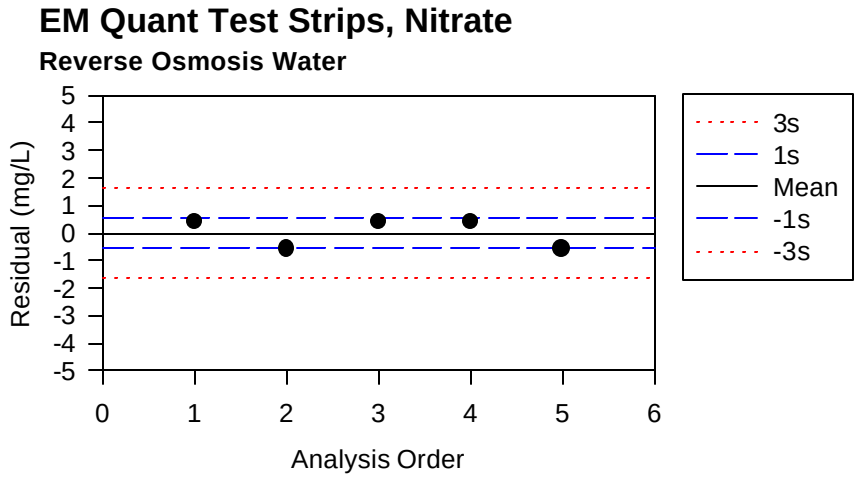



*Figure 115*

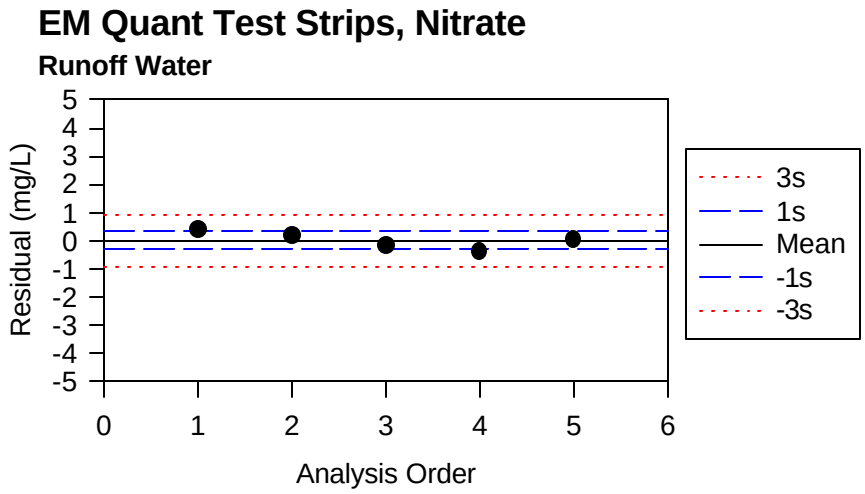



*Figure 116*

## 32.6 HACH Nitrate, Low Range

### *32.6.1 Method*

The HACH Nitrate LR method determines the amount of nitrate in a sample by cadmium reduction of all nitrate ($NO_3^-$) to nitrite ($NO_2^-$). The nitrite then forms a diazonium salt with sulfanimide. The diazonium salt is coupled chromotropic acid. The result is a highly colored compound in direct proportion to the original concentration of nitrate and nitrite in the sample.

To measure nitrate concentrations with the HACH Nitrate LR method, collect 30 mL in a beaker. Collect another 30 mL of sample to use as a blank. Add the contents of 1 NitraVer 6 Powder Pillow (Cd powder). Shake for 3 minutes. Allow the sample to set undisturbed for 2 minutes. Pour 25 ml of sample into the sample cell and add the contents of 1 NitriVer 3 Nitrite Reagent Powder Pillow to the sample cell. Mix and allow the to stand for 10 minutes. Zero the DR 2000 with the blank sample. Measure the concentration of nitrate, as N, in the sample using the DR 2000.

The major interferent with this test is that is measure nitrite and nitrate combined. The test reduces all nitrate to nitrite; any nitrite in the original sample will be detected as nitrate. Strong oxidizers and reducers will interfere with the dye formation and interfere in an unpredictable manner. Samples with high iron or copper concentrations will produce results decreased from the true value. The concentration

of cadmium metal in the reagent and in the waste sample causes these materials to be classified as a hazardous waste under Federal RCRA regulations. Disposal of these materials must therefore be done with care.

### *32.6.2 Observations*

The upper limit of this test is extremely low. This makes the test unusable for many applications without dilution of the sample. For higher concentrations, the HACH Nitrate MR method is recommended.

## 32.7 HACH Nitrate, Medium Range

### *32.7.1 Method*

The HACH Nitrate MR method determines the amount of nitrate in a sample by cadmium reduction of all nitrate ($NO_3^-$) to nitrite ($NO_2^-$). The nitrite is forms a diazonium salt with sulfanimide. The diazonium salt is coupled chromotropic acid. The result is a highly colored compound in direct proportion to the original concentration of nitrate and nitrite in the sample.

To measure nitrate concentrations with the HACH Nitrate MR method, collect at least 40 mL of sample in a 50 mL beaker. Break the tip of the ampoule beneath the surface of the sample. Allow the filled ampoule to set undisturbed for 5 minutes. Zero the DR 2000 using the blank sample in a 10 mL cuvette. Measure the sample using the DR 2000. The results are reported in mg/L as N.

The major interferent with this test is that it measures nitrite and nitrate combined. The test reduces all nitrate to nitrite; any nitrite in the original sample will be detected as nitrate. Strong oxidizers and reducers will interfere with the dye formation and interfere in an unpredictable manner. Samples with high iron or copper concentrations will produce results decreased from the true value. Again, the cadmium in the spent material causes these wastes to be classified as hazardous under Federal RCRA regulations.

### *32.7.2 Observations*

This test seems better suited to the concentrations found in water from manholes than the HACH Nitrate LR method. The reaction time is also shorter. However, this method was not pre-programmed into DR 2000 software version we had available. The program was included with the directions so that direct readout of the results in the desired units was possible. However, it took about 4 hours to enter the program. During programming, we made an error that caused the DR 2000 to stop functioning. The only remedy was to clear the DR 2000 of all user defined programs. There is no way to selectively delete user installed programs. Therefore, all user defined programs had to be re-entered. However, HACH instrument support was helpful during the situation.

*Table 124*

| Sample ID | Standard Conc. (mg/L) as NO3 | Order | RO (mg/L) as N | RO (mg/L) as NO3 | Recovery (%) | Order | Runoff (mg/L) as N | Runoff (mg/L) as NO3 | Runoff minus Blank (mg/L) as NO3 |
|---|---|---|---|---|---|---|---|---|---|
| NO3 X 0 | 0 | 4 | 0.6 | 2.64 | NA | 1 | 0.9 | 3.96 | 0.00 |
| NO3 X 1 | 0.999 | 5 | 0.7 | 3.08 | 308 | 8 | 1.2 | 5.28 | 1.32 |
| NO3 X 2 | 1.996 | 7 | 1.0 | 4.4 | 220 | 6 | 1.3 | 5.72 | 1.76 |
| NO3 X 3 | 2.991 | 10 | 1.2 | 5.28 | 177 | 9 | 1.8 | 7.92 | 3.96 |

*Table 125*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.992108606 |
| R Square | 0.984279487 |
| Adjusted R Square | 0.979039316 |
| Standard Error | 0.213188816 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 8.536931586 | 8.536931586 | 187.833463 | 0.000840523 |
| Residual | 3 | 0.136348414 | 0.045449471 | | |
| Total | 4 | 8.67328 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 2.462235631 | 0.16524582 | 14.90044125 | 0.000655958 | 1.936349189 | 2.988122073 | 1.936349189 | 2.988122073 |
| Standard Conc. (mg/L) as NO3 | 0.92766518 | 0.067686923 | 13.70523487 | 0.000840523 | 0.712254979 | 1.143075381 | 0.712254979 | 1.143075381 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L) as NO3* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 2.462235631 | 0.177764369 | 0.83383534 |
| 2 | 3.388973146 | -0.308973146 | -1.449293408 |
| 3 | 4.31385533 | 0.08614467 | 0.404076871 |
| 4 | 5.236882185 | 0.043117815 | 0.20225177 |
| 5 | 6.158053708 | 0.001946292 | 0.009129427 |

*Table 126*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.963943159 |
| R Square | 0.929186414 |
| Adjusted R Square | 0.905581885 |
| Standard Error | 0.532287403 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 11.15321036 | 11.15321036 | 39.36475175 | 0.008174335 |
| Residual | 3 | 0.849989638 | 0.283329879 | | |
| Total | 4 | 12.0032 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 4.045705618 | 0.412583877 | 9.805777299 | 0.002254234 | 2.73267835 | 5.358732885 | 2.73267835 | 5.358732885 |
| Standard Conc. (mg/L) as NO3 | 1.060328176 | 0.168999937 | 6.274133545 | 0.008174335 | 0.522494445 | 1.598161906 | 0.522494445 | 1.598161906 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L) as NO3* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 4.045705618 | -0.085705618 | -0.1610138 |
| 2 | 5.104973465 | 0.175026535 | 0.328819607 |
| 3 | 6.162120656 | -0.442120656 | -0.830605147 |
| 4 | 7.217147191 | 0.702852809 | 1.320438554 |
| 5 | 8.27005307 | -0.35005307 | -0.657639215 |

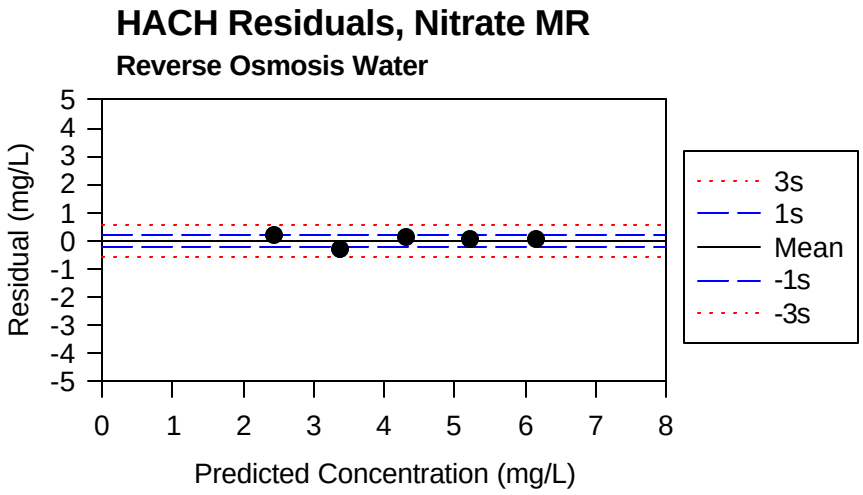

HACH Residuals, Nitrate MR
Reverse Osmosis Water
Residual (mg/L)
5
4
3
2
1
0
-1
-2
-3
-4
-5
0
1
2
3
4
5
6
7
8
Predicted Concentration (mg/L)
3s
1s
Mean
-1s
-3s

*Figure 117*

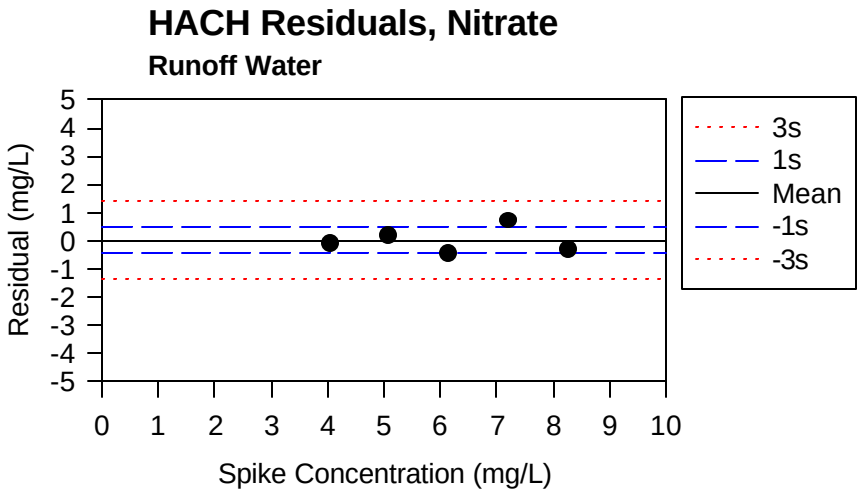



*Figure 118*

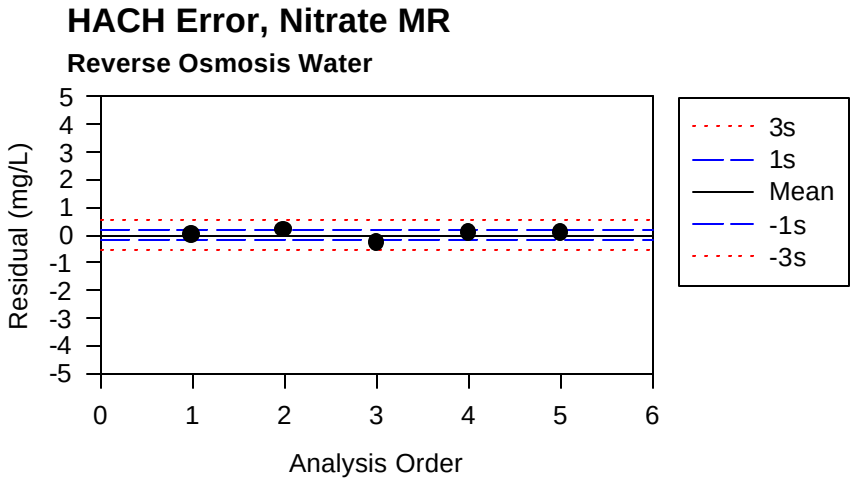



*Figure 119*

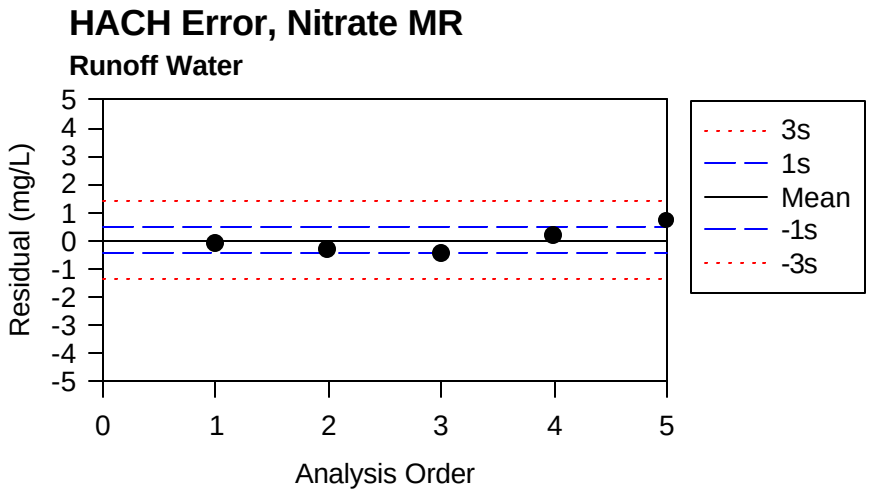



*Figure 120*

## 32.8 CHEMetrics Nitrate

### *32.8.1 Method*

The CHEMetrics Nitrate method determines the amount of nitrate in a sample by cadmium reduction of all nitrate ($NO_3^-$) to nitrite ($NO_2^-$). The nitrite then forms a diazonium salt with an unnamed primary aromatic amine. The diazonium salt is coupled with an unnamed organic molecule. The result is a highly colored compound in direct proportion to the original concentration of nitrate and nitrite in the sample.

To measure the nitrate concentration with the CHEMetrics method, collect 25 mL of sample. Add cadmium reagent from the foil pack. Shake for 3 minutes. Allow the sample to set undisturbed for 30 s. Immerse the tapered end of the ampoule into the sample and snap. Allow the ampoule to fill. Remove the ampoule from the solution and mix. Allow the ampoule to set undisturbed for 10 minutes. Use the visual comparator to measure the nitrate concentration. The concentration is expressed as mg/L N.

The major interferent with this test is that the test measures nitrate and nitrite combined, the same as many of the above described methods. The test reduces all nitrate to nitrite; any nitrite in the original sample will be detected as nitrate. Strong oxidizers and reducers will interfere with the dye formation and interfere in an unpredictable manner. Samples with high iron or copper concentrations will produce results decreased from the true value. Again, the use of the cadmium in this test likely causes the test wastes to be classified as hazardous.

### *32.8.2 Observations*

The quantitative capabilities of this test are not as good as some other tests. Like all visual comparators, the measurement depends on the color perception of the user.

*Table 127*

| Sample ID | Standard Conc. (mg/L) as NO3 | Order | RO (mg/L) as N | RO (mg/L) as NO3 | Recovery (%) | Order | Runoff (mg/L) as N | Runoff (mg/L) as NO3 | Runoff minus Blank (mg/L) as NO3 |
|---|---|---|---|---|---|---|---|---|---|
| NO3 X 0 | 0 | 6 | 0 | 0 | NA | 2 | 0.30 | 1.32 | 0 |
| NO3 X 1 | 0.999 | 1 | 0.2 | 0.88 | 88 | 10 | 0.60 | 2.64 | 1.32 |
| NO3 X 2 | 1.996 | 5 | 0.4 | 1.76 | 88 | 9 | 1.00 | 4.4 | 3.08 |
| NO3 X 3 | 2.991 | 4 | 0.8 | 3.52 | 118 | 3 | 1.00 | 4.4 | 3.08 |
| NO3 X 4 | 3.984 | 8 | 0.9 | 3.96 | 99 | 7 | 1.25 | 5.5 | 4.18 |

*Table 128*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.986393228 |
| R Square | 0.9729716 |
| Adjusted R Square | 0.963962133 |
| Standard Error | 0.32133873 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 11.15134426 | 11.15134426 | 107.9943609 | 0.00190142 |
| Residual | 3 | 0.309775738 | 0.103258579 | | |
| Total | 4 | 11.46112 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | -0.090117498 | 0.249074425 | -0.36180952 | 0.741477284 | -0.882784227 | 0.70254923 | -0.882784227 | 0.70254923 |
| Standard Conc. (mg/L) as NO3 | 1.060239468 | 0.102024254 | 10.39203353 | 0.00190142 | 0.735552453 | 1.38492648 | 0.735552453 | 1.384926482 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L) as NO3* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | -0.090117498 | 0.090117498 | 0.280443937 |
| 2 | 0.96906173 | -0.08906173 | -0.277158405 |
| 3 | 2.026120479 | -0.266120479 | -0.828161857 |
| 4 | 3.081058749 | 0.438941251 | 1.365976804 |
| 5 | 4.13387654 | -0.17387654 | -0.541100479 |

*Table 129*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.965268519 |
| R Square | 0.931743313 |
| Adjusted R Square | 0.908991085 |
| Standard Error | 0.500194392 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 10.24589671 | 10.24589671 | 40.95173791 | 0.007729355 |
| Residual | 3 | 0.750583289 | 0.25019443 | | |
| Total | 4 | 10.99648 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 1.625528521 | 0.387708107 | 4.192660637 | 0.0247464 | 0.391667129 | 2.859389912 | 0.391667129 | 2.859389912 |
| Standard Conc. (mg/L) as NO3 | 1.016284593 | 0.158810485 | 6.399354492 | 0.007729355 | 0.510878277 | 1.52169091 | 0.510878277 | 1.52169091 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L) as NO3* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 1.625528521 | -0.305528521 | -0.610819565 |
| 2 | 2.64079683 | -0.00079683 | -0.00159304 |
| 3 | 3.654032569 | 0.745967431 | 1.491355047 |
| 4 | 4.66523574 | -0.26523574 | -0.530265321 |
| 5 | 5.674406341 | -0.174406341 | -0.348677122 |

