PERCHLORATE SCREENING STUDY:
LOW CONCENTRATION METHOD FOR THE DETERMINATION OF PERCHLORATE IN AQUEOUS SAMPLES USING ION SELECTIVE ELECTRODES

LETTER REPORT OF FINDINGS FOR METHOD DEVELOPMENT STUDIES, INTERFERENCE STUDIES, AND SPLIT SAMPLE STUDIES, INCLUDING STANDARD OPERATING PROCEDURE

FINAL

2 OCTOBER 2001

Prepared for:

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY REGION IX
75 HAWTHORNE STREET
SAN FRANCISCO, CALIFORNIA 94105

DEPARTMENT OF THE ARMY
U.S. ARMY ENGINEER DISTRICT, SACRAMENTO
CORPS OF ENGINEERS
1325 J STREET, SACRAMENTO, CALIFORNIA 95814-2922

PREFACE

This letter report of findings has been prepared for the U.S. EPA according to the requirements of Contract No. DACA05-96-D-0003, Task Order 0062, between the United States (U.S.) Army Corps of Engineers - Sacramento District and Earth Tech, Inc. (Earth Tech). This letter report of findings includes the results of method development studies (Task 1), interference studies (Tasks 2 and 4), and split sample analyses (Task 5) for the *Low Concentration Method for the Determination of Perchlorate in Aqueous Samples Using Ion Selective Electrodes*. Also included as Attachment 1 is the standard operating procedure (SOP) for the method (Task 3).

The U.S. Army Corps of Engineers project manager is Mr. Randy Olsen. The U.S. EPA project manager is Mr. Richard Russell. The Earth Tech program manager for this project is Mr. Ray Sugiura, and the project manager and senior method development chemist is Mr. Christopher Davis.

Approved:

Christopher Davis
Project Manager

TABLE OF CONTENTS

Section **Page**

TABLE OF CONTENTS

Section **Page**

Tables

Attachments

Abstract: Method development was performed for the *Low Concentration Method for the Determination of Perchlorate in Aqueous Samples Using Ion Selective Electrodes* with a target detection limit (TDL) of 18 micrograms per liter (µg/L) to meet the California advisory action limit of 0.018 milligrams per liter (mg/L), equivalent to 18 µg/L, for perchlorate in water. The studies resulted in a method with a reporting limit (RL) set at 15 µg/L, supported by a low calibration point of 10 µg/L, and a method detection limit (MDL) of 3 µg/L, using a Sentek 367-75 Solid State Perchlorate Combination ISE with an Orion Model 290A Advanced Portable ISE/pH/mV/Temperature Meter.

Calibrations were performed with 10 µg/L, 20 µg/L, 40 µg/L, 60 µg/L, and 100 µg/L standards. Logarithmic calibration curves for perchlorate concentration versus millivolts plotted on Excel spreadsheets consistently achieved coefficients of determination (r^2) greater than 0.990 (equivalent to r greater than 0.995) for the final method. The method accuracy criterion of ±20% was met for standards throughout the linear range of 10 to 100 µg/L.

The use of 200 mL of standards and sample, use of a magnetic stirrer, and analysis at controlled temperature were found to be essential elements to achieve sensitivity for perchlorate near the 18 µg/L TDL and California action limit. The effect of temperature variation was found to be minimized to less than 3.0 µg/L perchlorate/°C above 22°C. At lower temperatures, variations of 3.0 µg/L/°C at 22°C to 10.9 µg/L/°C at 10°C were reported. Recalibration must be performed when temperature changes cause QC recoveries to exceed control limits.

Two ionic strength adjustor (ISA) solutions were studied and found acceptable for the low concentration method. Optimal ISA addition was determined to be 1.0 mL of Sentek Perchlorate ISAB (1.0 M sodium acetate) per 200 mL sample; or 2.0-5.0 mL of 0.4 M ammonium sulfate per 200 mL of sample (0.4-1.0 mL of Orion 930711 ISA) per 200 mL sample. Two times higher concentrations of ISA or ISAB may be used for samples with high background ionic strength with no expected loss of sensitivity.

Significant interferences were encountered for elevated concentrations of some anions. Interference due to carbonate and bicarbonate was eliminated by the acidification of all standards and samples to pH 4.0 with sulfuric acid. Correction factors must be applied for concentrations in excess of 0.12 mg/L nitrate-as-nitrogen (NO_3-N), 50 mg/L chloride, and 1.2 mg/L bromide. Some anions, notably nitrate, and possibly some organic chemicals, were found to reduce electrode sensitivity between analyses. Sample matrices with nitrate concentrations greater than 0.2 mg/L NO_3-N were found to require implementation of ISE reconditioning between every sample analysis.

Split sample analyses were performed for 60 samples with definitive confirmation by EPA Method 314.0. Non-detected ISE results were confirmed as non-detected in 54 of 55 samples, and detected results were confirmed with varying degrees of accuracy in five samples. Matrix spike analyses indicate the potential for false negatives at low perchlorate concentrations in samples with high levels of interfering anions, especially nitrate.

The method was found to perform well in matrices with low concentrations of anions, and is expected to be especially useful for matrices with less than 1000 mg/L chloride or 1.5 mg/L NO_3-N. Matrices with higher concentrations of these anions must be evaluated to determine if this method meets project objectives.

1.0 Task 1 – Evaluation of Solid State Probe Performance Characteristics

This section of the letter report of findings presents the results of method development for the *Low Concentration Method for the Determination of Perchlorate in Aqueous Samples Using Ion Selective Electrodes* (the low concentration method).

1.1 Background

In 1999 Earth Tech developed a screening method for the determination of perchlorate in soils using an Orion 938101 plastic membrane half-cell perchlorate ion specific electrode (ISE) with double junction reference electrode. The primary use for this method was to determine the concentration of perchlorate in soil samples by screening level analysis at or near the site of drilling operations to aid the field sampling crew in selecting samples for definitive-level analysis and in making decisions for further drilling locations. Ten percent of soil samples analyzed by this method were confirmed by definitive-level analysis. The method was determined to be effective, and the USEPA expressed an interest in developing a method for the determination of perchlorate in aqueous samples using solid state ISEs.

The soils method uses an extraction ratio of 10 grams (g) of soil to 100 milliliters (mL) of water, with analysis in general accordance with manufacturer specifications and USEPA quality assurance (QA) criteria. The 0.2 to 0.7 milligram per liter (mg/L) detection limits (DLs) for waters (equivalent to 200 to 700 micrograms per liter [µg/L]) specified by the manufacturers of perchlorate ISEs allow for DLs of 2.0 to 7.0 milligram per kilogram (mg/kg) in soils. Allowing for gradual loss of sensitivity, the reporting limit of 15 mg/kg used for the soils analyses meets the California Preliminary Remediation Goal (PRG) of 39 mg/kg in residential soils without modifying manufacturer specified analytical procedures.

As the California advisory action limit for perchlorate in waters is 0.018 mg/L (equivalent to 18 µg/L), the focus of the current study was to develop methodology for the determination of perchlorate at a target detection limit (TDL) of 18 µg/L, which is 12 to 40 times below manufacturer specified detection limits. The conceptual basis for the low concentration method is a low-level measurement procedure described in the instruction manual for the Orion 938101 plastic membrane half cell perchlorate ISE. This procedure was modified and developed in the current study to produce a method with a reporting limit (RL) set at 15 µg/L, supported by a low calibration point of 10 µg/L, and a method detection limit (MDL) of 3 µg/L, using solid state ISEs.

Aqueous perchlorate concentrations for this study were reported in µg/L, or parts per billion (ppb), as the range of interest for perchlorate is 10-100 ppb. Anion interferent concentrations were reported in mg/L, or parts per million (ppm), as concentrations of interferents studied were in the ppm range. Further references to perchlorate concentrations in this report are in ppb, and references to anion concentrations are in ppm. All such references are for aqueous solutions.

1.2 Equipment Comparison

Equipment and supplies were procured for the comparison of the Sentek 367-75 solid state perchlorate combination ISE (the Sentek ISE) to the Orion 938101 plastic membrane half-cell perchlorate ISE with double junction reference electrode (the Orion ISE). The Sentek ISE is a solid state sensor with built in reference element that does not require any filling solution or maintenance, and can be stored dry; whereas the Orion ISE utilizes a reference electrode that requires maintenance of both inner and outer chamber filling solutions, and must be stored in a special solution, or dismantled, cleaned, and stored dry. Perchlorate ISEs with similar characteristics are available from other manufacturers, and no requirement or recommendation of brand or manufacturer is implied.

In method development, the Sentek ISE was found to be sensitive to concentrations below 10 ppb. The Orion ISE was found to be sensitive to approximately 50-100 ppb (for details, refer to Section 1.3.1). Due to the lower detection limits, simplicity of the solid state ISE with built-in reference electrode, and ease of storage, the Sentek ISE was selected for the full method development studies, interference studies, and split sampling analyses.

Comparison of data acquisition systems for the read-out of millivolt readings was also performed. The Orion and Sentek ISEs were set up so millivolt readings could be read on both an Orion Model 290A Advanced Portable ISE/pH/mV/Temperature Meter and a Laval ELIT 8804 Computer Interface (Four Channel Serial Port RS232 Communication Port Connection and Laval ELIT Extended Software for ISE Interface 8804 for 10,000 Measuring Points). Data acquisition systems for ISEs with similar characteristics are available from other manufacturers, and no requirement or recommendation of brand or manufacturer is implied.

Millivolt readings were found to be consistent for each ISE on both instruments; however, the calibration features of both instruments were found to be difficult to use effectively. In calibration mode with the Orion 290A, it was difficult to determine when millivolt readings had adequately stabilized; and the Laval ELIT software was unable to integrate an appropriate curve and was tedious to use for saving data points. Both instruments were able to effectively readout in millivolts and monitor millivolt reading stability.

Millivolt readings from the meter or ELIT software were therefore manually logged into a bench logbook, then entered into an Excel spreadsheet which allowed graphic representation of the calibration curves with equation and output of the coefficient of determination (r^2), and direct output of concentration from millivolt readings (see presentation of data in the attached tables). After two weeks of running ISEs on both instruments, the meter was used alone for further analyses.

1.3 Method Development

1.3.1 Low Concentration Sensitivity Studies

Initially, aqueous perchlorate standards were prepared from reagent grade potassium perchlorate at 10 ppb, 25 ppb, 50 ppb, 100 ppb, and 500 ppb. Calibrations were then attempted using the Orion and Sentek ISEs with addition of different types and concentrations of ionic strength adjustor (ISA) solutions, including no ISA.