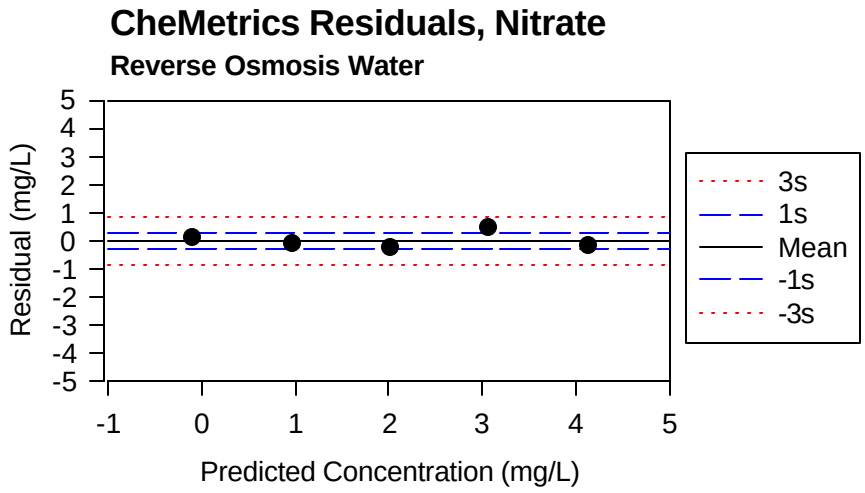

CheMetrics Residuals, Nitrate
Reverse Osmosis Water
Residual (mg/L)
5
4
3
2
1
0
-1
-2
-3
-4
-5
-1
0
1
2
3
4
5
Predicted Concentration (mg/L)
3s
1s
Mean
-1s
-3s

*Figure 121*

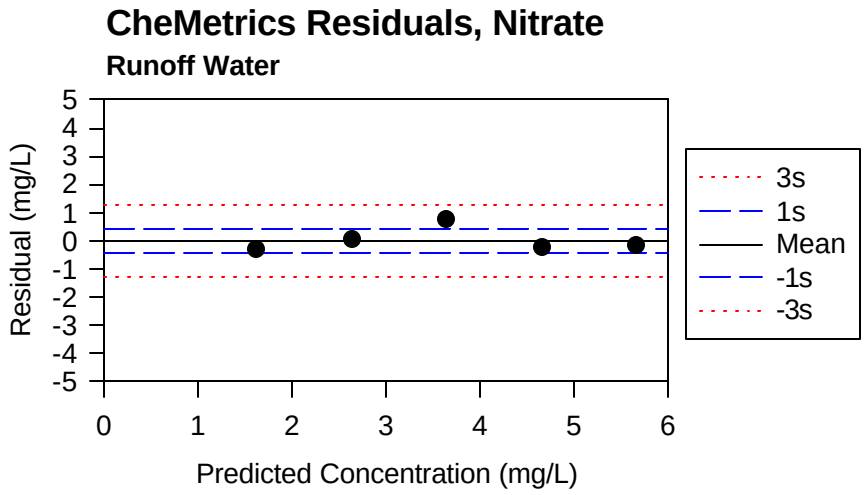



*Figure 122*

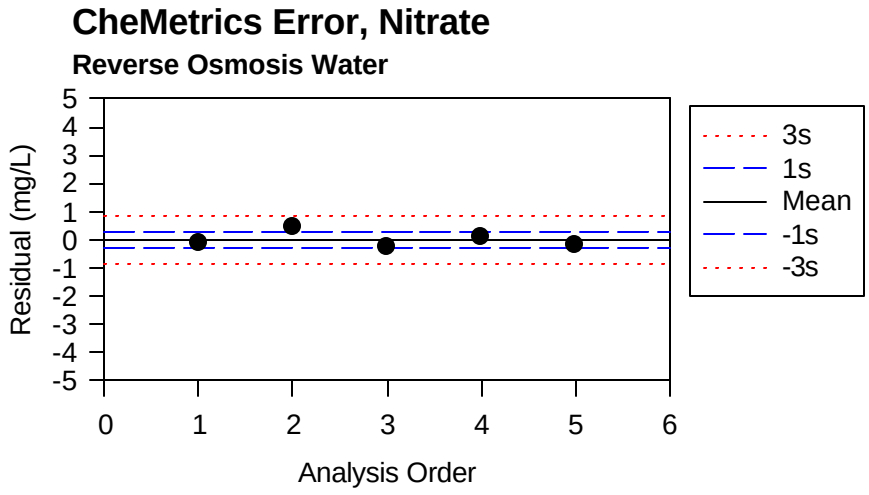



*Figure 123*

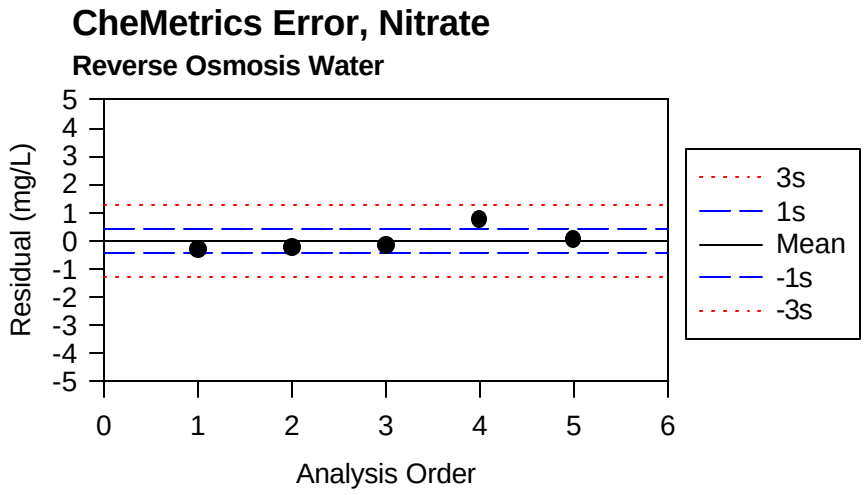

CheMetrics Error, Nitrate
Reverse Osmosis Water
Residual (mg/L)
5
4
3
2
1
0
-1
-2
-3
-4
-5
0
1
2
3
4
5
6
Analysis Order
3s
1s
Mean
-1s
-3s

*Figure 124*

# 33 pH Summary

# 34 pH

The evaluation of pH probes is different from the other evaluations presented in this report. There is no practical way to measure spike additions of pH to different samples matrices. The probes could be used to follow pH through the titration of a polyprotic acid such as $H_3PO_4$. However, the information would have limited value for comparison. The items of greatest interest to the evaluation of pH probes include ease of calibration, probe stability and longevity. Therefore, the analyses of pH probes will mostly be through parallel studies and comparisons with different buffers. The basic goal of these analyses is to "break" the probe. Many factors affect the quality of data generated with pH probes. The probes are acutely susceptible to poisoning with detergents, oils and other organic materials. To evaluate the effectiveness of each probe, the pH of 25 randomly selected water samples from manholes and 5 replicates of a composite of manhole samples are compared to the pH of the same sample as determined by the Sentron pH probe, our laboratory standard method for pH determinations.

*Table 130*

| Kit Name | Method | Capital cost | Expendable Cost (per sample) | Time Required (min) | Sample Vol. (ml) | Expertise Required |
|---|---|---|---|---|---|---|
| pH Testr 2 | electrode | Supplied with GDS's AquaVats kit | Supplied with GDS's AquaVats kit | 1 | *In situ* | none |
| Cole-Parmer pH Wand | electrode | $155.00 for kit | $92.00/ electrode | 5 | *in situ* | some |
| Horiba Twin pH | electrode | $235 for kit | $70.00 for sensor. $25.00 for standards. | 1 | *in situ* or drops | none |
| Sentron pH Probe | electrode | $595 for meter and electrode | none | 1 | *in situ* | none |
| EM Science ReflectoQuant pH | test paper | $500 for ReflectoQuant Meter | $0.89 | 2 | *in situ* | none |
| La Motte pH | Spectrophotometric | $895 for Smart Colorimeter | $0.22 | 5 | 10 | some |
| Fisher Scientific | test paper | $0.00 | small | 1 | *in situ* | none |

*Table 131*

| Kit Name | Precision | Shelf Life | Regular Maintenance | Safety Hazards | Useful Range (mg/L) |
|---|---|---|---|---|---|
| pHTestr 2 | not evaluated | not applicable | Weekly 1 point calibration. | None | unknown |
| Cole-Parmer pH Wand | 0.01300 | not applicable | Daily 3 point calibration. | None | 0-15 |
| Horiba Twin pH | 0.00843 | not applicable | Daily 2 point calibration. | None | 0-12 |
| Sentron pH Probe | 0.00632 | not applicable | Daily 3 point calibration. | None | 0-14 |
| EM Science ReflectoQuant pH | 0.08031 | not indicated | Clean ReflectoQuant optics. | None | 4 to 9 |
| La Motte pH | not evaluated | not indicated | Charge batteries. | None | 5-9.5 |
| Fisher Scientific Allegiant | 0.06577 | not indicated | none | None | 0-12 |

## 34.1 Sentron pH Probe

The Sentron pH probe is a solid state electrode device. However, it has the most rugged design of the methods evaluated. The Sentron electrode, unlike the others, is designed to be cleaned should it become poisoned by organic material. The probe can use a single point verification or a two point calibration. The probe is programmed to recognize pH standards of 4.0, 7.0 and 10.0. This probe produces an error message when the measured pH of a sample is outside the calibration limits of the probe.

## 34.2 Cole-Parmer pH Wand

The Cole-Parmer pH Wand is the traditional field pH probe. The design is a conventional glass electrode encased in plastic. The plastic sheath helps protect the glass electrode during field use. The meter is programmed to recognize pH 4.01, 7.00 and 10.00 calibration standards. To calibrate the meter, the probe is placed in any of the three standards. The solution should be stirred constantly with a gentle motion throughout measurement. After approximately 1 minute, the meter should read the approximate concentration of the standard. Initially, the pH reading will vary wildly as the probe comes to equilibrium with the sample, but after a few minutes the reading should "settle" to a narrow range of values. When this occurs, press the calibration button to enter the value and proceed to the next standard. After all three calibrations have been entered, the meter will check the slope of the calibration. If the calibration is unsuccessful, the meter will display an error message instructing the user to calibrate again. After calibration, the meter may be used to measure sample pH in exactly the same manner as measuring the calibration standards.

*Table 132*

| Cole-Parmer pH Wand | | | Sentron | | |
|---|---|---|---|---|---|
| Sample ID | Order | Response | Sample ID | Order | Response |
| 2464 | 7 | 6.78 | 2464 | 10 | 6.9 |
| 2473 | 24 | 6.78 | 2473 | 29 | 6.6 |
| 2491 | 12 | 7.43 | 2491 | 25 | 7.4 |
| 2501 | 3 | 7.69 | 2501 | 20 | 7.4 |
| 2511 | 11 | 7.36 | 2511 | 16 | 7.3 |
| 2530 | 23 | 6.72 | 2530 | 13 | 7.0 |
| 2539 | 15 | 7.52 | 2539 | 6 | 7.3 |
| 2548 | 21 | 7.15 | 2548 | 7 | 6.9 |
| 2585 | 2 | 7.11 | 2585 | 18 | 7.3 |
| 2595 | 27 | 7.79 | 2595 | 2 | 7.4 |
| 2613 | 26 | 7.70 | 2613 | 1 | 7.4 |
| 2629 | 6 | 6.86 | 2629 | 26 | 6.9 |
| 2638 | 1 | 7.51 | 2638 | 19 | 7.3 |
| 2656 | 10 | 7.67 | 2656 | 15 | 7.6 |
| 2666 | 30 | 7.51 | 2666 | 8 | 7.2 |
| 2674 | 22 | 7.60 | 2674 | 27 | 7.4 |
| 2695 | 19 | 7.65 | 2695 | 24 | 7.4 |
| 2722 | 17 | 7.13 | 2731 | 22 | 7.2 |
| 2731 | 18 | 7.30 | 2740 | 30 | 7.3 |
| 2740 | 4 | 7.35 | 2749 | 9 | 7.4 |
| 2749 | 13 | 7.49 | 2774 | 11 | 7.0 |
| 2774 | 9 | 7.07 | 2783 | 4 | 7.6 |
| 2783 | 29 | 8.00 | 2783 | 12 | 7.7 |
| 2801 | 8 | 7.35 | 2801 | 28 | 7.3 |
| 2810 | 5 | 7.07 | 2810 | 17 | 7.1 |
| | | | | | |
| JD 001 | 14 | 7.27 | JD 001 | 14 | 7.0 |
| JD 002 | 20 | 7.36 | JD 002 | 21 | 7.1 |
| JD 003 | 16 | 7.31 | JD 003 | 23 | 7.1 |
| JD 004 | 25 | 7.45 | JD 004 | 5 | 7.1 |
| JD 005 | 28 | 7.50 | JD 005 | 3 | 7.1 |
| average | | 7.38 | average | | 7.08 |
| standard deviation | | 0.10 | standard deviation | | 0.04 |
| COV | | 1.30 | COV | | 0.63 |

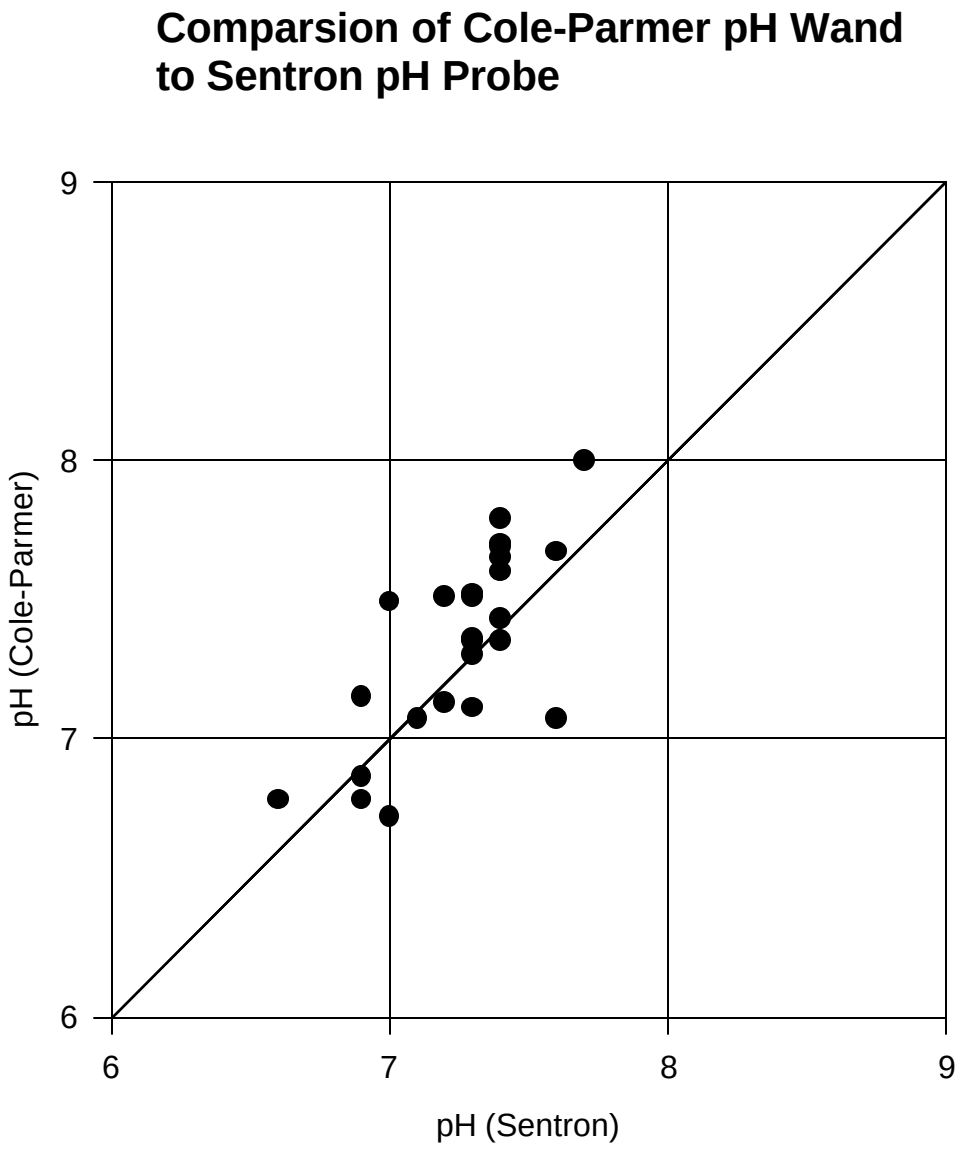



*Figure 125*

### 34.3 Horiba Twin pH

The Horiba Twin pH meter is constructed similar to the Horiba Twin Conductivity Meter. The pH is determined using a solid state electrode, not the traditional glass electrode. This meter uses a 2 point calibration at pH 4.0 and 7.0. The probe is built into the meter. To measure the sample, fill the sample well with a few drops of sample. The meter will display a “smiley face” when the probe has reached

equilibrium with the sample solution. Like the Horiba Twin Conductivity meter, the end of the probe may be immersed in a sample for direct measurement. This probe is sensitive to surfactants and has a very fragile thin glass covering over the electrode that is easily broken.