Difficulties were initially encountered with both ISEs, including similar and inverted millivolt readings for decreasing perchlorate concentrations below 100 ppb. Experimentation with the following parameters improved the linearity of the millivolt readings significantly. The volume of the standards was changed from 50 mL to 200 mL, the use of a magnetic stirrer was implemented, stronger perchlorate solutions were used for preconditioning of the perchlorate ISE, and reconditioning was performed on a more frequent basis. These protocols significantly improved stabilization time, linearity, accuracy, and precision. Standards at 10 ppb, 20 ppb, 40 ppb, 60 ppb, and 100 ppb were used to focus of the calibration range to the concentrations of interest. In the initial trials with the orion plastic membrane half-cell ISE with double junction reference electrode, calibrations were unable to indicate an ability to differentiate between standards below 100 ppb, as presented in Table 1-1. Although several combinations of ISA were tried, the lower limit of sensitivity for the Orion

ISE was determined to be 100 ppb. Therefore, the Orion ISE was not used for method development due to unacceptable performance at the TDL.

In the initial trials with the Sentek 367-75 solid state combination ISE, calibrations demonstrated the ability to differentiate standards from 20 ppb to 100 ppb, as presented in Table 1-1. Subsequent calibration curves for the Sentek ISE were acceptable and able to include all standards down to 10 ppb, therefore, the Sentek ISE was chosen for method development. All further references to method development are for the Sentek ISE, unless otherwise specified.

1.3.1.1 Calibration Curves

After the initial trials, full calibrations including 10 ppb, 20 ppb, 40 ppb, 60 ppb, and 100 ppb standards were run on a daily basis, with one Sentek ISE set up for readings on the Orion 290A meter, and one Sentek ISE set up for readings on the Laval ELIT computer interface. Logarithmic calibration curves for perchlorate concentration versus millivolt readings were prepared on Excel spreadsheets. Initially, coefficients of determination (r^2) were greater than 0.980 (equivalent to r greater than 0.990) for all of the calibration curves. However, as method development progressed and the effects of different variables were determined, calibration curves with r^2 greater than 0.990 (equivalent to r greater than 0.995) were consistently achieved, with r^2 for most curves exceeding 0.995 (refer to Table 1-2 for examples of calibration curves with r^2 approximately equal to 0.98 and 0.99). For the final low concentration method, coefficients of determination greater than 0.990 are considered necessary to demonstrate acceptable linearity.

1.3.1.2 Method Detection Limit Studies

An initial MDL study was performed on January 4, 2001 according to requirements specified in 40 CFR Part 136, using 10 consecutive replicate analyses of a 25 ppb standard with 2 mL of 0.4 molar (M) ISA in 200 mL of standard, and no pH adjustment. The MDL was determined to be 3 ppb, as presented in Table 1-3. The 3 ppb MDL was confirmed in a second MDL study on January 24 through 29, 2001, as presented in Table 1-4. Fifteen non-consecutive analyses were performed on a 20 ppb standard on four different days, using 1mL of Sentek ISAB in 200mL standard and pH adjustment to pH 4.0. The MDL standards were analyzed intermittently between field sample analyses to provide an MDL for working conditions.

Periodic tests of method blanks, 5 ppb standards, and 10 ppb perchlorate standards indicated acceptable differentiation of millivolt readings at 5-10 ppb for a distilled water matrix. Although the MDLs were 3 ppb, results for standards less than 5 ppb could not generally be considered differentiable from results for blanks.

1.3.1.3 Practical Quantitation Limit

The practical quantitation limit (PQL), or reporting limit (RL), was set at 15 ppb, which is five times the MDL, and 20% below the 18 ppb project TDL and California action limit. The quality control (QC) criterion for accuracy is ±20% for this method (refer to Section 1.3.1.5, below). Results reported as non-detected (ND) at the PQL or MDL can be considered to indicate the absence of perchlorate at that concentration. If results are to be reported as detected between the PQL and MDL, such results should be considered estimated as quantiatively and qualitatively uncertain due to possible matrix effects. However, results below the PQL of 15 ppb should not be reported as detections unless the matrix is demonstrated to be free of positive interferences.

For samples with chloride concentrations above 50 ppm, perchlorate readings less than 50 ppb require subtraction of a correction factor due to positive interference according to Table 4.7; and perchlorate readings greater than 60 ppb require dilution and reanalysis due to potential negative interference, as indicated in Table 4.2C. For samples with nitrate concentrations above 0.12 ppm nitrate-as-nitrogen (NO_3-N) or bromide concentrations greater than 1.2 ppm, perchlorate readings require subtraction of a correction factor due to positive interference according to Tables 4.8 and 4.9, respectively. For a full description of the matrix interference studies, refer to the Task 4 Letter Report of Findings, Section 4.0; and Sections 1.3.2.7, 1.3.2.8, and 1.3.2.9, below.

1.3.1.4 Linear Range

The linear range for the low concentration method is considered to be 10-100 ppb perchlorate. Linearity and percent recoveries are acceptable from 10 ppb to 100 ppb; however, the calibration curves flatten off above 100 ppb. To determine concentrations of perchlorate above 100 ppb, samples can be diluted such that they are within the linear range, or if the concentration exceeds 500 ppb, calibration can be performed to include standards at higher concentrations with stronger ISA concentrations according to ISE manufacturer recommendations. Due to the potential for positive bias matrix interference, dilution and reanalysis of samples with perchlorate readings in the upper half of the linear range is recommended.

Perchlorate ISEs are listed by the manufacturers as having a usable range from 200-700 ppb through 99,500 ppm if appropriately calibrated. As the focus of this investigation is the determination of perchlorate at concentrations below the manufacturer specified range, analysis of high concentration perchlorate samples is not included in this Letter Report of Findings.

1.3.1.5 Quality Assurance/Quality Control

Quality assurance/quality control (QA/QC) criteria were applied to all analyses to ensure usable quality of the data during method development and split sample analyses. The sequences and concentrations of QC samples were varied during method development, but generally followed typical EPA requirements for QC, as summarized in this section. Complete QA/QC requirements are specified in Section 8.0 of the Standard Operating Procedure (SOP) for the *Low Concentration Method for the Determination of Perchlorate in Aqueous Samples Using Ion Selective Electrodes* presented in the Letter Report of Findings for Task 3, Section 3.0, Attachment 1.

Initial calibrations were performed using 5 initial calibration standards (ICAL), with the low standard at a concentration below the PQL. A blank calibration standard is not recommended in ISE manufacturer protocols and was not included for the low concentration method as linearity to the origin is not expected for ISE methods. The logarithmic calibration curves were required to meet a correlation coefficient criterion of $r^2 \geq 0.990$ ($r \geq 0.995$). In addition, millivolt readings for each ICAL standard were converted to perchlorate concentrations to verify ±20% accuracy throughout the linear range.

Second source standards were analyzed as laboratory control samples/initial calibration verification check samples (LCS/ICV) with each analytical run. Continuing calibration verification check samples (CCV) and method blanks/initial or continuing calibration blanks (MB/ICB or CCB) were analyzed at a frequency exceeding one per 10 samples. Matrix spikes and duplicate analyses were analyzed during split sample analyses at a frequency in excess of one per 20 samples to determine matrix specific accuracy and precision. Corrective actions were implemented when QC sample recoveries exceeded the ±20% method accuracy criterion.

All standards were made from reagent grade salts dissolved in deionized water and diluted to the concentrations required with high accuracy/high precision pipettes. In addition to glass pipettes, a variable volume pipettor with tip ejector was found to be extremely useful for accurate pipetting. ICVs, LCSs, and CCVs were prepared at varying concentrations, including 20, 25, 40, and 50 ppb. Check standards at 5 ppb or 10 ppb were also analyzed for some analytical runs.

The following analytical sequence is recommended as a result of method development: ICALs at 10, 20, 40, 60, and 100 ppb; ICV/LCS at 25 ppb or 50 ppb; MB/ICB; 10 samples or less; CCV at 20 ppb; MB/CCB; 10 samples or less; LCS; CCB; etc. In addition, a check sample at 10 ppb and/or 5 ppb may be considered appropriate after the ICAL or ICB to demonstrate sensitivity and the ability to differentiate between a low concentration standard and a blank, depending on project objectives, especially for clean matrices or if results are to be reported below the PQL.

Although mid-range check standards (50 ppb for the specified linear range) are normally used for EPA methods, concentrations for check standards for this method at 20-25 ppb may be preferable to demonstrate accuracy and sensitivity near the 18 ppb TDL and California action limit. The concentration of the ICV/LCS may be set at 50 ppb to check mid-range accuracy if appropriate for project objectives, but at least one check standard (the CCV) should be set at 20-25 ppb.

Accuracy should meet a ±20% criterion, precision should meet a 20 relative percent difference (RPD) criterion, and MBs/ICBs/CCBs should be less than 7.5 ppb or a level appropriate to project objectives, generally specified as one-half the PQL or project RL.

In general, the method demonstrated the ability to perform within the specified QC criteria. Method development indicated that when ISE sensitivity was diminished by the matrix, QC sample recoveries at all concentrations were affected. Corrective actions included re-conditioning the ISE module with acidified blanks and 100-2000 ppb perchlorate solutions (refer to Section 1.3.2.1, below), verification and correction of operating temperature (refer to Section 1.3.2.3, below), or recalibration and reanalysis of affected samples. The most significant QC failures were due to matrix interferences that caused a positive bias followed by loss of sensitivity. Analysis of QC samples between every field sample allowed the problematic samples to be singled out and the matrix interference to be identified as carbonate/bicarbonate. Nitrate was later found to cause similar interference during interference studies. Adjustment of pH to 4.0 was implemented to eliminate carbonate/bicarbonate interference, and all samples were successfully reanalyzed (refer to Sections 1.3.2.6, 4.1, and 4.2). Implementation of reconditioning between samples acceptably mitigated the loss of sensitivity due to nitrate (refer to Sections 1.3.2.1, 1.3.2.8, and 4.4).

1.3.2 Method Variables

Samples and standards were analyzed at different concentrations in different sequences on many different dates, varying certain parameters such as ISE module conditioning, sample volume, stirring, temperature, amounts and composition of ISA, pH, and matrix effects. The effects of different variables are discussed in this section.