*Table 133*

| Horiba Twin | | | Sentron | | |
|---|---|---|---|---|---|
| Sample ID | Order | Response | Sample ID | Order | Response |
| 2464 | 8 | 7.28 | 2464 | 10 | 6.90 |
| 2473 | 23 | 7.00 | 2473 | 29 | 6.60 |
| 2491 | 6 | 7.73 | 2491 | 25 | 7.40 |
| 2501 | 16 | 7.91 | 2501 | 20 | 7.40 |
| 2511 | 4 | 7.69 | 2511 | 16 | 7.30 |
| 2530 | 24 | 7.27 | 2530 | 13 | 7.00 |
| 2539 | 14 | 7.73 | 2539 | 6 | 7.30 |
| 2548 | 11 | 7.19 | 2548 | 7 | 6.90 |
| 2585 | 26 | 7.73 | 2585 | 18 | 7.30 |
| 2595 | 27 | 7.91 | 2595 | 2 | 7.40 |
| 2613 | 21 | 8.00 | 2613 | 1 | 7.40 |
| 2629 | 5 | 7.28 | 2629 | 26 | 6.90 |
| 2638 | 28 | 7.94 | 2638 | 19 | 7.30 |
| 2656 | 3 | 7.92 | 2656 | 15 | 7.60 |
| 2666 | 2 | 7.64 | 2666 | 8 | 7.20 |
| 2674 | 25 | 7.83 | 2674 | 27 | 7.40 |
| 2695 | 18 | 7.83 | 2695 | 24 | 7.40 |
| 2722 | 20 | 7.46 | 2731 | 22 | 7.20 |
| 2731 | 19 | 7.55 | 2740 | 30 | 7.30 |
| 2740 | 9 | 7.64 | 2749 | 9 | 7.40 |
| 2749 | 10 | 7.76 | 2774 | 11 | 7.00 |
| 2774 | 12 | 7.37 | 2783 | 4 | 7.60 |
| 2783 | 29 | 8.11 | 2783 | 12 | 7.70 |
| 2801 | 1 | 7.55 | 2801 | 28 | 7.30 |
| 2810 | 7 | 7.46 | 2810 | 17 | 7.10 |
| | | | | | |
| JD 001 | 15 | 7.46 | JD 001 | 14 | 7.00 |
| JD 002 | 17 | 7.55 | JD 002 | 21 | 7.10 |
| JD 003 | 13 | 7.55 | JD 003 | 23 | 7.10 |
| JD 004 | 22 | 7.55 | JD 004 | 5 | 7.10 |
| JD 005 | 30 | 7.64 | JD 005 | 3 | 7.10 |
| average | | 7.60 | average | | 7.08 |
| standard deviation | | 0.06 | standard deviation | | 0.04 |
| COV | | 0.84 | COV | | 0.63 |

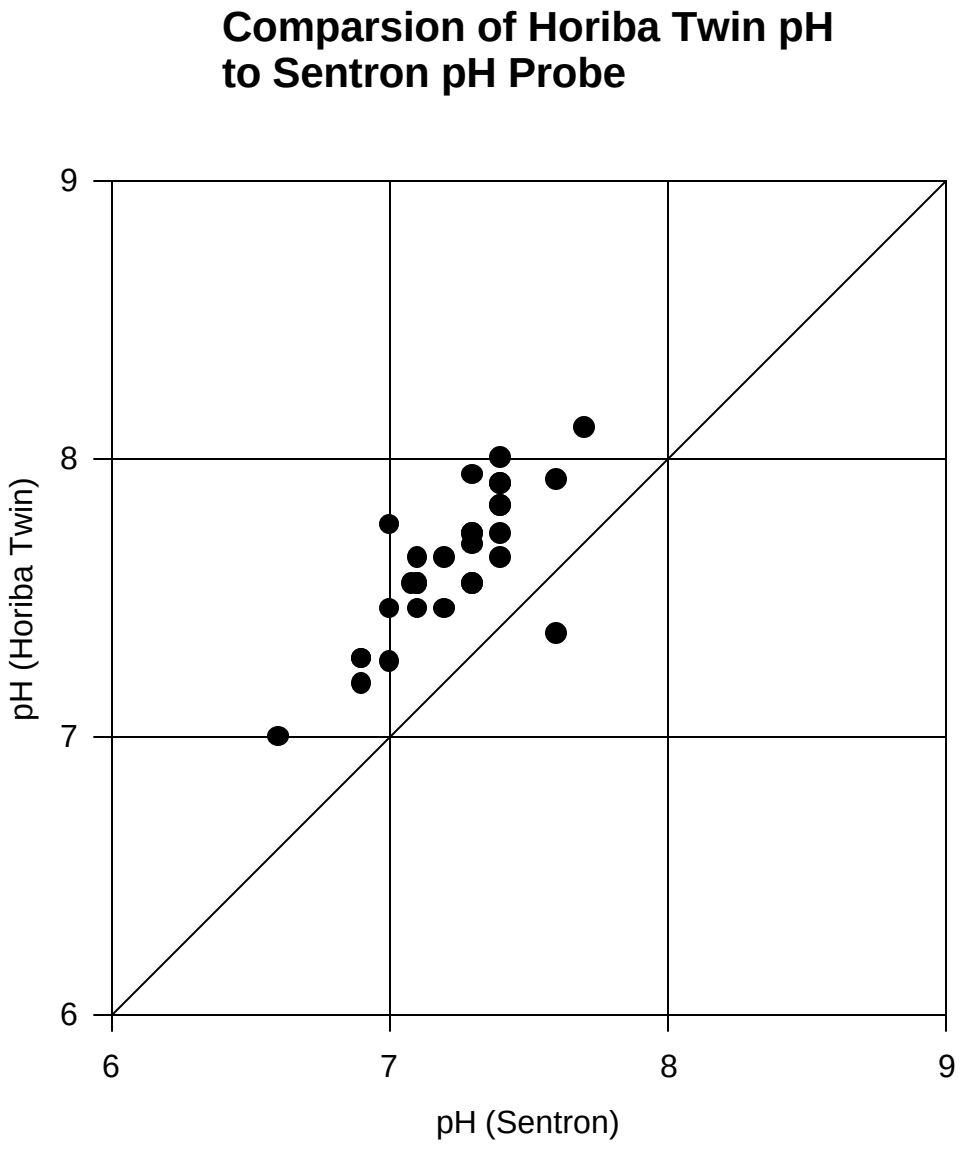



*Figure 126*

### 34.4 EM Science Quant pH Test Strips

The EM Science Quant pH Test Strips are modernized litmus paper tests for pH. The test strip is impregnated with universal indicator. The pH of the sample is determined by immersing the strip into the sample. A 1 minute color development time is required. At the conclusion of the 1 minute period, the

test strip is analyzed using the RQFlex Reflectometer. The meter is calibrated with bar code strips shipped with each set of reagents. The calibration is permanent until a new set of strips are used. This eliminates the need for frequent re-calibration required by the electrode methods. As seen, there was a very poor correlation between these test strips and the pH meter.

*Table 134*

| EM Quant Test Strips | | | Sentron | | |
|---|---|---|---|---|---|
| Sample ID | Order | Response | Sample ID | Order | Response |
| 2464 | 8 | 5 | 2464 | 10 | 6.90 |
| 2473 | 30 | 7 | 2473 | 29 | 6.60 |
| 2491 | 16 | 6.6 | 2491 | 25 | 7.40 |
| 2501 | 7 | 7.2 | 2501 | 20 | 7.40 |
| 2511 | 11 | 6.9 | 2511 | 16 | 7.30 |
| 2530 | 14 | 6.5 | 2530 | 13 | 7.00 |
| 2539 | 29 | 6.8 | 2539 | 6 | 7.30 |
| 2548 | NA | NA | 2548 | 7 | 6.90 |
| 2585 | 2 | 5.0 | 2585 | 18 | 7.30 |
| 2595 | 18 | 7.2 | 2595 | 2 | 7.40 |
| 2613 | 21 | 6.9 | 2613 | 1 | 7.40 |
| 2629 | 9 | 6.9 | 2629 | 26 | 6.90 |
| 2638 | 1 | 6.9 | 2638 | 19 | 7.30 |
| 2656 | 24 | 6.6 | 2656 | 15 | 7.60 |
| 2666 | 22 | 6.9 | 2666 | 8 | 7.20 |
| 2674 | 6 | 4.9 | 2674 | 27 | 7.40 |
| 2695 | 21 | 6.7 | 2695 | 24 | 7.40 |
| 2731 | 28 | 4.5 | 2731 | 22 | 7.20 |
| 2740 | 3 | 6.6 | 2740 | 30 | 7.30 |
| 2749 | 12 | 5.2 | 2749 | 9 | 7.40 |
| 2774 | 5 | 6.0 | 2774 | 11 | 7.00 |
| 2783 | 4 | 7.3 | 2783 | 4 | 7.60 |
| 2783 | 23 | 7.3 | 2783 | 12 | 7.70 |
| 2801 | 26 | 6.8 | 2801 | 28 | 7.30 |
| 2810 | 4 | 5 | 2810 | 17 | 7.10 |
| | | | | | |
| JD 001 | 20 | 5.8 | JD 001 | 14 | 7.00 |
| JD 002 | 13 | 6.9 | JD 002 | 21 | 7.10 |
| JD 003 | 25 | 6.9 | JD 003 | 23 | 7.10 |
| JD 004 | 17 | 6.9 | JD 004 | 5 | 7.10 |
| JD 005 | 15 | 7.2 | JD 005 | 3 | 7.10 |

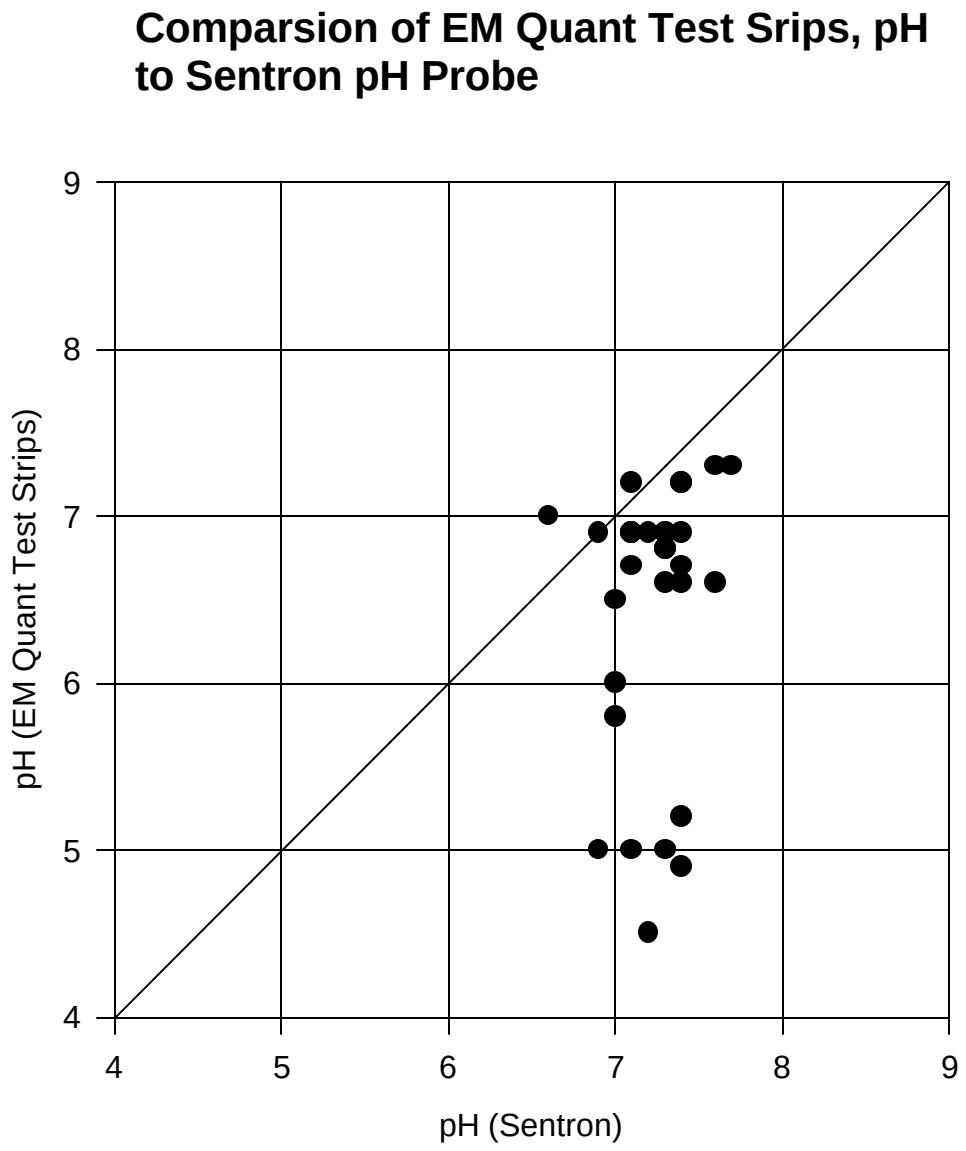



*Figure 127*

## 34.5 La Motte pH

The La Motte pH method is the most complicated of the evaluated methods. It requires some estimate of the pH of the sample before measurement (within 2 pH units). Depending on the estimated pH of the sample, one of three indicator solutions is added to a 10 mL sample. The pH is then determined using the La Motte Smart Colorimeter. The useful range of this instrument is the most limited. However, the calibration is stored in the La Motte Smart

Colorimeter and need not be updated. This test was not evaluated further because of its limited range and *a priori* requirements.

## 34.6 Fisher Scientific Alkacid Test Strips

The Alkacid Test Strips are another improvement over simple litmus paper. The strips are impregnated with universal indicator. To measure the pH of a sample, simply immerse the strip, or dot a drop on the paper, and immerse the strip in the sample. Compare the color change (immediate) to the color chart printed on package. The measurement scale is accurate to within 1 pH unit. As seen, there was a very poor correlation between these test strips and the pH meter.

*Table 135*

| Fisher Alkacid Test Paper | | | Sentron | | |
|---|---|---|---|---|---|
| Sample ID | Order | Response | Sample ID | Order | Response |
| 2464 | 26 | 7 | 2464 | 10 | 6.90 |
| 2473 | 14 | 7 | 2473 | 29 | 6.60 |
| 2491 | 11 | 7 | 2491 | 25 | 7.40 |
| 2501 | 17 | 7 | 2501 | 20 | 7.40 |
| 2511 | 5 | 6 | 2511 | 16 | 7.30 |
| 2530 | 1 | 6 | 2530 | 13 | 7.00 |
| 2539 | 16 | 7 | 2539 | 6 | 7.30 |
| 2548 | 4 | 7 | 2548 | 7 | 6.90 |
| 2585 | 7 | 5 | 2585 | 18 | 7.30 |
| 2595 | 8 | 7 | 2595 | 2 | 7.40 |
| 2613 | 24 | 7 | 2613 | 1 | 7.40 |
| 2629 | 6 | 5 | 2629 | 26 | 6.90 |
| 2638 | 30 | 7 | 2638 | 19 | 7.30 |
| 2656 | 21 | 7 | 2656 | 15 | 7.60 |
| 2666 | 23 | 6 | 2666 | 8 | 7.20 |
| 2674 | 27 | 5 | 2674 | 27 | 7.40 |
| 2695 | 2 | 6 | 2695 | 24 | 7.40 |
| 2731 | 13 | 6 | 2731 | 22 | 7.20 |
| 2740 | 19 | 7 | 2740 | 30 | 7.30 |
| 2749 | 28 | 7 | 2749 | 9 | 7.40 |
| 2774 | 12 | 6 | 2774 | 11 | 7.00 |
| 2783 | 29 | 6 | 2783 | 4 | 7.60 |
| 2783 | 22 | 7 | 2783 | 12 | 7.70 |
| 2801 | 20 | 7 | 2801 | 28 | 7.30 |
| 2810 | 10 | 5 | 2810 | 17 | 7.10 |
| | | | | | |
| JD 001 | 3 | 7 | JD 001 | 14 | 7.00 |
| JD 002 | 6 | 7 | JD 002 | 21 | 7.10 |
| JD 003 | 9 | 7 | JD 003 | 23 | 7.10 |
| JD 004 | 18 | 7 | JD 004 | 5 | 7.10 |
| JD 005 | 3 | 7 | JD 005 | 3 | 7.10 |

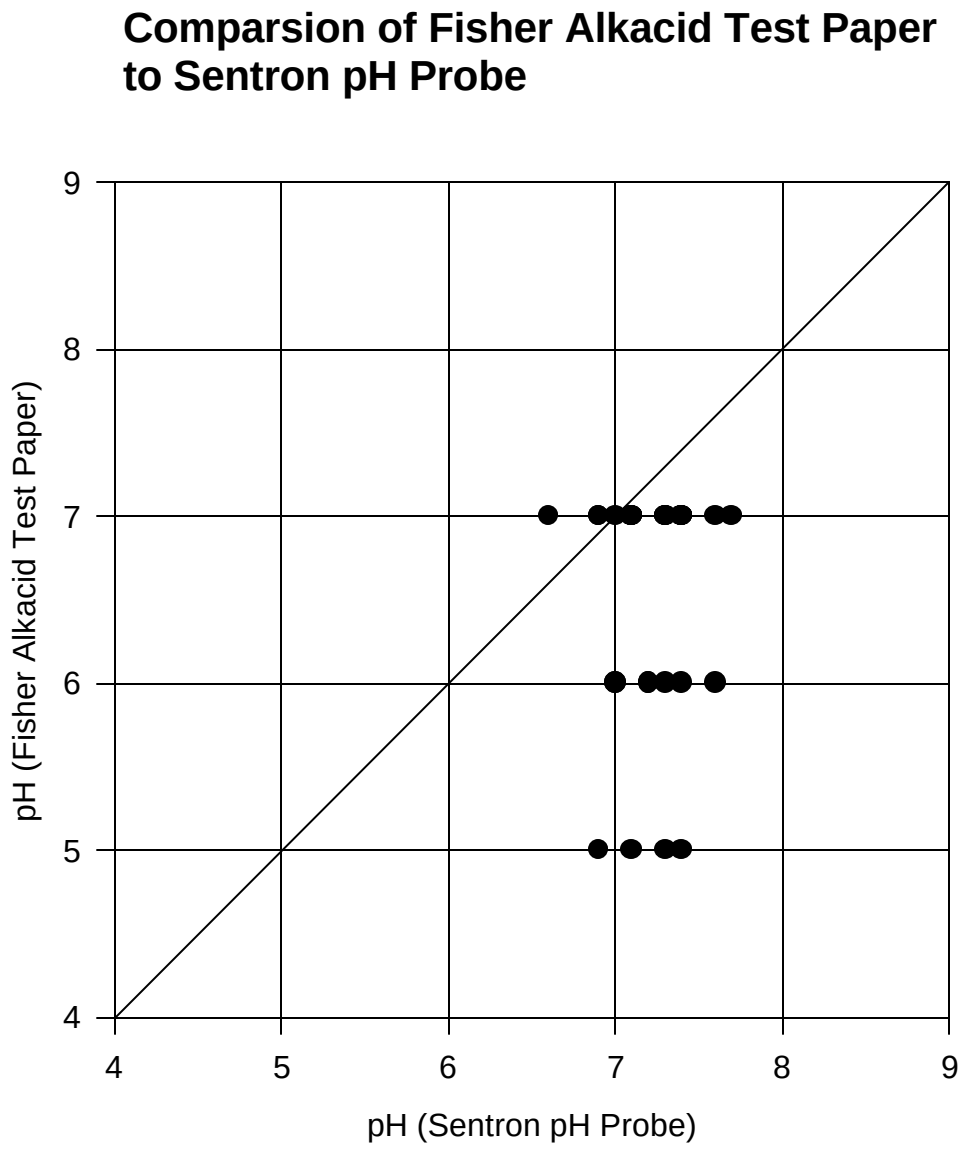



*Figure 128*

## 34.7 pHTestr2 pH Meter

### *34.7.1 Method*

The pH meter provided in the GDS AquaVats test kit is the pHTestr 2, with automatic temperature control. This is a small, lightweight device. Calibration is completed by submerging the bottom of the meter in a buffer solution, then pressing the CAL button. Once the meter has reached a steady reading, the HOLD/CON button is pressed. If the solution does not reach the specified buffer (4.0, 7.0, or 10.0), the instruction are to simply add or subtract the deviation amount from each of the data readings. One disadvantage of this particular piece of equipment is that you cannot calibrate it to an exact buffer value. The only reagents required for this procedure is the buffer used for calibration, which is non-hazardous and can be disposed of easily.

### *34.7.2 Observations*

Figure 5 compares the pHTestr 2 observations against the buffer values. The comparisons were good, with a maximum deviation of about 0.5 pH unit for the pH 10 buffer. The deviations for the pH 4 test were 0.1 pH unit, while most of the replicate readings using the pH 7 buffer were less than 0.1 pH unit.