1.3.2.1 Perchlorate ISE Module Conditioning

ISE manufacturers recommend preconditioning ISE modules in perchlorate solutions prior to use. Periodic reconditioning of the ISE is also recommended during the analytical sequence. For maximum effectiveness, conditioning solutions should be prepared the same as the standards and samples, including ISA and pH adjustment, as appropriate. Sentek recommends conditioning their perchlorate ISE modules in a perchlorate solution at a concentration equivalent to the lowest calibration standard for 10 minutes. Orion specifies preconditioning a new unit in 100 ppm solution for one-to-two hours, and storing the unit in the same solution between analyses; however, the Orion unit was not used in method development, and no recommendations for conditioning the Orion ISE are included in this section.

For the Sentek ISE, the manufacturer-specified working range is 200 ppb to 99,500 ppm and the low standard would be 200-500 ppb; whereas for the low concentration method, the low standard is 10 ppb. During method development with the Sentek ISE, conditioning solution concentrations of 10 ppb, 50 ppb, 500 ppb, 2 ppm, and 50 ppm were tried. Conditioning with 10 ppb was found to be ineffective, and 50 ppm was found to destabilize low-end sensitivity. A 500 ppb solution was found to work well for preconditioning of the ISE module.

During field sample analyses, stabilization of the millivolt readings generally took longer than for calibration standards, most likely due to chemical contaminants from the samples blocking perchlorate electrode or reference electrode conductivity sites in the ISE module. When time required for millivolt readings to stabilize became excessive, or if low recoveries for check standard recoveries were encountered after analysis of field samples, reconditioning of the ISE in a 100 ppb perchlorate solution acidified to pH 4 was generally found to work effectively, decreasing stabilization time and increasing sensitivity and accuracy. In addition, the acidification of samples and blanks was found to increase sensitivity without adversely affecting performance.

Some anions, notably nitrate, and possibly some organic chemicals, appeared to be the cause of electrode sensitivity loss. During method development, sample matrices with nitrate concentrations greater than 0.2 ppm NO_3-N were found to require implementation of reconditioning between every sample analysis to maintain sensitivity. As concentrations of nitrate increased, stronger solutions of perchlorate were required to recondition the ISE in a reasonable amount of time, with 2000 ppb perchlorate solutions found most effective in maintaining sensitivity and accuracy when analyzing samples with nitrate concentrations above 2.0 ppm NO_3-N.

Therefore, for the low concentration method, preconditioning the Sentek perchlorate ISE with a 500 ppb perchlorate solution daily prior to analyses, and reconditioning with 100-2000 ppb perchlorate solutions at a frequency applicable to the matrix being analyzed is specified in the method. Reconditioning frequency may range from the use of a 100 ppb perchlorate standard once or twice a day or once per analytical sequence of 10 field samples (12 analyses including MB and CCV) for cleaner matrices, to use of a 2000 ppb solution between every sample for samples with high nitrate or other loss-of-sensitivity interferents.

Reconditioning includes soaking the perchlorate ISE in deionized water acidified to pH 4.0 for one minute to clean interfering ions from the electrode membrane; followed by immersion in a 100-2000 ppb perchlorate solution acidified to pH 4 for one to six minutes, depending on time required for millivolt readings to stabilize, to regenerate perchlorate sites in the ISE membrane. The ISE should then be allowed to restabilize in a blank prior to sample analysis.

Use of 500 or 2000 ppb concentration solutions should be progressively implemented when the 100 ppb solution is found not to regenerate sensitivity within four to six minutes, or after analysis of any sample with known high concentrations of nitrate. Use of stronger solutions does not adversely affect accuracy, but requires additional time for the ISE to restabilize in a blank before sample analysis.

Acid blanks and perchlorate conditioning solutions should be adjusted with ISA and sulfuric acid the same as the standards and samples. All reconditioning protocols applied to field sample analyses must be applied to analyses of QC samples as well.

Even when reconditioning is not required due to nitrate, routinely storing the ISE briefly in a 20 ppb perchlorate standard followed by a thorough rinse between each sample was found to help maintain sensitivity in general. This can lead to faster analysis times because millivolt readings stabilize more quickly, with fewer reanalyses required due to declining check standard recoveries.

When sensitivity for a specific ISE module is found to decrease with extended use, Sentek recommends using an abrasive such as fine emery paper to renew the exposed PVC surface of the electrode. See manufacturer directions for this procedure. If sensitivity cannot be restored, the ISE module must be replaced. Note that exposure to samples containing organic solvents may permanently degrade the electrode membrane.

1.3.2.2 Sample Volume and Stirring

The initial studies were conducted using 50 mL of standard and no stirring mechanism. The Orion ISE was not able to differentiate between 20 to 100 ppb standards under these conditions, and the Sentek ISE was not able to meet linearity requirements. The use of 200 mL and a magnetic stirrer made a significant difference in the ability of the Sentek ISE to perform at the required concentrations. Therefore, the use of 200 mL of standards and sample, and the use of a magnetic stirrer are considered to be essential elements for the determination of perchlorate near the 18 ppb TDL. Note that due to low volumes of sample provided for the first round of split samples, sample volumes of 120 mL were successfully analyzed; however, the use of 200 mL is recommended.