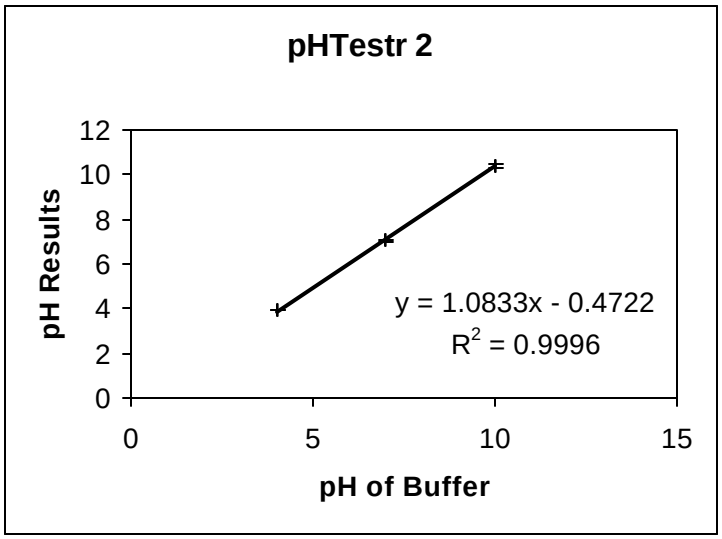



Figure 5

# 35 Potassium Summary

# 36 Potassium

Three methods for determining potassium concentrations were evaluated: HACH, La Motte and the Horiba Cardy. The La Motte procedure was also adapted for use with the DR 2000 spectrophotometer for comparison. The HACH and La Motte methods both use tetraphenylborate to determine the concentration of potassium. The Horiba Cardy is an ion selective electrode for potassium.

| Kit Name | Method | Capital cost | Expendable Cost (per sample) | Time Required (min) | Sample Vol. (ml) | Expertise Required |
|---|---|---|---|---|---|---|
| HACH Potassium Tetraphenylborate | Spectrophotometric | $1495 for DR 2000 | $2.99 | 30 | 25 | some |
| Horiba CARDY | ISE | $235 for kit | $60.00/ electrode | 5 | drops | little |
| La Motte Potassium | colorimeter | $895 for Smart Colorimeter | $0.29 | 15 | 10 | some |
| La Motte Potassium Reagent Set, HACH DR 2000 Spectrophotometer | Spectrophotometric | $1495 for DR 2000 | $0.29 | 15 | 10 | some |

*Table 136*

*Table 137*

| Kit Name | Precision | Shelf Life | Regular Maintenance | Safety Hazards | Upper Limit of Useful Range (mg/L) |
|---|---|---|---|---|---|
| HACH Potassium Tetraphenylborate | not evaluated | not indicated | New calibration with each set of reagents. Charge batteries. | | 7.0* |
| Horiba CARDY | 0.04141 | not applicable | Daily 1 point calibration. Monthly 2 point calibration. | None | unknown |
| La Motte Potassium | not evaluated | not indicated | Charge batteries. | | <10.0 |
| La Motte Potassium Reagent Set, HACH DR 2000 Spectrophotometer | 0.06217 | not indicated | New calibration with each set of reagents. Charge batteries. | | 7 |

## 36.1 Spiked Samples

The RO summaries for the HACH and HACH adaptation of the La Motte method refer to the calibration curves developed for those methods. Therefore, the slope may differ significantly from 1 and the detection limits are not comparable to the other methods.

*Table 138*

Reverse Osmosis

| Kit Name | Adjusted $R^2$ | Standard Error | Intercept | p-Value | Slope | p-Value | Detection Limit ($\alpha$=0.05) (mg/L) | Limit of Quantification ($\alpha$=0.05) (mg/L) |
|---|---|---|---|---|---|---|---|---|
| HACH Potassium Tetraphenylborate | 0.9856 | 0.5993 | -0.4858 | 0.2183 | 8.1387 | 5.3935E-06 | 0.5235 | 1.5328 |
| Horiba CARDY | 0.8931 | 0.9055 | 0.4476 | 0.4070 | 0.5307 | 8.3196E-04 | 1.9724 | 3.4972 |
| La Motte Potassium | 0.8035 | 1.6971 | 0.4881 | 0.6723 | 1.3484 | 2.5166E-02 | 3.3459 | 6.2038 |
| La Motte Potassium Reagent Set, HACH DR 2000 | 0.9714 | 0.8440 | -0.0803 | 0.8701 | 8.7709 | 3.0000E-05 | 1.3410 | 2.7623 |

*Table 139*

Runoff

| Kit Name | Adjusted $R^2$ | Standard Error | Intercept | p-Value | Slope | p-Value | Detection Limit ($\alpha$=0.05) (mg/L) | Limit of Quantification ($\alpha$=0.05) (mg/L) |
|---|---|---|---|---|---|---|---|---|
| HACH Potassium Tetraphenylborate | 0.9562 | 0.9581 | 1.2805 | 0.0577 | 0.8998 | 8.7798E-05 | 2.8941 | 4.5076 |
| Horiba CARDY | 0.7699 | 1.2206 | 0.6473 | 0.3762 | 0.4595 | 5.8872E-03 | 2.8255 | 4.8811 |
| La Motte Potassium | 0.9875 | 0.3085 | 1.1785 | 0.0084 | 1.0462 | 3.8770E-04 | 1.6980 | 2.2175 |
| La Motte Potassium Reagent Set, | 0.9339 | 1.2838 | -0.6722 | 0.4194 | 1.0537 | 2.4714E-04 | 1.4898 | 3.6517 |

## Potassium Measurements in Reverse Osmosis Water

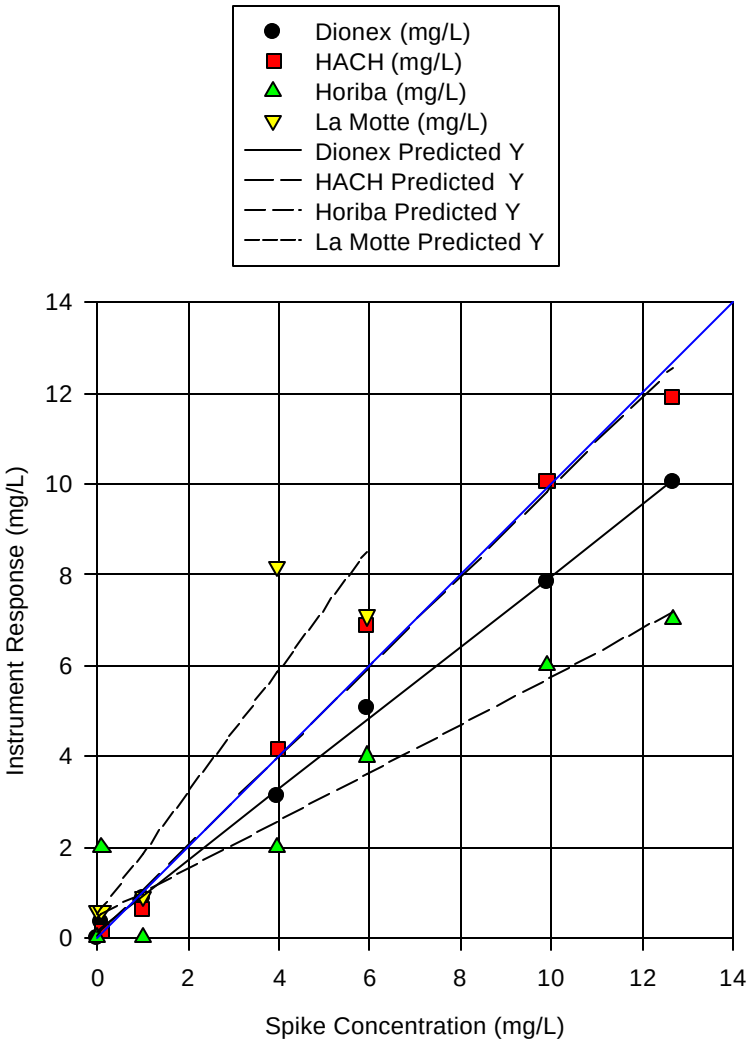



*Figure 129*

## Potassium Measurements in Runoff Water

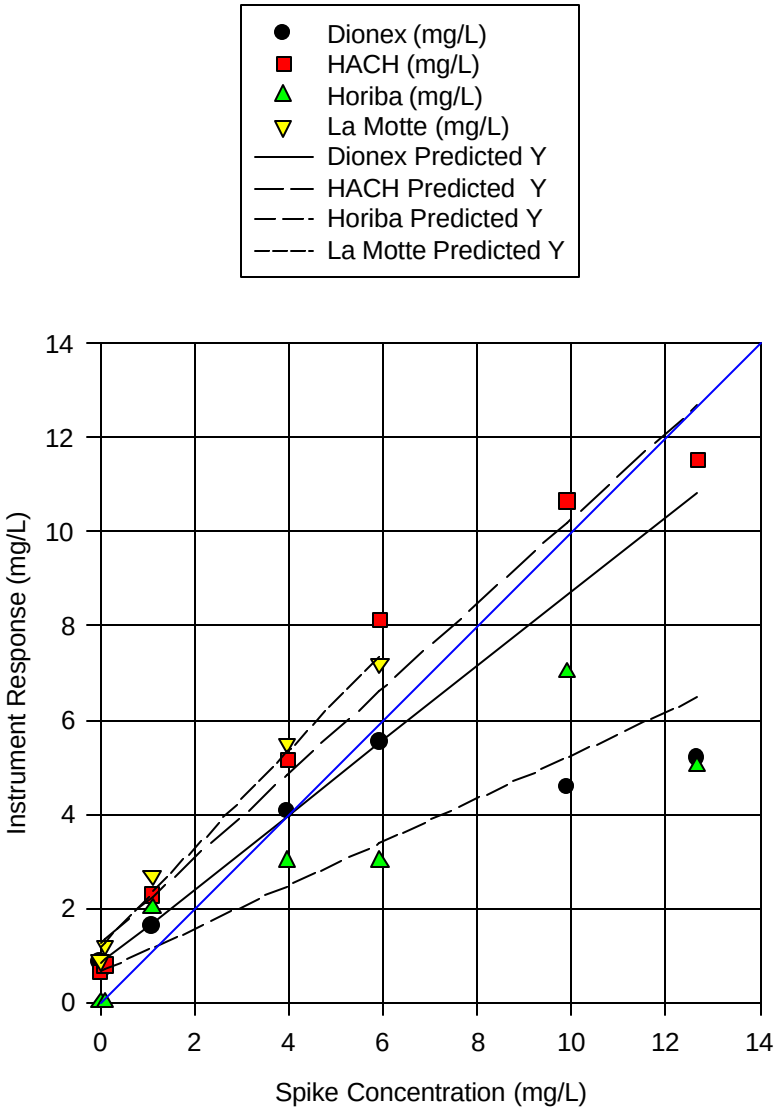



*Figure 130*

## 36.2 Parallel Analyses

The comparisons of the Horiba Cardy and the modified La Motte methods to the standard ion chromatograph (IC) method shows under-predictions compared to the laboratory standard IC. The Horiba and La Motte methods were both too low by about 50%. The sample with very high concentration (about 160 mg/L) was greatly under-predicted by the field instruments. These results indicate negative matrix interferences from the water collected from telecommunication manholes, especially for the samples having very high road salt concentrations.

*Table 140*

| Sample ID | Dionex DX-100 Ion Chromatograph (mg/L) | Order | Horiba (mg/L) | Order | LM Adapted (abs) | LM Adapted (mg/L) |
|---|---|---|---|---|---|---|
| 2464 | 6.61 | 10 | 3 | 2 | 0.341 | 2.29 |
| 2473 | 63.64 | 33 | 51 | 10 | 2.119 | 16.76 |
| 2491 | 63.91 | 18 | 33 | 17 | 2.175 | 17.22 |
| 2501 | 16.67 | 32 | 8 | 19 | 0.963 | 7.35 |
| 2511 | 15.59 | 15 | 8 | 9 | 0.908 | 6.90 |
| 2530 | 11.22 | 34 | 3 | 23 | 0.45 | 3.18 |
| 2539 | 28.33 | 6 | 13 | 1 | 1.458 | 11.38 |
| 2548 | 55.49 | 38 | 28 | 20 | 1.953 | 15.41 |
| 2585 | 1.17 | 12 | 0 | 16 | 0.054 | -0.05 |
| 2595 | 12.42 | 7 | 7 | 6 | 0.712 | 5.31 |
| 2613 | 34.13 | 35 | 28 | 28 | 2.06 | 16.28 |
| 2629 | 9.19 | 4 | 8 | 15 | 0.914 | 6.95 |
| 2638 | 10.56 | 19 | 5 | 13 | 0.505 | 3.62 |
| 2656 | 70.02 | 11 | 25 | 27 | 2.078 | 16.43 |
| 2666 | 6.87 | 39 | 4 | 22 | 0.631 | 4.65 |
| 2674 | 5.49 | 22 | 3 | 24 | 0.42 | 2.93 |
| 2695 | 4.62 | 16 | 2 | 29 | 0.501 | 3.59 |
| 2722 | 9.67 | 8 | 9 | 3 | 0.658 | 4.87 |
| 2731 | 2.76 | 36 | 1 | 8 | 0.068 | 0.07 |
| 2740 | 3.88 | 21 | 0 |  | 0.178 | 0.96 |
| 2749 | 5.93 | 23 | 3 | 18 | 0.6 | 4.40 |
| 2774 | 3.88 | 20 | 3 | 26 | 0.668 | 4.95 |
| 2783 | 158.21 | 31 | 11 | 21 | 2.526 | 20.07 |
| 2801 | 19.58 | 37 | 10 | 11 | 0.94 | 7.16 |
| 2810 | 7.06 | 1 | 2 | 14 | 0.42 | 2.93 |
|  |  |  |  |  |  |  |
| JD001 | 22.71 | 27 | 10 | 12 | 1.371 | 10.67 |
| JD002 | 16.92 | 30 | 11 | 5 | 1.18 | 9.12 |
| JD003 | 21.36 | 28 | 11 | 25 | 1.503 | 11.75 |
| JD004 | 16.55 | 29 | 11 | 7 | 1.308 | 10.16 |
| JD005 | 17.79 | 26 | 11 | 4 | 1.301 | 10.10 |

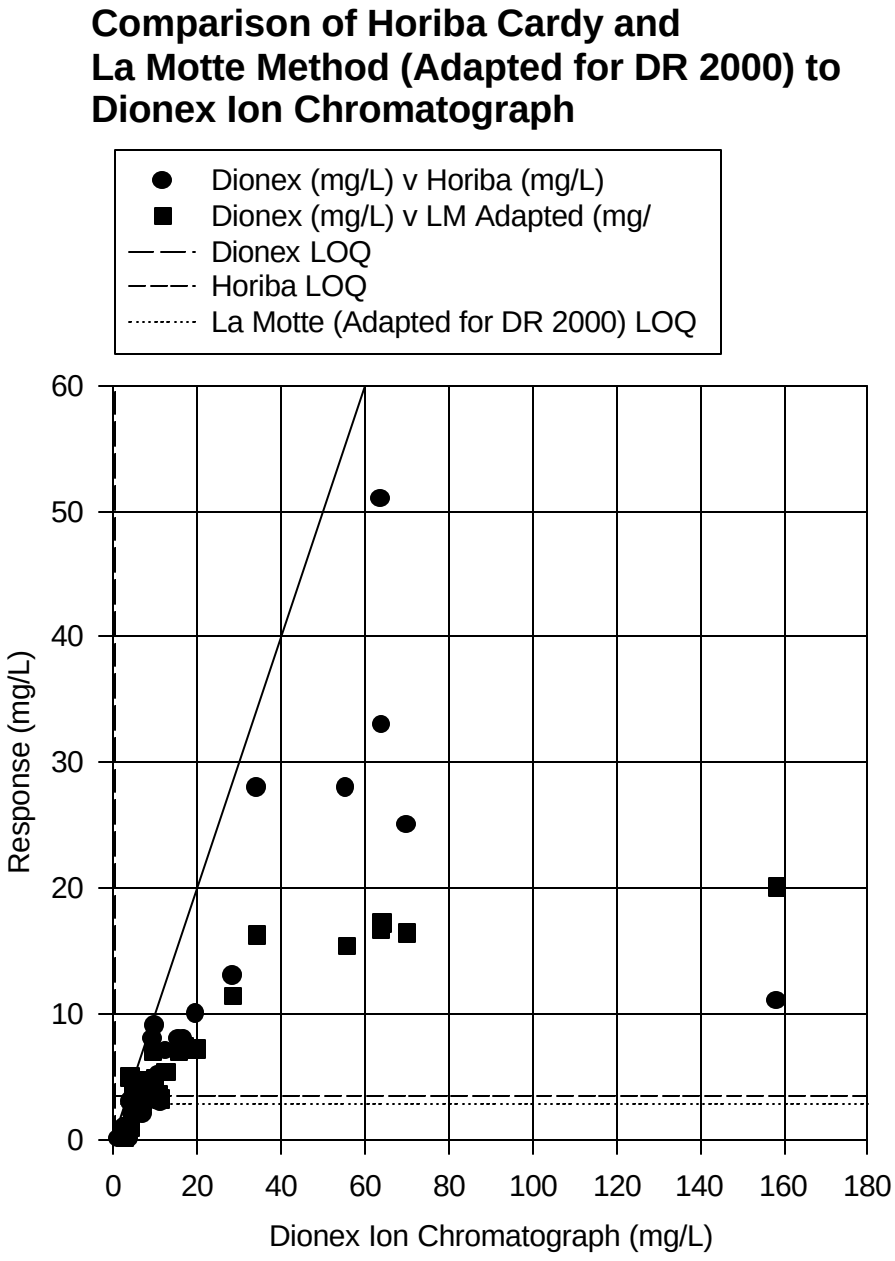



*Figure 131*

## 36.3 HACH Potassium

### *36.3.1 Method*

The HACH Potassium test determines the potassium concentration using tetraphenylborate salts. This procedure adds a large doses of sodium tetraphenylborate to the sample. The potassium in the sample reacts with the sodium tetraphenylborate to form insoluble potassium tetraphenylborate. The insoluble potassium tetraphenylborate increases the turbidity of the sample solution. The increased turbidity is measured using the DR 2000 spectrophotometer.

The HACH procedure requires 50 ml of sample (25 ml sample and 25 ml blank). The procedure can be completed in about 15 minutes. Potassium 1 Reagent (EDTA, sodium salt) and Potassium 2 Reagent (formaldehyde, methanol, and water) are added to reduce interferences with the method. After these reagents dissolve, Potassium Reagent 3 (sodium tetraphenylborate) is added. The sample is shaken for 30 s. The solution is allowed to stand for another 3 minutes. Strict adherence to the timing scheme is required for consistent results. The DR 2000 spectrophotometer is used to measure the absorbance of the blank and the sample at the end of the 3 minute reaction time. The difference in absorbance estimates the turbidity of the sample. The difference in absorbance (turbidity) between the blank and sample is directly proportional to the potassium concentration.

The presence of magnesium ($Mg^{2+}$), ammonium ($NH_4^+$) and calcium ($Ca^{2+}$) ions can interfere with the reaction by competing in the reaction with tetraphenylborate (HACH 1992). These salts will result in a reported potassium concentration larger than is actually present in the sample.

Measuring turbidity with a standard spectrophotometer is cause for concern. Spectrophotometers measure color absorbance measurements in homogenous solutions with a light beam passing through the solution. Therefore, the measurement depends on the amount of light passing through the sample. The detector is placed opposite the light source. Turbidity is the scattering of light from particles. Turbidity is measured by the amount of light scattered from the beam path. The detector is placed at a right angle to the light path to eliminate the detection of light passing through the sample. To compensate, the procedure includes a definite timing scheme. The scheme must be followed exactly in order to compare results from different samples.

### *36.3.2 Observations*

The method is not pre-programmed into the library of software shipped with the instrument. The method can be programmed by the user. Alternatively, the user may prepare an external calibration and measure the absorbance of each sample. The potassium concentration may be calculated later based on the regression equation relating absorbance to known concentration. HACH recommends that a new calibration curve be prepared each time a new batch of reagents is used. To evaluate this method, we used the second calibration alternative. The spiked samples prepared in reverse osmosis water were used to create a calibration curve. This curve was then used to determine the concentration of potassium in the runoff samples. The calibration data is presented below with the runoff data.