1.3.2.3 Temperature Effects

During method development, millivolt readings were found to be very slow in stabilizing at temperatures below 19°C. As temperatures increased above 20°C, readings were found to stabilize much more readily. At 16-20°C, readings for the lowest concentration standards could take 10 minutes to stabilize enough to read. At 20-25°C, the same standards took less than five minutes to stabilize. In addition, the millivolt readings increase with temperature, lowering the concentration readout for perchlorate. Calibrations and sample analyses should be performed an approximately constant temperature.

A study of the effect on temperature was conducted on January 29, 2001, as presented in Table 1-5. For a standard with a true value of 20 ppb perchlorate and a found value of 19.9 ppb at 25.5°C, the following changes in concentration with respect to temperature were noted. The most significant effects were noted at lower temperatures. With temperature increases from 10.0°C to 12.5°C, a 27.2 ppb decrease in the reading for perchlorate was noted (10.9 ppb/°C). From 19°C to 21.5°C the decrease was 7.8 ppb (3.1 ppb/°C) and from 21.5°C to 24.0°C the decrease was 5.5 ppb (2.2 ppb/°C). At higher temperatures, the effect was less pronounced. From 27.5°C to 32.5° the decrease was 7.0°C (1.4 ppb/°C). Additional temperature studies for other concentrations (method blank, 10 ppb, and 50 ppb) are suggested for future study.

As with all ISE methods, accuracy is best if calibration standards and samples are analyzed at the same temperature. However, as a field screening method this may not always be possible. The effect of temperature variation will be minimized as long as the temperature exceeds 22°C and is kept constant to within a few degrees. If the temperature changes such that QC sample results are not within control limits, a recalibration must be performed (refer to Task 3 Letter Report of Findings).

As the temperature of all standards and samples must be the same for accurate analysis, all standards or samples stored in a cooler or refrigerator must be allowed to warm to ambient temperature before analysis. Due to the stability of perchlorate in aqueous samples at room temperatures, samples and working standards may remain at room temperature overnight. Samples or standards should not be warmed by exposure to sunlight or other light sources, as perchlorate concentrations may be affected by ultraviolet light.

1.3.2.4 Ionic Strength Adjustors (ISA)

ISA solutions are made from the same chemicals present in the reference electrodes for each ISE. For ISE analyses to succeed, all standards and samples must be at approximately the same background ionic strength. Therefore, ISA is added to all standards and samples.

Two ISAs were used in method development, and both were found to work acceptably. The manufacturer-recommended standard amount of ISA for the Orion ISE is 2 mL of 2.0 molar (M) ammonium sulfate per 100 mL sample when operating in the normal operating range (0.7 – 98,500 ppm). The Orion low-level measurement procedure specifies use of 1 mL 0.4 M ISA per 100 mL sample (10% of the standard Orion ISA). Sentek specifies use of 2 mL of their 1.0M sodium acetate “Perchlorate ISAB” per 100 mL sample (ISAB refers to the buffering capacity of this ISA) when operating in the normal operating range (0.2 – 98,500 ppm). The Orion ammonium sulfate ISA is referred to hereafter as “ISA,” and the Sentek sodium acetate ISA is referred to hereafter as “ISAB.” Approximately half the method development work and half the sample analyses were performed with each type of ISA.

Initial studies included an attempt to use no ISA. The attempt to use no ISA was not successful, and is considered inappropriate for determination of perchlorate at the low concentrations required to meet the TDL.

On January 9, 2001 calibrations were performed using 2 mL, 3 mL, 4 mL, 5 mL, and 11 mL of 0.4 M ISA per 200 mL sample to determine the effects of differing ISA concentrations on method parameters, as presented in Table 1-6. The calibration with the best coefficient of determination and the steepest slope was the 5 mL of 0.4 M ISA per 200 mL sample, approximately equivalent in concentration to 25% of the standard Orion amount of ISA. Similar coefficients of determination and slopes resulted from use of the ISAB at 25% of the manufacturer recommended amount during subsequent method development.

Therefore, 25% of the standard ISAB or 10-25% of standard Orion ISA were determined to be appropriate for the low concentration method. These levels of ionic strength adjustment maintain linearity down to the lowest calibration standard, support check standards of 5 ppb, and the resulting conductivities in the standards appropriately adjust the background ionic strength to functionally equivalent levels for standards and field samples.

Parallel calibrations using 2 mL and 5 mL of 0.4 M ISA per 200 mL sample were maintained on January 10, 2001; and 5 mL and 10 mL of 0.4 M ISA per 200 mL sample were maintained on January 12, 2001. Field samples were analyzed with both concentrations of ISA for each of these dates during investigation of matrix effects related to sample conductivity (refer to Table 1-7). Perchlorate readings for the analyses of QC samples and field samples from the parallel calibration curves were within 5% (refer to readings highlighted in bold in Table 1-7), demonstrating that effectively there was no difference in accuracy for the different ISA concentrations. After January 12, 2001, 1 mL of 1M ISAB per 200 mL sample was used for further method development studies (25% of manufacturer-recommended strength).

Millivolt readings for the different amounts of ISA were not significantly different for each level of ICAL standard in the calibrations for each date or for the different samples and QC samples in Tables 1-6 and 1-7. Further indication that accuracy and precision are not affected by the different ISA solutions was provided by the results of the MDL studies. MDL studies using ISA (Table 1-3) and ISAB (Table 1-4) independently provided MDLs of 3 ppb. The acceptable calibrations and low concentration check standards achieved with both ISA and ISAB demonstrate that there was no difference in sensitivity for the different ISA/ISAB concentrations. Thus, different levels of background ionic strength adjustment in samples do not appear to significantly affect perchlorate readings, as long as minimum adjustment equivalent to 10% of the Orion ISA or 25% of the Sentek ISAB are used.