*Table 141*

| Sample ID | Spike Conc. (mg/L) | Order | RO Response (abs) | Order | Runoff Response (abs) | Runoff Response (mg/L) |
|---|---|---|---|---|---|---|
| K X O | 0 | 4 | 0.028 | 8 | 0.140 | 0.65 |
| K X 1 | 0.1000 | 5 | 0.079 | 3 | 0.158 | 0.80 |
| K X 2 | 0.9980 | 2 | 0.136 | 12 | 0.340 | 2.28 |
| K X 3 | 3.9683 | 9 | 0.572 | 1 | 0.692 | 5.15 |
| K X 4 | 5.9289 | 6 | 0.907 | 9 | 1.056 | 8.11 |
| K X 5 | 9.9000 | 10 | 1.297 | 13 | 1.368 | 10.7 |
| K X 6 | 12.6706 | 9 | 1.523 | 7 | 1.476 | 11.5 |

*Table 142*

Calibration Regression

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.993975425 |
| R Square | 0.987987146 |
| Adjusted R Square | 0.985584575 |
| Standard Error | 0.599334403 |
| Observations | 7 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 147.7112254 | 147.7112254 | 411.220811 | 5.39345E-06 |
| Residual | 5 | 1.796008634 | 0.359201727 | | |
| Total | 6 | 149.507234 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | -0.485771541 | 0.345153568 | -1.407406983 | 0.218328268 | -1.373015584 | 0.401472501 | -1.373015584 | 0.401472501 |
| RO Response (abs) | 8.138717765 | 0.401345544 | 20.2785801 | 5.39345E-06 | 7.107027886 | 9.170407645 | 7.107027886 | 9.170407645 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Spike Conc. (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | -0.257887444 | 0.257887444 | 0.430289739 |
| 2 | 0.157187162 | -0.057207162 | -0.095451157 |
| 3 | 0.621094075 | 0.376905925 | 0.62887417 |
| 4 | 4.16957502 | -0.20132502 | -0.33591434 |
| 5 | 6.896045472 | -0.967195472 | -1.613782667 |
| 6 | 10.0701454 | -0.1701354 | -0.28387391 |
| 7 | 11.90949562 | 0.761069685 | 1.269858164 |

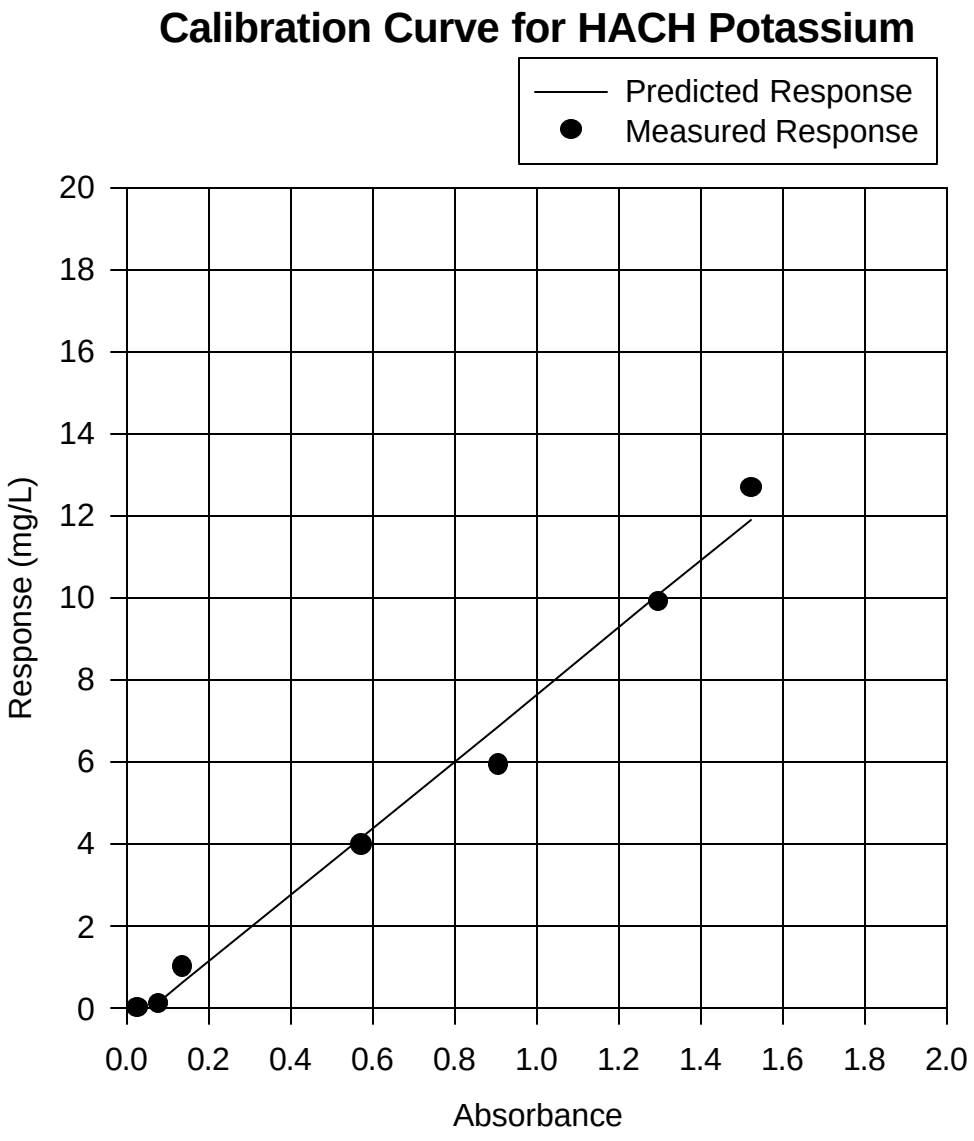

Calibration Curve for HACH Potassium
Predicted Response
Measured Response
Response (mg/L)
20
18
16
14
12
10
8
6
4
2
0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Absorbance

*Figure 132*

*Table 143*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.98156114 |
| R Square | 0.963462272 |
| Adjusted R Square | 0.956154726 |
| Standard Error | 0.958143183 |
| Observations | 7 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 121.0386318 | 121.0386318 | 131.8448523 | 8.77982E-05 |
| Residual | 5 | 4.590191792 | 0.918038358 | | |
| Total | 6 | 125.6288236 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 1.280537976 | 0.521856988 | 2.453810152 | 0.057665611 | -0.060935927 | 2.622011879 | -0.060935927 | 2.622011879 |
| Spike Conc. (mg/L) | 0.899768737 | 0.078360881 | 11.48237137 | 8.77982E-05 | 0.698336009 | 1.101201466 | 0.698336009 | 1.101201466 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 1.280537976 | -0.62688903 | -0.654274895 |
| 2 | 1.370496854 | -0.570350989 | -0.59526697 |
| 3 | 2.178507176 | 0.102885323 | 0.107379904 |
| 4 | 4.851045268 | 0.295175884 | 0.308070745 |
| 5 | 6.615131855 | 1.493582564 | 1.558830236 |
| 6 | 10.18825747 | 0.459736887 | 0.479820653 |
| 7 | 12.68111652 | -1.154140638 | -1.204559673 |

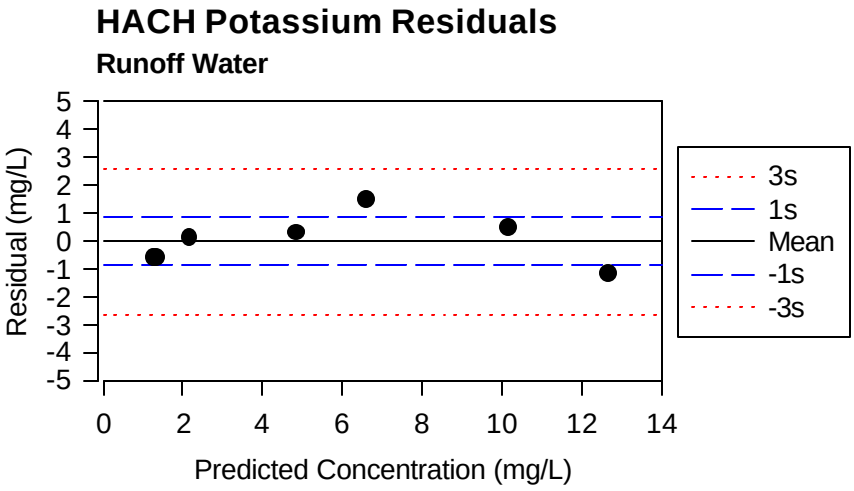

HACH Potassium Residuals
Runoff Water
Residual (mg/L)
5
4
3
2
1
0
-1
-2
-3
-4
-5
0
2
4
6
8
10
12
14
Predicted Concentration (mg/L)
3s
1s
Mean
-1s
-3s

*Figure 133*

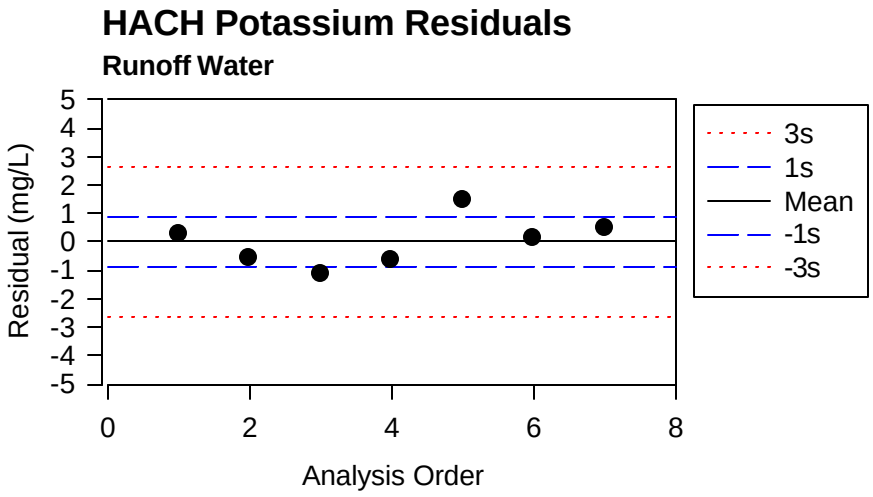



*Figure 134*

## 36.4 Horiba Cardy, Potassium

### *36.4.1 Method*

The Horiba Cardy uses an ion selective electrode to determine the potassium concentration in the sample. The procedure is simple. Place a swatch of sample paper over the electrode. Place 1-2 drops of sample solution on the sample paper. Record the displayed concentration.

The Horiba Cardy must be calibrated before use. There are two calibration procedures included with the kit, a single point verification and a two point calibration. Horiba recommends a two point calibration once per month and a single point verification once per day. To perform the two point calibration, measure the response for the first calibration solution and adjust the dial on the top of the meter until the instrument reads the correct concentration. Rinse the electrode. Measure the second calibration solution and adjust the slope set screw (located under a rubber plug on the face of the meter) until it reads the correct value. Rinse the electrode and measure the first calibration solution again. If the meter does not read the correct value within 2 mg/L, repeat the entire procedure. To perform a single point re-calibration, measure the first standard solution and adjust the top knob.

### *36.4.2 Observations*

This procedure may be the simplest method of all the potassium test kits. There is almost no opportunity for user error once the instrument is calibrated. The directions indicate that the use of the paper swatches over the electrode is optional. However, we found that the instrument response was much more stable using the swatch than placing the sample directly on the electrode.

The meter is designed to measure a very broad range of potassium concentrations. The designed range extends far above the values that typically indicate a problem. Thus, this application will usually operate within a very narrow region on the extreme low end of the instrument's range, possibly increasing the error for most water measurements.

*Table 144*

| Sample ID | Spike Conc. (mg/L) | Order | RO Response (mg/L) | Recovery (%) | Order | Runoff Response (mg/L) |
|---|---|---|---|---|---|---|
| K RO O | 0 | 11 | 0 | NA | 8 | 0 |
| K RO 1 | 0.1000 | 7 | 2 | 2000 | 14 | 0 |
| K RO 2 | 1.0976 | 12 | 0 | 0 | 1 | 2 |
| K RO 3 | 3.9683 | 9 | 2 | 50 | 5 | 3 |
| K RO 4 | 5.9289 | 3 | 4 | 67 | 10 | 3 |
| K RO 5 | 9.9000 | 4 | 6 | 61 | 2 | 7 |
| K RO 6 | 12.6706 | 6 | 7 | 55 | 13 | 5 |

*Table 145*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.95440294 |
| R Square | 0.910884973 |
| Adjusted R Square | 0.893061967 |
| Standard Error | 0.905460243 |
| Observations | 7 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 41.90070875 | 41.90070875 | 51.10725995 | 0.000831963 |
| Residual | 5 | 4.099291254 | 0.819858251 | | |
| Total | 6 | 46 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.447580444 | 0.494567066 | 0.904994438 | 0.406960056 | -0.823742594 | 1.718903482 | -0.823742594 | 1.718903482 |
| Spike Conc. (mg/L) | 0.530723576 | 0.07423814 | 7.148934183 | 0.000831963 | 0.339888674 | 0.721558478 | 0.339888674 | 0.721558478 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.447580444 | -0.447580444 | -0.494312641 |
| 2 | 0.500642187 | 1.499357813 | 1.655906844 |
| 3 | 1.030094846 | -1.030094846 | -1.137647792 |
| 4 | 2.553624275 | -0.553624275 | -0.611428586 |
| 5 | 3.594160919 | 0.405839081 | 0.448213032 |
| 6 | 5.701749156 | 0.298250844 | 0.32939143 |
| 7 | 7.172148173 | -0.172148173 | -0.190122288 |

*Table 146*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.899041262 |
| R Square | 0.808275191 |
| Adjusted R Square | 0.76993023 |
| Standard Error | 1.22064559 |
| Observations | 7 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 31.40726458 | 31.40726458 | 21.07904545 | 0.005887231 |
| Residual | 5 | 7.44987828 | 1.489975656 | | |
| Total | 6 | 38.85714286 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.64732522 | 0.666722932 | 0.970905888 | 0.376186774 | -1.066537838 | 2.361188278 | -1.066537838 | 2.361188278 |
| Spike Conc. (mg/L) | 0.459486496 | 0.100079997 | 4.59119216 | 0.005887231 | 0.202223095 | 0.716749898 | 0.202223095 | 0.716749898 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.64732522 | -0.64732522 | -0.530313816 |
| 2 | 0.69326468 | -0.69326468 | -0.567949195 |
| 3 | 1.15165085 | 0.84834915 | 0.695000381 |
| 4 | 2.470682509 | 0.529317491 | 0.433637327 |
| 5 | 3.371551734 | -0.371551734 | -0.304389527 |
| 6 | 5.196246129 | 1.803753871 | 1.477704819 |
| 7 | 6.469278877 | -1.469278877 | -1.203689989 |

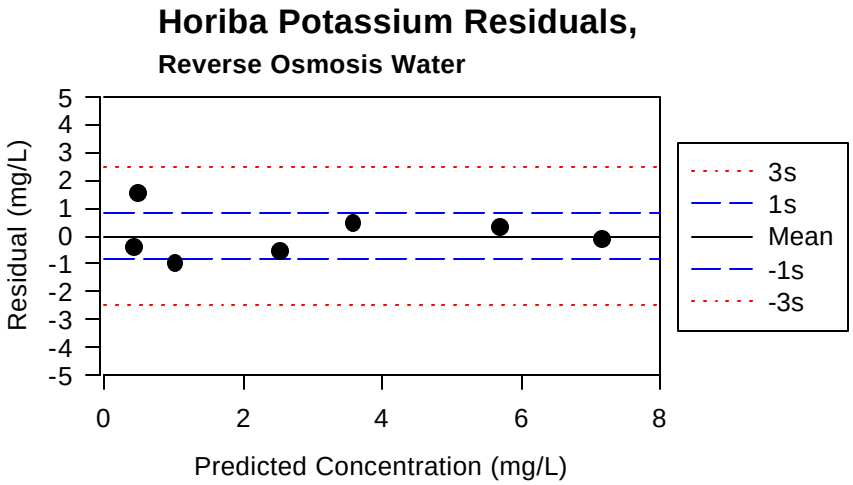

Horiba Potassium Residuals,
Reverse Osmosis Water
Residual (mg/L)
5
4
3
2
1
0
-1
-2
-3
-4
-5
0
2
4
6
8
Predicted Concentration (mg/L)
3s
1s
Mean
-1s
-3s

*Figure 135*

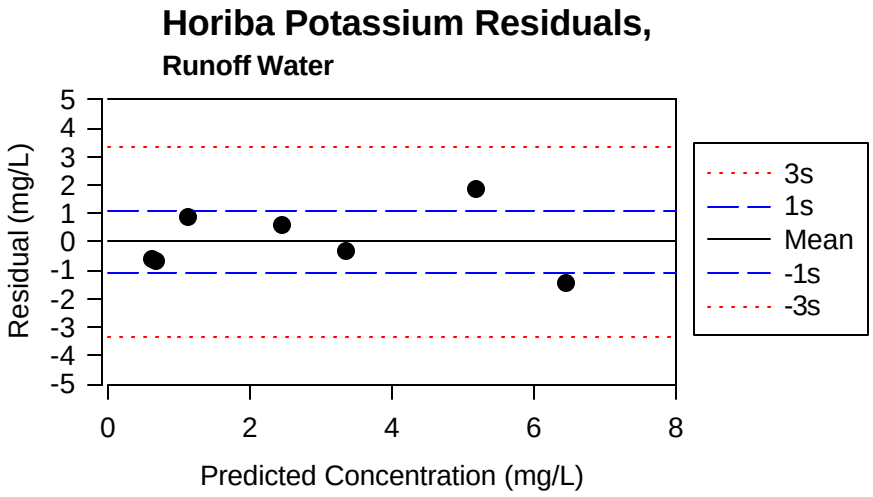



*Figure 136*

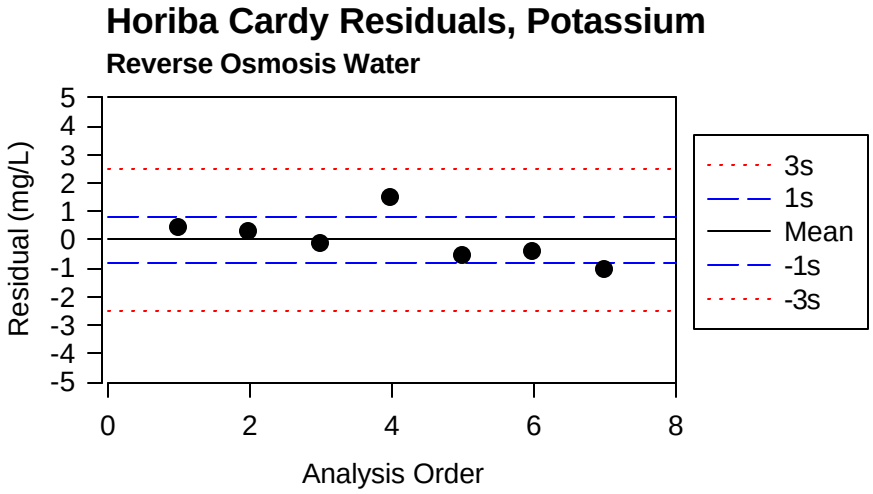



*Figure 137*

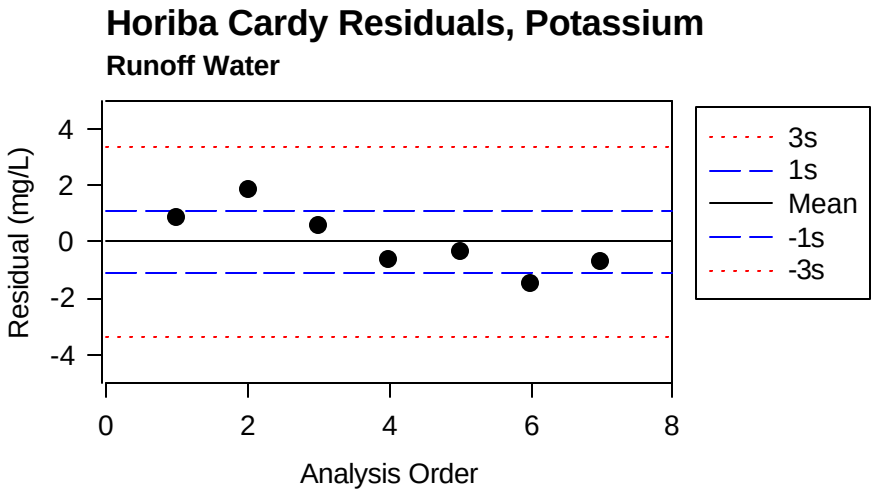



*Figure 138*

## 36.5 La Motte Potassium

### *36.5.1 Method*

The La Motte Potassium test determines potassium concentration using tetraphenylborate salts to the sample. These procedure adds a large doses of sodium tetraphenylborate. The potassium in the sample reacts with the sodium tetraphenylborate to form insoluble potassium tetraphenylborate. The insoluble potassium tetraphenylborate increases the turbidity of the sample solution. The increased turbidity is measure using the Smart Colorimeter spectrophotometer.

The La Motte procedure requires 10 ml of sample. The procedure can be completed in about 10 minutes. The sample is zeroed using the scan blank function. Four drops of 1.0 N sodium hydroxide (NaOH), are added to mask interference. Add one scoop (0.05 g) of sodium tetraphenylborate to the solution. Shake until all the powder has dissolved. The solution is allowed to stand for another 5 minutes. Shake again, and measure using the Smart Colorimeter. Strict adherence to the timing sequence is required for consistent results. The difference in absorbance (turbidity) between the blank and sample is directly proportional to the potassium concentration.

The presence of magnesium ($Mg^{2+}$), ammonium ($NH_4^+$) and calcium ($Ca^{2+}$) ions can interfere with the reaction by competing in the reaction with tetraphenylborate (HACH 1992). These salts will result in a reported potassium concentration larger than is actually present in the sample.

Measuring turbidity with a standard spectrophotometer is cause for concern. Spectrophotometers measure color absorbance measurements in homogenous solutions with a light beam passing through the solution.

Therefore, the measurement depends on the amount of light passing through the sample. The detector is placed opposite the light source. Turbidity is the scattering of light from particles. Turbidity is measured by the amount of light scattered from the beam path. The detector is placed at a right angle to the light path to eliminate the detection of light passing through the sample. To compensate, the procedure includes a definite timing scheme. The scheme must be followed exactly in order to compare results from different samples.

### *36.5.2 Observations*

This test operates in exactly the same manner as the HACH Potassium method. The only difference in the methods is the choice of masking reagents. The sodium hydroxide mask seems to operate better than the combination of reagents in the HACH method. We explored using this reagent system with the HACH DR 2000 spectrophotometer.

*Table 147*

| Sample ID | Spike Conc. (mg/L) | Order | RO Response (mg/L) | Recovery (%) | Order | Runoff Response (mg/L) |
|---|---|---|---|---|---|---|
| K RO O | 0 | 6 | 0.6 | NA | 7 | 0.9 |
| K RO 1 | 0.1000 | 4.0000 | 0.6 | 600 | 5 | 1.2 |
| K RO 2 | 1.0976 | 9.0000 | 0.9 | 82 | 3 | 2.7 |
| K RO 3 | 3.9683 | 2.0000 | 8.2 | 207 | 8 | 5.5 |
| K RO 4 | 5.9289 | 10.0000 | 7.1 | 120 | 1 | 7.2 |
| K RO 5 | 9.9000 | 9.0000 | over-range | | n.t. | over-range |

*Table 148*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.923378129 |
| R Square | 0.852627169 |
| Adjusted R Square | 0.803502892 |
| Standard Error | 1.697073398 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 49.98782565 | 49.98782565 | 17.35653366 | 0.025165615 |
| Residual | 3 | 8.640174351 | 2.880058117 | | |
| Total | 4 | 58.628 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 0.488063969 | 1.044875325 | 0.467102589 | 0.672259678 | -2.837198769 | 3.813326707 | -2.837198769 | 3.813326707 |
| Spike Conc. (mg/L) | 1.348366961 | 0.323650741 | 4.166117336 | 0.025165615 | 0.318364891 | 2.378369031 | 0.318364891 | 2.378369031 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.488063969 | 0.111936031 | 0.065958273 |
| 2 | 0.622873698 | -0.022873698 | -0.01347832 |
| 3 | 1.968011741 | -1.068011741 | -0.629325604 |
| 4 | 5.838721164 | 2.361278836 | 1.391382859 |
| 5 | 8.482329428 | -1.382329428 | -0.814537209 |

*Table 149*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.995290448 |
| R Square | 0.990603076 |
| Adjusted R Square | 0.987470768 |
| Standard Error | 0.308479365 |
| Observations | 5 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 30.09452144 | 30.09452144 | 316.2534021 | 0.0003877 |
| Residual | 3 | 0.285478555 | 0.095159518 | | |
| Total | 4 | 30.38 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | 1.178525586 | 0.189928424 | 6.20510379 | 0.008434086 | 0.574088006 | 1.782963165 | 0.574088006 | 1.782963165 |
| Spike Conc. (mg/L) | 1.046212008 | 0.05883044 | 17.7835149 | 0.0003877 | 0.858987115 | 1.2334369 | 0.858987115 | 1.2334369 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 1.178525586 | -0.278525586 | -0.902898598 |
| 2 | 1.283125862 | -0.083125862 | -0.269469767 |
| 3 | 2.326832519 | 0.373167481 | 1.20969998 |
| 4 | 5.330156385 | 0.169843615 | 0.550583391 |
| 5 | 7.381359648 | -0.181359648 | -0.587915006 |

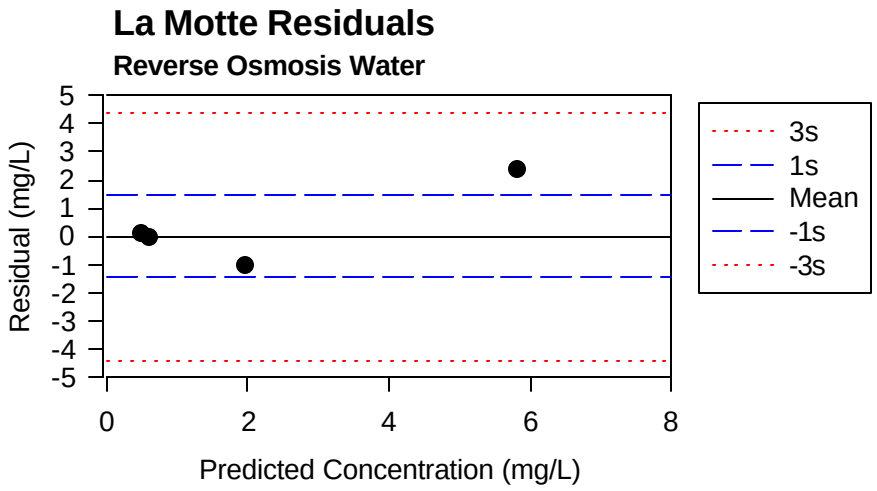



*Figure 139*

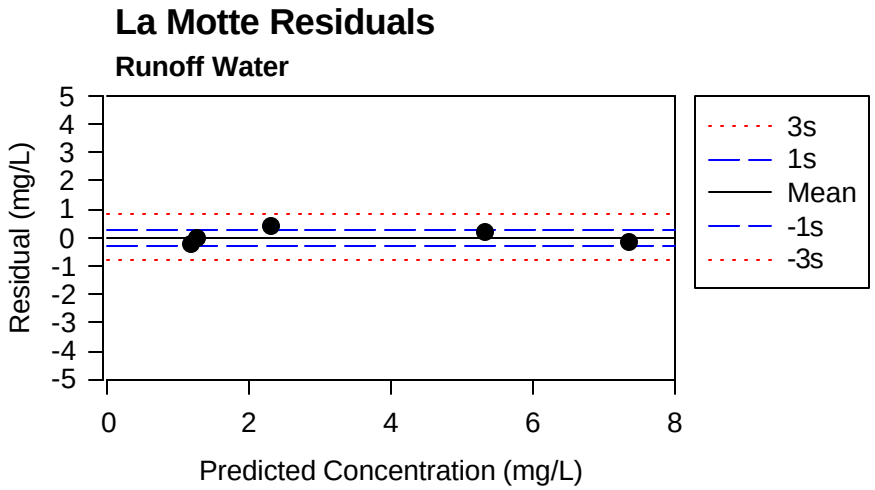



*Figure 140*

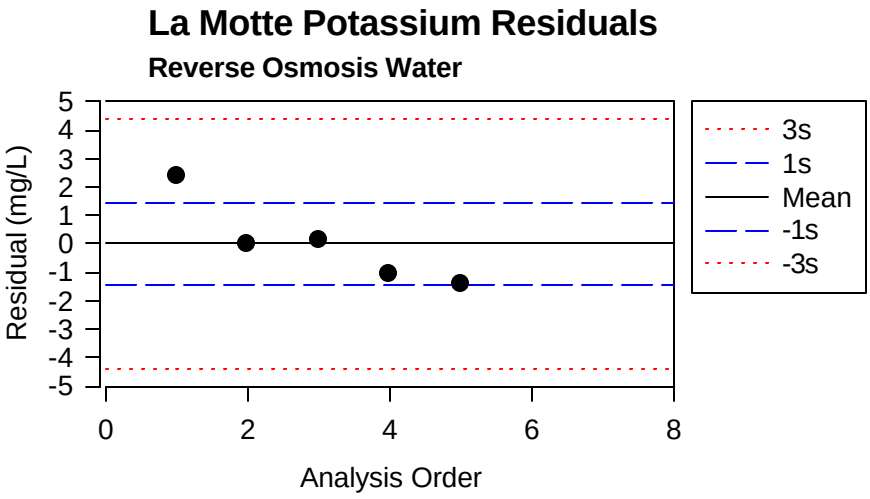

La Motte Potassium Residuals
Reverse Osmosis Water
Residual (mg/L)
5
4
3
2
1
0
-1
-2
-3
-4
-5
0
2
4
6
8
Analysis Order
3s
1s
Mean
-1s
-3s

*Figure 141*

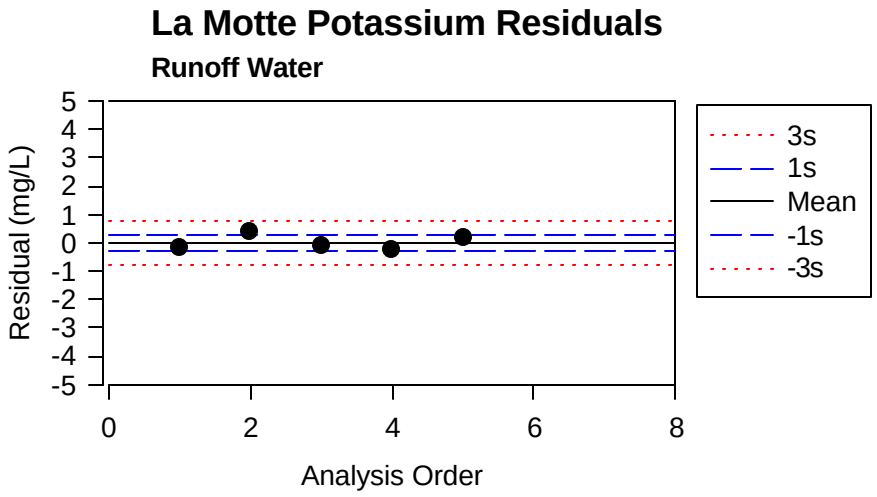



*Figure 142*

## 36.6 Use of La Motte Reagents and HACH Spectrophotometer

### *36.6.1 Method*

This adaptation of the La Motte method is simply using the better La Motte Potassium reagents with the better HACH DR 2000 Spectrophotometer substituted for the Smart Colorimeter. The measurements were made at 650 nm wavelengths as instructed by the HACH method.

### *36.6.2 Observations*

The method seemed to work just fine. The reverse osmosis samples were again used to construct a calibration curve. The data points suggest a second order fit. However, there is no difference in the linear and second order equation over the range described here. A plot of the calibration data suggest that the relationship between absorbance and concentration for this method may be quadratic. Therefore, the data is presented for both a linear and quadratic fit.

*Table 150*

| Sample ID | Conc. (mg/L) | Order | abs. | Order | Abs. | Predicted Conc. (mg/L) Quadratic Fit |
|---|---|---|---|---|---|---|
| K RO 0 | 0 | 7 | 0.003 | 3 | 0.010 | 0.01 |
| K RO 1 | 0.1000 | 5 | 0.017 | 5 | 0.027 | 0.16 |
| K RO 2 | 0.9980 | 1 | 0.205 | 7 | 0.240 | 2.02 |
| K RO 3 | 3.9683 | 6 | 0.588 | 2 | 0.618 | 5.34 |
| K RO 4 | 5.9289 | 7 | 0.776 | 1 | 0.862 | 7.48 |
| K RO 5 | 9.9000 | 4 | 1.140 | 6 | 1.218 | 10.60 |

*Table 151*

Calibration Regression

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.988016562 |
| R Square | 0.976176726 |
| Adjusted R Square | 0.971412072 |
| Standard Error | 0.844008502 |
| Observations | 7 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 145.9454823 | 145.9454823 | 204.8787959 | 2.99995E-05 |
| Residual | 5 | 3.561751757 | 0.712350351 | | |
| Total | 6 | 149.507234 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | -0.080297 | 0.466670533 | -0.172063575 | 0.870135075 | -1.279909836 | 1.119315836 | -1.279909836 | 1.119315836 |
| abs. | 8.770941738 | 0.612770317 | 14.31358781 | 2.99995E-05 | 7.195768065 | 10.34611541 | 7.195768065 | 10.34611541 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Conc. (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | -0.053984175 | 0.053984175 | 0.063961648 |
| 2 | 0.068809009 | 0.031170991 | 0.036932081 |
| 3 | 0.103892776 | 0.894107224 | 1.059358077 |
| 4 | 5.077016742 | -1.108766742 | -1.313691437 |
| 5 | 6.725953788 | -0.797103788 | -0.944426254 |
| 6 | 9.918576581 | -0.018566581 | -0.021998097 |
| 7 | 11.72539058 | 0.945174721 | 1.119863981 |

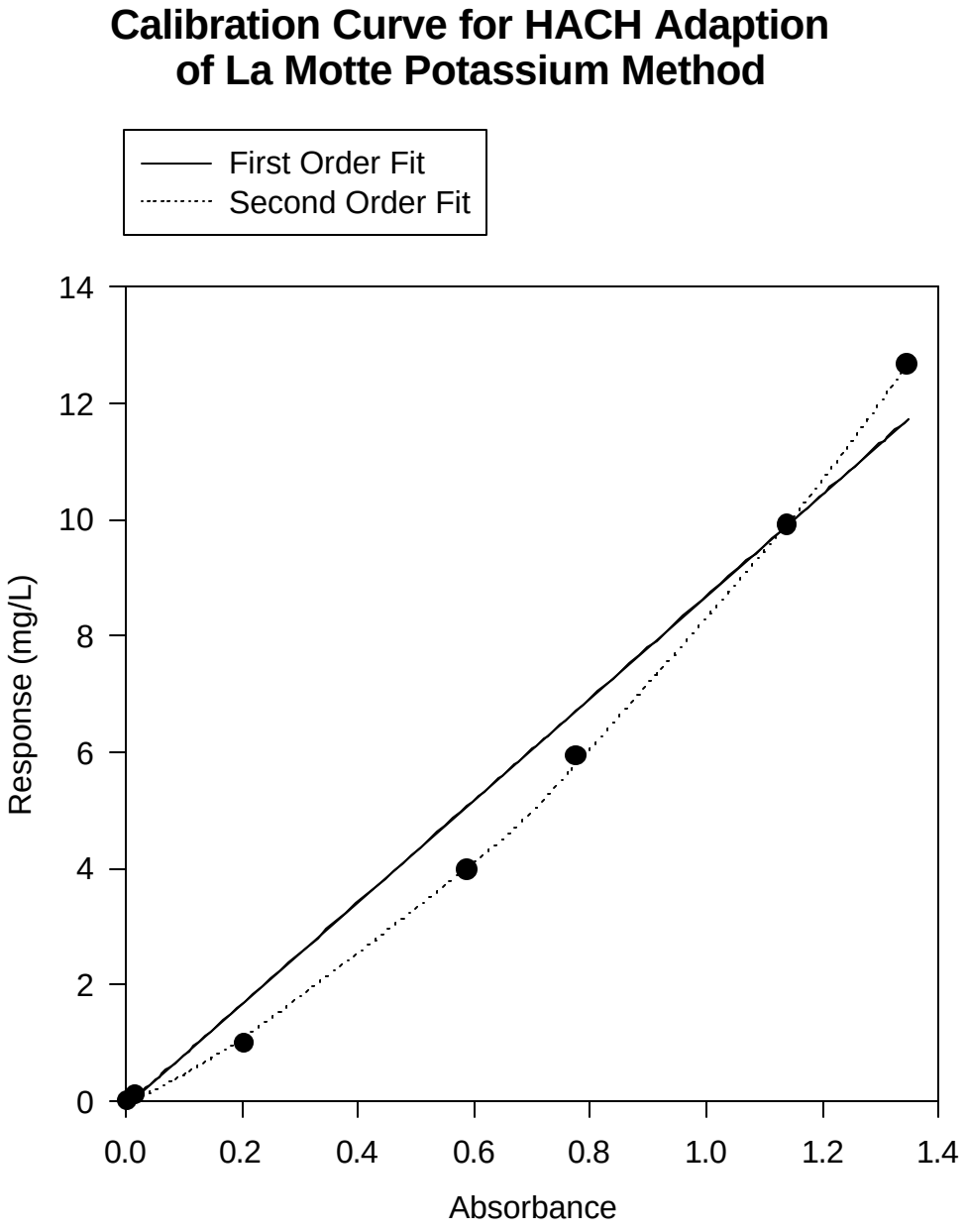

Calibration Curve for HACH Adaption of La Motte Potassium Method
First Order Fit
Second Order Fit
Response (mg/L)
Absorbance
0
2
4
6
8
10
12
14
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4

*Figure 143*

*Table 152*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.972048362 |
| R Square | 0.944878018 |
| Adjusted R Square | 0.933853621 |
| Standard Error | 1.28383294 |
| Observations | 7 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 141.2660989 | 141.2660989 | 85.70791367 | 0.000247137 |
| Residual | 5 | 8.241135088 | 1.648227018 | | |
| Total | 6 | 149.507234 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* | *Upper 95.0%* |
|---|---|---|---|---|---|---|---|---|
| Intercept | -0.67221452 | 0.764343253 | -0.879466806 | 0.419401865 | -2.637018192 | 1.292589153 | -2.637018192 | 1.292589153 |
| X Variable 1 | 1.053729085 | 0.11381998 | 9.257856862 | 0.000247137 | 0.76114599 | 1.346312181 | 0.76114599 | 1.346312181 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Y* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | -0.66440384 | 0.66440384 | 0.517515807 |
| 2 | -0.507286501 | 0.607266501 | 0.473010531 |
| 3 | 1.461301336 | -0.463301336 | -0.360873538 |
| 4 | 4.954851581 | -0.986601581 | -0.76848128 |
| 5 | 7.209947506 | -1.281097506 | -0.997869323 |
| 6 | 10.50016943 | -0.60015943 | -0.467474709 |
| 7 | 10.61107579 | 2.059489513 | 1.604172512 |