As the conductance of a sample matrix is proportional to the common anions present in the matrix, conductivities of ISA standards (refer to Table 1-8) and samples (refer to Table 1-9) were measured in microsiemens/cm (uS/cm) or microMhos/cm (uMhos/cm), which are considered equivalent terms, during the ISA studies and during split sample analyses to determine relative ionic strengths. Studies of the conductivity of different concentrations of ISA with no pH adjustment were performed on January 8, 2001 (refer to Table 1-8A). The lowest concentration ISA in this study (2 mL 0.4 M ISA per 200 mL sample) was the concentration specified in the Orion low-level procedure, equivalent to 10% of the standard Orion ISA. The highest concentration ISA was approximately equivalent, when corrected for additional volume, to 50% of the standard Orion ISA. Additional studies of the conductivity of different concentrations of ISA at pH 4, and ISAB without pH adjustment and at pH 4 were performed on April 23, 2001 and May 1, 2001 (refer to Tables 1-8B through 1-8D). Conductivity did not significantly change for the ISA solutions with acidification to pH 4, as very little acid was required to effect pH changes (Tables 1-8A and 1-8B). More significant conductivity changes were effected by acidification for the ISAB solutions with acidification to pH 4 due to the buffering capacity of ISAB (Tables 1-8C and 1-8D).

The ionic strengths for ISA and ISAB adjusted solutions are approximately the same for the amounts of ISA used for method development and recommended for the low concentration method. For the ISA, 2 mL of 0.4 M ammonium sulfate per 200 mL of sample produces a 3.96 millimolar (mM) solution with 11.88 milliequivalents per liter (meq/L) of individual ions; whereas for the ISAB, I mL of 1.0 M sodium acetate produces a 4.98 mM solution with 9.95 meq of individual ions per liter (refer to Tables 1-8E and 1-8F, highlighted data; and Table 1-8F graph). Note that each formula weight of ammonium sulfate contributes three ions and sodium acetate contributes two ions. Although the ISA ionic strength adjustment (meq/L) is slightly higher than the ISA adjustment, the conductivity for the ISA adjusted solution is significantly higher due to the higher conductivity of the ions in ammonium sulfate than those in sodium acetate (refer to labeled points on Table 1-8E graph).

Therefore, for the low concentration perchlorate method, either the Sentek ISAB can be used at 25% of manufacturer-specified strength or the Orion ISA can be used at 10-25% of the standard manufacturer-specified strength. For the Sentek ISAB, the use of 1 mL of Sentek Perchlorate ISAB (1.0 M sodium acetate) per 200 mL sample is recommended. For the Orion ISA, the use of 2-5 mL of 0.4 M ammonium sulfate per 200 mL of sample, or 0.4-1.0 mL of Orion 930711 ISA (2.0 M ammonium sulfate) per 200 mL sample is recommended. Further study is recommended to determine whether higher adjustment by ISA or ISAB may be appropriate for samples with high background ionic strength, including samples with high levels of nitrate.

All standards and samples should be spiked with proportionally equivalent concentrations of the same ISA. Different concentrations of ISA or ISAB should not be used interchangeably within a calibration, although minor changes in ISA are not expected to significantly affect data quality. Note that concurrent calibrations can be maintained for any differences in adjustments to samples (such as pH, ISA/ISAB concentration, or temperature) by making the same adjustments to the standards.

1.3.2.5 Matrix Effects

As method development progressed, split samples from Edwards AFB were analyzed to determine whether definitive analytical results for perchlorate by ion chromatography (IC) according to EPA Method 314.0 could be reproduced by ISE using the low concentration method (refer to Table 1-9), and to investigate method performance for a field matrix. These analyses immediately indicated both positive and negative matrix interferences, so matrix interferences were systematically evaluated, starting with conductivity, then specific anions (refer to Section 4.0 and Tables 4-1 through 4-6).

Although a direct relationship between false positive readings and conductivity was noted, some samples caused significant loss of electrode sensitivity as well. From background information on the sampling locations, the most likely significant interferents were determined to be carbonate/bicarbonate, chloride, and nitrate. Bromide, fluoride, iodide, phosphate, and other anions such as thiocyanate were also identified as interferents in the ISE manufacturer specifications. Carbonate/bicarbonate, chloride, bromide, fluoride, nitrate, and phosphate were investigated in the current study.

Addition of sulfuric acid to adjust all samples and standards to pH 4.0 was found to effectively remove carbonate/bicarbonate interference (see Section 1.3.2.6, below). Corrections must be applied for chloride, nitrate, and bromide interference if applicable to the matrix (see Sections 1.3.2.7, 1.3.2.8, and 1.3.2.9, below). If anion concentrations are not available for field samples and are suspected to be causing false positives or other unacceptable interference, ion-specific ISEs can be used to determine chloride, nitrate, and/or bromide with the same ISE meter used for the perchlorate determinations. Alternatively, analysis by the method of standard additions (MSA) may be used to compensate for unknown anion interference (refer to Section 4.9), especially for perchlorate readings less than 30 ppb. However, further studies of the effectiveness of MSA to compensate for anion interferences are required.