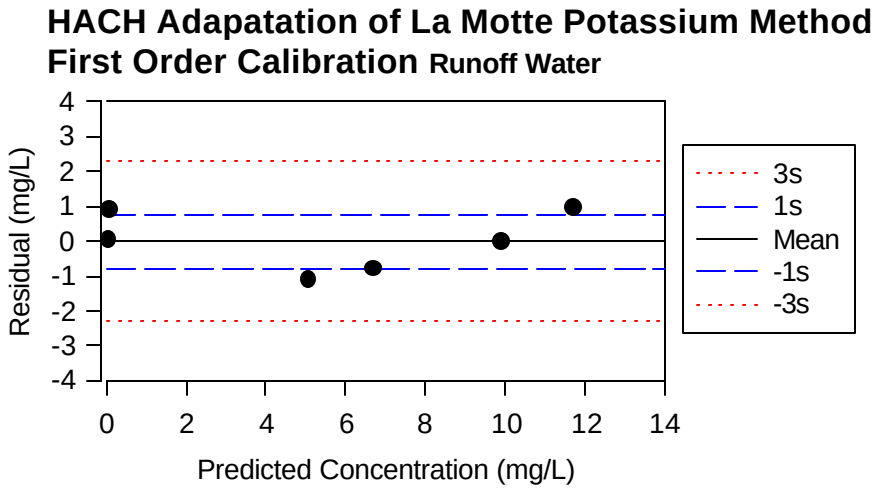

HACH Adapatation of La Motte Potassium Method
First Order Calibration Runoff Water
Residual (mg/L)
4
3
2
1
0
-1
-2
-3
-4
0
2
4
6
8
10
12
14
Predicted Concentration (mg/L)
3s
1s
Mean
-1s
-3s

*Figure 144*

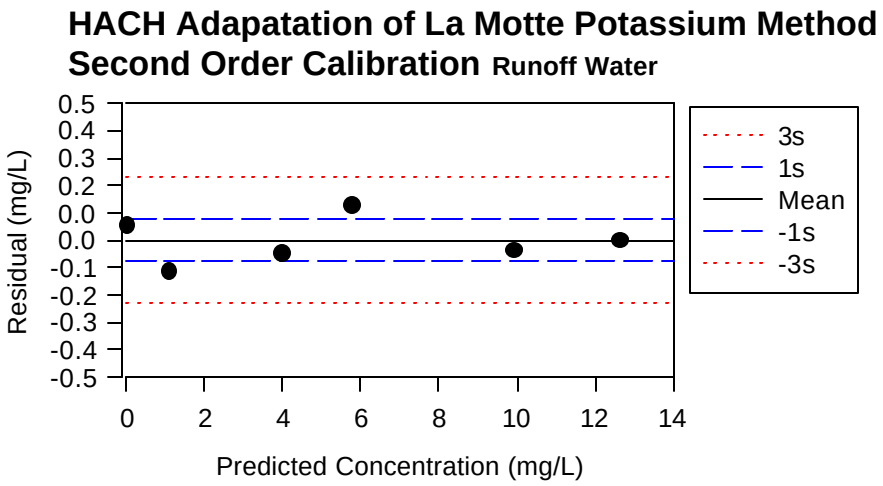

HACH Adapatation of La Motte Potassium Method
Second Order Calibration Runoff Water
Residual (mg/L)
0.5
0.4
0.3
0.2
0.0
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
0
2
4
6
8
10
12
14
Predicted Concentration (mg/L)
3s
1s
Mean
-1s
-3s

*Figure 145*

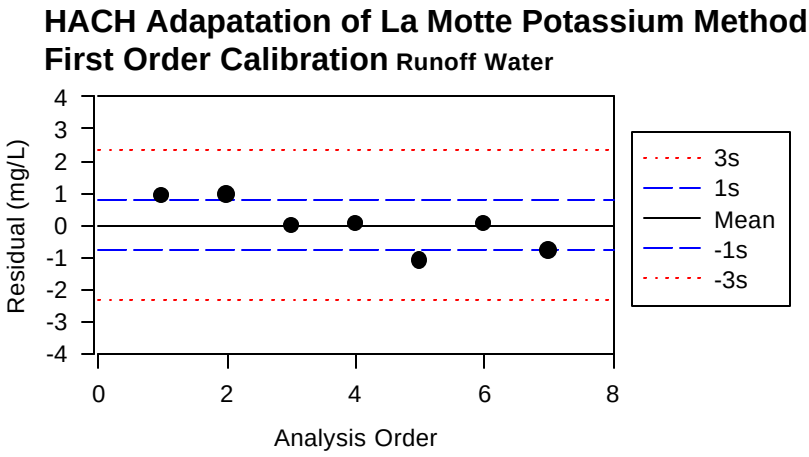

HACH Adapatation of La Motte Potassium Method
First Order Calibration Runoff Water
Residual (mg/L)
4
3
2
1
0
-1
-2
-3
-4
0
2
4
6
8
Analysis Order
3s
1s
Mean
-1s
-3s

*Figure 146*

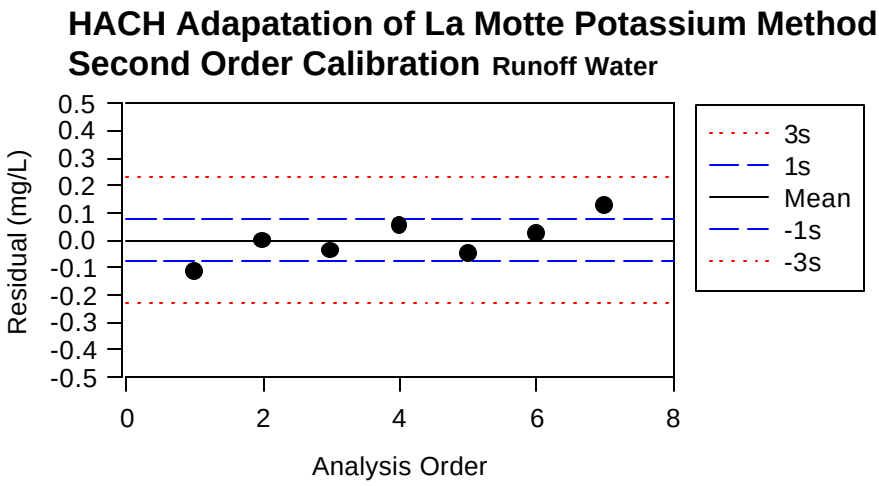

HACH Adapatation of La Motte Potassium Method
Second Order Calibration Runoff Water
Residual (mg/L)
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
0
2
4
6
8
Analysis Order
3s
1s
Mean
-1s
-3s

*Figure 147*

# Toxicity Summary

# 37 Toxicity

## 37.1 Azur Environmental's DeltaTox PS1

The DeltaTox was evaluated during a beta site test for Azur Environmental. It was used to evaluate a number of water samples obtained from manholes during this project, especially by comparing its ease of use and results to that expected from the Azur Microtox test. The DeltaTox uses a specialized strain of freeze-dried luminescent bacteria as biosensors to detect the biological effects of contaminants. It is based on the same principles as the full-scale Microtox test that is most commonly used in the laboratory. Its major features are its small size, battery operation, and rapid analysis time for small numbers of samples. The bacteria strain selected for the DeltaTox was selected for temperature intolerance, making it possible to operate under ambient conditions (10 to 28°C). The test reagent (the freeze-dried bacteria) is quickly rehydrated immediately before the test begins.

### *37.1.1 Method*

The DeltaTox PS1 System provides two standardized testing procedures for acute toxicity measurement and assessment. The first is the Q-Tox Procedure which has been developed for quick toxicity screening. This test procedure is preferred when several samples must be tested quickly or when only a rough estimate of the toxicity level is desired. The second test procedure is the B-Tox Procedure. It is a basic toxicity screening test which is preferred when a more precise result is desired.

The differences between the DeltaTox and Microtox analyzers are the following:
The Microtox samples must be osmotically adjusted, while the DeltaTox samples do not. The Microtox samples are incubated at 15°C prior to exposure to the bacteria, while the DeltaTox samples are exposed to the reagent at ambient temperatures.

In general, the DeltaTox is designed to test 9 samples and 1 control at the same time. The test procedure for the Q-Tox and B-Tox is as follows:

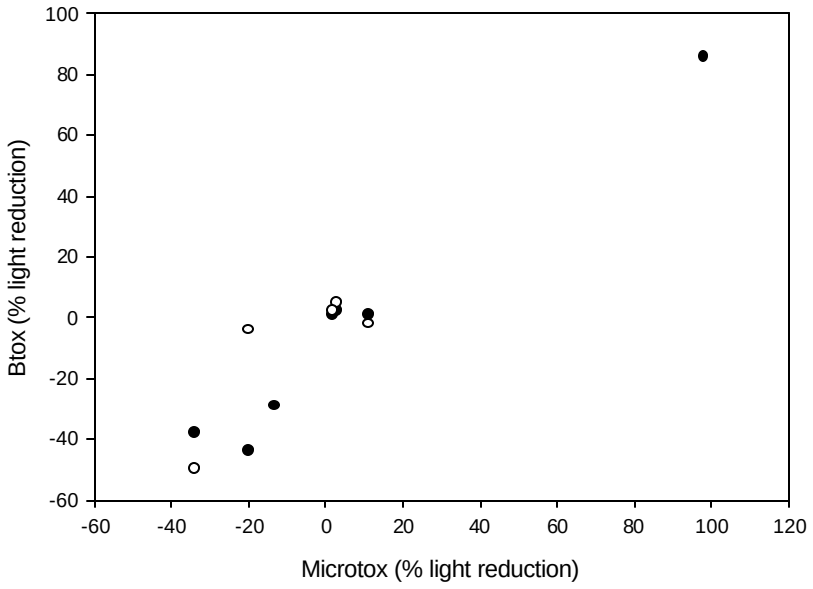
- Set the mode of the machine (Q-Tox or B-Tox).
- Reconstitute a vial of reagent by adding reconstitution solution to the freeze-dried reagent, and mixing.
- Expose sample to 500 µL of reagent (amount of sample varies: 1 mL for the B-Tox procedure; 0.5 mL for the Q-Tox procedure). The other difference in the two procedures is that the reagent is tested at zero time for the B-Tox procedure prior to exposure to the sample.
- The samples are exposed to the reagent for 15 minutes (the exposure time can be manually set, with 15 minutes as the default) using the timer on the DeltaTox analyzer.
- Once the timer sounds, the samples are analyzed and the percent light reduction recorded. The results also can be saved for a later download through an RS-232 port.

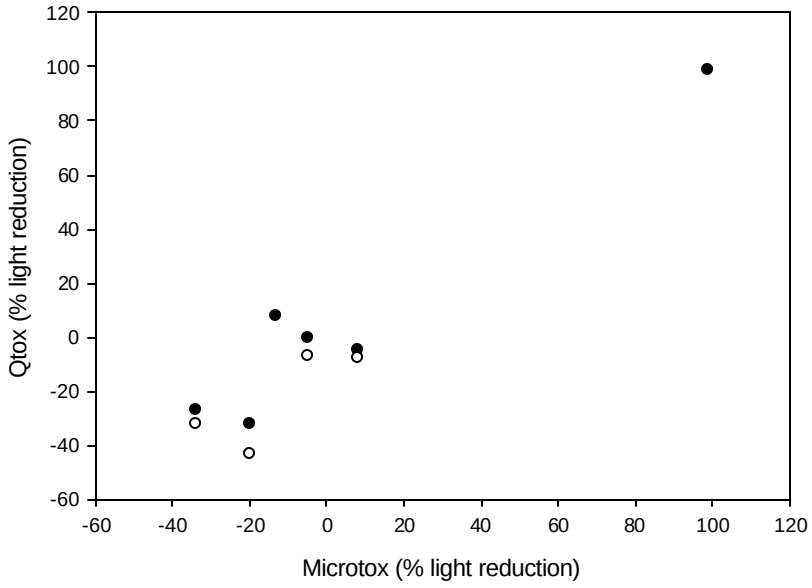
### *37.1.2 Observations of DeltaTox Procedure, Compared to Microtox Procedure*

During the characterization tests of water found in manholes (presented in the companion report), all samples were tested using the Microtox procedure. During our beta site evaluation of the DeltaTox instrument, some of the samples were also tested using the DeltaTox (both Q-tox and B-tox), as shown in Figures 1 and 2. About 7 samples were analyzed using all three test procedures and were replicated

with the DeltaTox. These figures show that the replicates were quite close and that both the Q-tox and the B-tox procedures agreed reasonably well with the Microtox procedures. During these comparison tests, only one sample in each set was considered toxic, and the

others were non-toxic. In fact, several of the samples caused an enhanced light output.


Btox (% light reduction)
Microtox (% light reduction)
100
80
60
40
20
0
-20
-40
-60
-60
-40
-20
0
20
40
60
80
100
120




### *37.1.3 Correlations between Luminescent Bacteria Toxicity Tests and other Toxicity Tests*

During earlier EPA-funded research, UAB evaluated various laboratory toxicity tests using 20 stormwater and CSO samples, specifically comparing Azur's luminescent bacteria Microtox test with other toxicity tests. We found that the most promising results are associated with using several complementary tests, instead of any one individual test method. However, simple screening toxicity tests (such as using the Azur Microtox® test) are useful during preliminary assessments or for treatability tests. The stormwater and CSO samples were split and sent to four laboratories for analyses using 14 different bioassay tests. Conventional bioassay tests were conducted using freshwater organisms at the EPA's Duluth, MN, laboratory and using marine organisms at the EPA's Narragansett Bay, RI, laboratory. In addition, other bioassay tests, using bacteria, were also conducted at the Environmental Health Sciences Laboratory at Wright State University, Dayton, Ohio. The tests represented a range of organisms that included fish, invertebrates, plants, and microorganisms. The conventional bioassay tests conducted simultaneously with the Microtox™ screening test for the samples were all short-term tests. However, some of the tests were indicative of chronic toxicity (life cycle tests and the marine organism sexual reproduction tests, for example), whereas the others would be classically considered as indicative of acute toxicity (Microtox™ and the fathead minnow tests, for example). The following list shows the major tests that were conducted by each participating laboratory:

- University of Alabama at Birmingham, Environmental Engineering Laboratory
  Microtox™ bacterial luminescence tests ( 10-, 20-, and 35-minute exposures) using the marine *Photobacterium phosphoreum.*

- Wright State University, Biological Sciences Department
  Macrofaunal toxicity tests:

*Daphnia magna* (water flea) survival; *Lemma minor* (duckweed) growth; and *Selenastrum capricornutum* (green alga) growth.

Microbial activity tests (bacterial respiration):

Indigenous microbial electron transport activity;

Indigenous microbial inhibition of β-galactosidase activity;

Alkaline phosphatase for indigenous microbial activity;

Inhibition of β-galactosidase for indigenous microbial activity; and

Bacterial surrogate assay using *O*-nitrophenol-β-D-galactopyranside activity and *Escherichia coli*.

- EPA Environmental Research Laboratory, Duluth, Minnesota

  *Ceriodaphnia dubia* (water flea) 48-h survival; and

  *Pimephales promelas* (fathead minnow) 96-h survival.

- EPA Environmental Research Laboratory, Narragansett Bay, Rhode Island

  *Champia parvula* (marine red alga) sexual reproduction (formation of cystocarps after 5 to 7 d exposure); and

  *Arbacua punctulata* (sea urchin) fertilization by sperm cells.

Table 1 summarizes the results of the toxicity tests. The *C. dubia. P. promelas,* and C. *Parvula* tests experienced problems with the control samples, and those results are therefore uncertain. The *A. pustulata* tests on the stormwater samples also had a potential problem with the control samples. The CSO test results (excluding the fathead minnow tests) indicated that from 50% to 100% of the samples were toxic, with most tests identifying the same few samples as the most toxic. The toxicity tests for the stormwater samples indicated that 0% to 40% of the samples were toxic. The Microtox™ screening procedure gave similar rankings for the samples as the other toxicity tests.

**Table 1. Fraction of Samples Rated as Toxic**

| Sample series | Combined sewer overflows, % | Stormwater, % |
|---|---|---|
| Microtox™ marine bacteria | 100 | 20 |
| *C. Dubia* | 60 | 0[a] |
| *P. promelas* | 0[a] | 0[a] |
| *C. parvula* | 100 | 0[a] |
| *A. punctulata* | 100 | 0[a] |
| *D. magna* | 63 | 40 |
| *L. minor* | 50[a] | 0 |

[a] Results uncertain due to laboratory errors, see text

## *37.1.4 Correlations between Toxicity Screening and other Observed Parameters during Characterization Study of Water found in Manholes*

During our recent characterization tests using water samples collected from telecommunication manholes (presented in the companion report), we statistically evaluated relationships between the Microtox results and the other measured constituents (including many metallic and organic toxicants, in both filtered and unfiltered forms, plus conventional parameters) in an attempt to identify the most likely water and/or site characteristics adversely affecting acute water toxicity.

The toxicity screening tests (using the Azur Microtox® method) conducted on both unfiltered and filtered water samples from telecommunication manholes indicated a wide range of toxicity. About 60% of the samples are not considered toxic (less than a I25 light reduction of 20%, the light reduction associated with the phosphorescent bacteria after a 25 minute exposure to undiluted samples), about 20% are considered moderately toxic, while about 10% are considered toxic (light reductions of greater than 40%), and 10% are considered highly toxic (light reductions of greater than 60%). Samples from residential areas generally had greater toxicities than samples from commercial and industrial areas. Samples from newer areas were also more toxic than from older areas. Further statistical tests of the data, in addition to reviews of critical concentration effects, indicated that the high toxicity levels were likely associated with periodic high concentrations of salt (in areas using deicing salt), heavy metals (especially filterable zinc, with high values found in most areas) and pesticides (associated with newer residential areas).

Pearson correlation tests were used to examine simple relationships between toxicity and other measured parameters. There were relatively high correlations between filtered and total forms of toxicity (0.79), with the filtered samples being about 90% as toxic as the unfiltered samples. Other correlations are shown on Table 2, indicating common, but relatively weaker, relationships between filtered and unfiltered forms of zinc with toxicity (pesticide results were not available for these evaluations).

*Table 2. Pearson Correlations with Microtox Toxicity*

| **Independent and Dependent Variables** | **Pearson Coefficient** | **Regression slope term** |
|---|---|---|
| zinc (µg/L) and toxicity (% light decrease) | 0.5 | 0.046 |
| filtered zinc and toxicity (same as above) | 0.55 | 0.058 |
| zinc and filtered toxicity (same as above) | 0.5 | 0.045 |
| filtered zinc and filtered toxicity (same as above) | 0.56 | 0.057 |

One method to examine complex relationships between measured parameters is by using hierarchical cluster analyses. Figure 3 is a tree diagram (dendogram) produced by SYSTAT, version 8, using the water quality data for water samples collected from manholes. A tree diagram illustrates both simple and complex relationships between parameters. Parameters having short branches linking them are more closely related than parameters linked by longer branches. In addition, the branches can encompass more than just two parameters. The length of the short branches linking only two parameters are indirectly comparable to the Pearson correlation coefficients (very short branches signify correlation coefficients close to 1). The main advantage of a cluster analyses is the ability to identify complex relationships that cannot be observed using a simple correlation matrix. There are relatively few complex relationships shown on this diagram. As an example, total toxicity is closely related to filtered toxicity and then to zinc and filtered zinc, but not any other parameter.

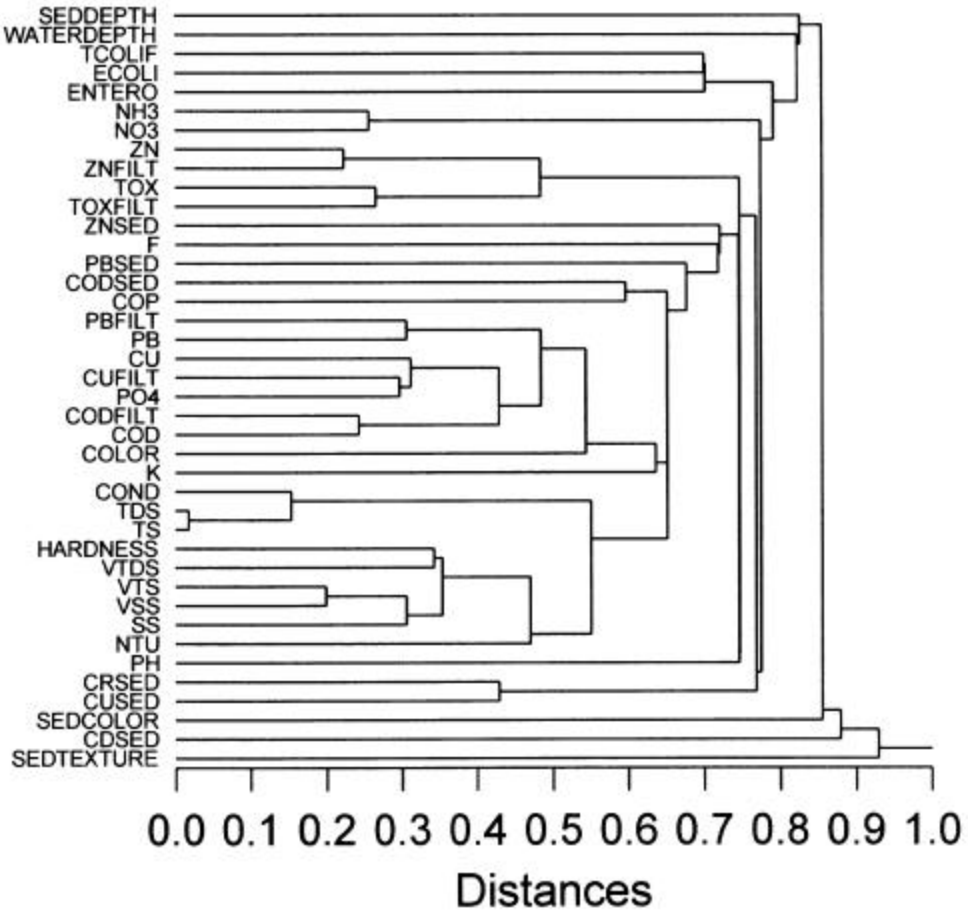



*Figure 3. Dendogram showing complex relationships between constituents and parameters measured in water and sediment from telecommunication manholes*

.

Another important tool to identify relationships and natural groupings of samples or locations is with principal component analyses (PCA). The data was autoscaled before PCA in order to remove the artificially large influence of constituents having large values compared to constituents having small values. PCA is a sophisticated procedure where information is sorted to determine the components (usually constituents) needed to explain the variance of the data. Typically, very large numbers of constituents are available for PCA analyses and a relatively small number of sample groups are to be identified. Component loadings for each principal component were calculated using SYSTAT, version 8, as shown in Table 3 (with the percent of the total variance explained for each component also shown).

*Table 3. Loadings for Principal Components*

| Principal component (% variance explained) | 1 (20.8%) | 2 (14.2%) | 3 (10.1%) | 4 (9.4%) | 5 (7.7%) |
|---|---|---|---|---|---|
| Total solids | **0.771** | **-0.557** | 0.011 | 0.190 | 0.104 |
| TDS | **0.723** | **-0.629** | 0.030 | 0.131 | 0.036 |
| SS | 0.424 | 0.322 | -0.111 | 0.311 | 0.353 |
| Turbidity | 0.306 | 0.463 | -0.110 | 0.381 | 0.381 |
| pH | 0.106 | 0.117 | -0.338 | -0.416 | -0.206 |
| Toxicity | 0.269 | 0.173 | 0.339 | 0.154 | **-0.674** |
| COD | **0.726** | 0.304 | 0.057 | -0.052 | -0.037 |
| Color | 0.464 | 0.431 | -0.059 | -0.122 | 0.062 |
| Conductivity | **0.649** | **-0.593** | 0.041 | 0.193 | 0.058 |
| Fluoride | 0.280 | -0.186 | -0.177 | -0.478 | -0.045 |
| Nitrate | 0.170 | 0.183 | **0.816** | -0.283 | 0.181 |
| Phosphate | **0.571** | 0.233 | -0.154 | -0.466 | 0.034 |
| Hardness | 0.385 | -0.291 | 0.046 | 0.041 | -0.278 |
| Ammonia | 0.107 | 0.088 | **0.821** | -0.284 | 0.296 |
| Potassium | 0.344 | 0.031 | -0.179 | **-0.518** | -0.124 |
| Zinc | 0.206 | 0.355 | 0.265 | 0.370 | **-0.613** |
| Copper | **0.521** | **0.523** | -0.211 | -0.103 | -0.056 |
| Lead | 0.298 | 0.488 | -0.121 | 0.335 | 0.092 |

These first five components account for about 65% of the total variance of the data. The first two components are mostly affected by total solids, TDS, COD, conductivity, phosphate, and copper. The third component is affected mostly by nitrate and ammonia, the forth component by potassium, and the fifth component by toxicity and zinc, again showing the re-occurring relationship between these two parameters.

Kurskal-Wallis nonparametric analyses were used like a one-way analysis of variance test to identify groupings of data that had significant differences between the groups, compared to within the groups. Most of the groupings had a large and relatively even number of observations in each subgroup. Table 4 lists the probabilities that the observed concentrations are the same amongst all of the categories. Probabilities smaller than 0.05 are considered significant and are indicated in bold. Age of surrounding area, land use and geographical region all significantly affected the unfiltered toxicity of the water found in telecommunication manholes, while age of the surrounding area, season, and geographical area significantly affected the unfiltered toxicity values.

*Table 4. Kurskal-Wallis Probabilities that Concentrations are the same in each Category*

| mg/L, unless otherwise noted | **Total Number of Detectable Observations** | **Age** | **Season** | **Land Use** | **EPA Rain Region** |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| Toxicity | 384 | **0.001** | 0.29 | **0.024** | **0** |
| Toxicity, filtered | 596 | **0.048** | **0** | 0.078 | **0.001** |

A full factorial analysis was also used to evaluate the data and to create models that may be useful for prediction. Since the experimental design was a full two-level factorial design, the following groupings were used to define the two levels used for each main factor, based on the number of observations in each grouping, the previous grouping evaluations, and the initial exploratory data analyses:

- age: old and medium combined (group A, given a + sign), vs. new (group B, given a - sign)
- season: winter and fall combined (group A, given a + sign), vs. summer and spring combined (group B, given a - sign)
- land use: commercial and industrial areas combined (group A, given a + sign), vs. residential areas (group B, given a - sign)
- region: EPA rain regions 1, 2, 8, and 9 (northern tier) (group A, given a + sign), vs. regions 3, 4, 5, 6, and 7 (milder) (group B, given a - sign)

The 597 available sets of data observations were therefore divided into 16 categories corresponding to the complete factorial design. Some samples did not have the necessary site information needed to correctly categorize the samples and were therefore not usable for these analyses. The “Group A” categories were assigned “+” values and the “Group B” categories were assigned “-” values in the experimental design matrix for the main factors. The 16 factorial groups account for all possible combinations of the four main factors. Twelve to more than 100 samples were represented in each factorial group and were used to calculate the means and standard errors. Amongst the significant models identified, the factorial analysis also identified a significant model for filtered toxicity (significant models were not identified for unfiltered toxicity), with significant land use and age effects alone:

$$\text{Filtered toxicity (I25\%)} = 44.7 - 7.5\ L - 6.7\ A$$

- If both land use (commercial and industrial areas) and age (old or medium) are +, then the predicted filtered toxicity is lowest, at 30.5%

- If both land use (residential) and age (new) are -, then the predicted filtered toxicity is highest, at 60%

- For mixed conditions, the filtered toxicity is intermediate, at about 45%.

These model results are opposite to what was initially expected. It was originally thought that old industrial areas would have water having the highest toxicity. However, new residential areas had water that was significantly more toxic.

# 38 Zinc Summary

# 39 Zinc

## 39.1 La Motte Zinc

### *39.1.1 Method*

The La Motte Zinc method detects zinc through color absorbance. Sodium cyanide forms complexes with all metals in solution. The addition of formaldehyde destroys the zinc complexes first. The zinc then reacts with Zincon indicator (2-carboxy-2'-hydrosy-5'-sulfoformazyl benzene) to form a blue complex. The absorbance of the zincon complex is in direct proportion to the original zinc concentration.

To measure the zinc concentration of a sample, prepare the dilute zinc indicator solution. Measure 5.0 mL of concentrated zinc indicator. Add 17.8 mL of methanol to the concentrated indicator. Mix the solution. The storage life of the dilute indicator is 1 month.

Measure 10.0 mL of sample and zero the Smart colorimeter. Add 0.1 g of sodium ascorbate to remove manganese interferences. Add 0.5 g of Zinc buffer powder to adjust the pH of the sample. Shake for 1 minute. Add 3 drops of 10% sodium cyanide solution. Mix thoroughly. Add 1.0 mL of dilute Zinc indicator. Mix again. Add 4 drops of 37% formaldehyde. Cap and invert 15 times. Scan the sample to determine the Zinc concentration.

Other metals will react with zincon. Despite the masking agents, the method sequence must not be interrupted since kinetics serve as a reaction control. Table 1 lists other metals that will interfere with the results at the given concentration.

*Table 153*

| Ion | conc. (mg/L) | Ion | conc. (mg/L) |
|---|---|---|---|
| $Cd^{2+}$ | 1 | $Cr^{3+}$ | 10 |
| $Al^{3+}$ | 5 | $Ni^{2+}$ | 20 |
| $Mn^{2+}$ | 5 | $Cn^{2+}$ | 30 |
| $Fe^{3+}$ | 7 | $Co^{2+}$ | 30 |
| $Fe^{2+}$ | 9 | $CrO_4^{2-}$ | 50 |

***39.1.2***

***39.1.3***

***39.1.4***

### *39.1.5 Observations*

Although the La Motte zinc method uses hazardous reagents, sodium cyanide and formaldehyde, the manufacturer has attempted to limit the exposure to the user. The sodium cyanide is provided as a dilute solution in a sealed dropper. This packaging greatly reduces the risk of accidental poisoning. However,

the formaldehyde is shipped in a reagent bottle and requires the use of a medicine dropper. It would be much better if the formaldehyde solution were also shipped in a dropper bottle.

*Table 154*

| Sample ID | spike conc.(mg/L) | Order | RO Response(mg/L) | Recovery (%) | Order | Runoff Response(mg/L) |
|---|---|---|---|---|---|---|
| Zn X 0 | 0.00 | 10 | 0.13 | NA | 7 | 0.12 |
| Zn X 1 | 0.10 | 1 | 0.14 | 140 | 8 | 0.19 |
| Zn X 2 | 0.20 | 5 | 0.19 | 95 | 12 | 0.22 |
| Zn X 3 | 1.00 | 4 | 0.96 | 96 | 5 | 0.22 |
| Zn X 4 | 2.00 | 6 | 1.84 | 92 | 2 | 1.70 |
| Zn X 5 | 3.00 | 11 | 2.71 | 91 | 9 | 2.68 |

*Table 155*

Reverse Osmosis

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.999373289 |
| R Square | 0.998746971 |
| Adjusted R Square | 0.998433713 |
| Standard Error | 0.042565267 |
| Observations | 6 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 5.776502792 | 5.776502792 | 3188.26396 | 5.89027E-07 |
| Residual | 4 | 0.007247208 | 0.001811802 | | |
| Total | 5 | 5.78375 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* |
|---|---|---|---|---|---|---|---|
| Intercept | 0.068908421 | 0.023894933 | 2.883808986 | 0.044841007 | 0.002565315 | 0.135251528 | 0.002565315 |
| spike conc.(mg/L) | 0.883958308 | 0.015655057 | 56.46471429 | 5.89027E-07 | 0.840492812 | 0.927423804 | 0.840492812 |

RESIDUAL OUTPUT

| *Observation* | *Predicted RO Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.068908421 | 0.061091579 | 1.43524482 |
| 2 | 0.157295414 | -0.017295414 | -0.406326917 |
| 3 | 0.245664732 | -0.055664732 | -1.307750101 |
| 4 | 0.951983654 | 0.008016346 | 0.18833068 |
| 5 | 1.833296262 | 0.006703738 | 0.157493149 |
| 6 | 2.712851517 | -0.002851517 | -0.066991631 |

*Table 156*

Runoff

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.998743033 |
| R Square | 0.997487645 |
| Adjusted R Square | 0.996859556 |
| Standard Error | 0.057966792 |
| Observations | 6 |

ANOVA

| | *df* | *SS* | *MS* | *F* | *Significance F* |
|---|---|---|---|---|---|
| Regression | 1 | 5.336359404 | 5.336359404 | 1588.131804 | 2.36896E-06 |
| Residual | 4 | 0.013440596 | 0.003360149 | | |
| Total | 5 | 5.3498 | | | |

| | *Coefficients* | *Standard Error* | *t Stat* | *P-value* | *Lower 95%* | *Upper 95%* | *Lower 95.0%* |
|---|---|---|---|---|---|---|---|
| Intercept | 0.089889392 | 0.032540912 | 2.762350134 | 0.050727184 | -0.00045885 | 0.180237634 | -0.00045885 |
| spike conc.(mg/L) | 0.849614321 | 0.021319575 | 39.85137142 | 2.36896E-06 | 0.790421567 | 0.908807074 | 0.790421567 |

RESIDUAL OUTPUT

| *Observation* | *Predicted Runoff Response (mg/L)* | *Residuals* | *Standard Residuals* |
|---|---|---|---|
| 1 | 0.089889392 | 0.030110608 | 0.519445831 |
| 2 | 0.174842328 | 0.015157672 | 0.261488881 |
| 3 | 0.259778278 | -0.039778278 | -0.686225283 |
| 4 | 0.938654947 | 0.031345053 | 0.540741556 |
| 5 | 1.785726359 | -0.085726359 | -1.478887421 |
| 6 | 2.631108696 | 0.048891304 | 0.843436436 |

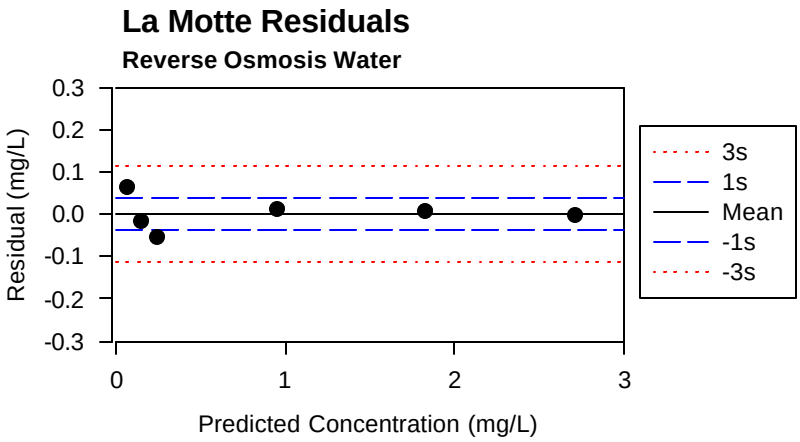

La Motte Residuals
Reverse Osmosis Water
Residual (mg/L)
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
0
1
2
3
Predicted Concentration (mg/L)
3s
1s
Mean
-1s
-3s

*Figure 148*

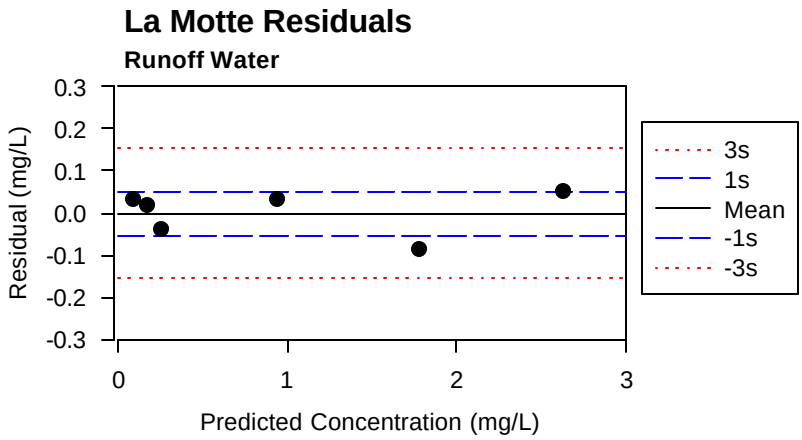



*Figure 149*

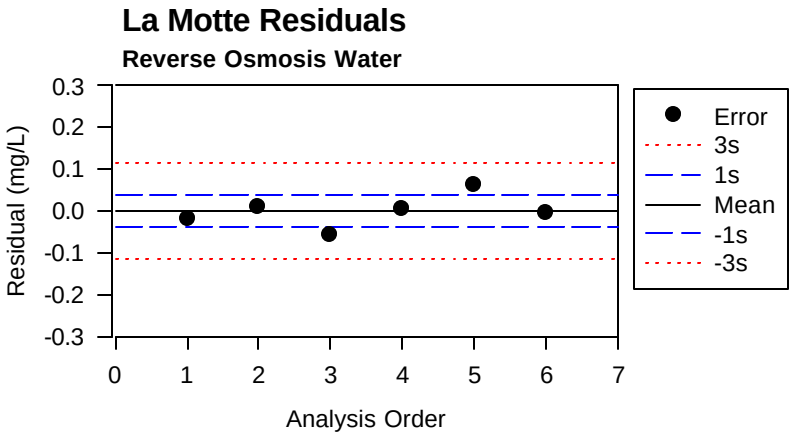



*Figure 150*

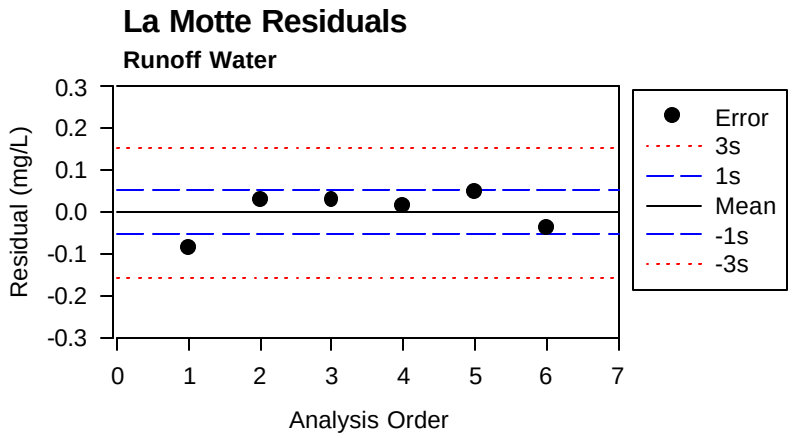

La Motte Residuals
Runoff Water
Residual (mg/L)
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
0
1
2
3
4
5
6
7
Analysis Order
Error
3s
1s
Mean
-1s
-3s

*Figure 151*

## 39.2 HACH Zinc

The HACH Zinc Method uses the same chemical reaction to determine the zinc concentration. The HACH method uses cyclohexanone instead of formaldehyde to selectively release the zinc from the complex. However, this method is unacceptable for field use without modification. The cyanide supplied with the kit is in a crystal form. The user must open this bottle and measure the cyanide to be used. This greatly increases the risk of cyanide exposure to the user and the environment. If the cyanide is spilled into an acidic environment, extremely poisonous hydrogen cyanide gas will be formed. This test was not evaluated because of serious safety concerns.

## 39.3 EM Science Quant Test Strips for Zinc

### *39.3.1 Method*

The EM Science Zinc Test Strips measure zinc concentration in the same manner as the EM Science Lead Test Strips measure lead. The user adds 10 drops of 1.0 M sodium hydroxide to mask other metals that also react with dithizone. The test strip is immersed in sample for 2 s, then the strip is allowed to dry for 15 s. Measurements are quantified by comparison with the color scale printed on the strip container.

The method is actually designed for zinc concentrations much greater than those represented in our spiked samples. Therefore, no data is available on detection limit of this method. However, the method was used to evaluate the parallel samples.