Additional interference from organic chemicals is also considered possible, and further study is recommended. For a detailed description of the interference studies, refer to the Task 4 Letter Report of Findings, Section 4.0.

1.3.2.6 pH Adjustment

The most troublesome patterns of interference in the initial attempts to analyze split samples from Edwards AFB were false positives followed by low perchlorate readings and low recoveries of QC check standards. After some experimentation, specific samples were isolated that caused a false positive bias with loss of sensitivity for the subsequent analyses (for example, see samples P-6, P-7, P-8, P-9, P-14, P-16, and P-19 in Table 4-10). Suspecting carbonate/bicarbonate as the interferent, tests on sodium bicarbonate spiked standards at pHs of 8.0 (bicarbonate present), 6.7 (carbonate present), and 4.0 (no carbonate/bicarbonate) determined that the effect could be eliminated by acidification to pH 4.0 with sulfuric acid (refer to Tables 4-1, 4-2, 4-11, and 4-12).

Subsequent testing of field samples and sodium bicarbonate spiked standards with all calibration standards, spiked standards, and field samples acidified to pH 4.0 demonstrated the ability of the method to work effectively at this pH with no loss of sensitivity after analysis of samples high in carbonate/bicarbonate. Due to the high prevalence of carbonate and/or bicarbonate in environmental samples and potential difficulties in determining levels of carbonate/bicarbonate in field samples to be analyzed by this method, the acidification of all standards and samples to pH 4.0 with sulfuric acid has been incorporated into the low concentration method. In addition, the acidification of standards and samples to pH 4.0 results in steeper, more linear calibration curves, and appears to aid in the maintenance of sensitivity of the perchlorate ISE modules.

For a detailed discussion of the carbonate/bicarbonate interference studies, refer to the Letter report of Finding for Task 4, Sections 4.1 and 4.2.

1.3.2.7 Chloride Correction

A correlation was noted between historical levels of chloride at sample locations, with apparent false positives reported for perchlorate in samples with 100-500 ppm chloride by this method. These false positives were reduced to non-detected levels when chloride and other interference correction factors were applied (refer to Task 5 Letter Report of Findings).

A chloride interference study was performed on January 18 and 22, 2001 to determine the relationship between chloride and bias for perchlorate readings. At pH 4.0, positive bias of 0-12 ppb perchlorate was noted for chloride concentrations of 0-500 ppm in standards with less than 30 ppb perchlorate. For standards with perchlorate above 30 ppb, the bias becomes less significant, then becomes negative at higher concentrations. At pH 7.0, bias is insignificant at low concentrations and negative at higher concentrations. Tables presenting chloride bias at pH 4.0 and pH 7.0 are presented in Tables 4-2A, 4-2B, and 4-2C.

The ISE manufacturer recommended protocol for the removal of chloride and several other ions listed as interferents is addition of silver sulfate to all standards and samples. The addition of silver sulfate would be costly, would result in additional waste disposal problems, would create solids in the solutions which would be difficult to remove and when stirred for analysis could potentially interfere, and would generally impose unacceptable difficulties on the use of this method as a field screening method.

Since the interferences due to chloride are relatively small, Table 4-7 was developed to correct perchlorate readings for chloride interference. In general, chloride interference is expected to cause significant accuracy problems only when perchlorate readings are between the RL (suggested to be 15 ppb) and 45 ppb (at pH 4.0), in which case chloride could contribute significantly to positive bias. The data indicate that for readings above this level, chloride interference is negligible or may cause negative interference. For perchlorate readings above 40 ppb, sample dilutions can be used to determine if interference is affecting results in such a way as to affect project objectives.

If chloride concentrations are not available for field samples and chloride levels are suspected to be causing false positives or positive bias, a chloride ISE can be used to determine chloride using the same ISE meter to be used for the perchlorate determinations. Alternatively, analysis by MSA may be used to compensate for unknown anion interference, especially for perchlorate readings less than 30 ppb, although further studies of the effectiveness of MSA to compensate for anion interferences are required (refer to Section 4.9). Definitive-level analyses should be performed whenever project objectives may be affected by indeterminate bias.

For a detailed discussion of the chloride interference studies, refer to the Letter report of Finding for Task 4, Section 4.3.

1.3.2.8 Nitrate Correction

An initial nitrate interference study was performed on February 18, 2001 to determine the relationship between nitrate and bias for perchlorate readings. Additional nitrate interference studies were performed April 30 and May 1, 2001 to verify the findings of the initial study and extend the range of concentrations studied. At pH 4.0, positive bias of 2.75 ppb to greater than 70 ppb perchlorate was noted for concentrations of 0.11 ppm to 10 ppm NO_3-N in standards with no perchlorate. (Note that nitrate is most commonly measured and reported in mg/L nitrate-as-nitrogen [ppm NO_3-N]. The same results when reported as nitrate are 4.43 times the results reported as nitrogen.) The data indicate positive interference at all concentrations of nitrate in all concentration standards of perchlorate, with potential interference of two or more times the RL at high levels of nitrate (refer to Tables 4-3A and 4-3B).

There is no suggested method for removal of nitrate interference in ISE product literature. Therefore, the application of correction factors to perchlorate readings according to Table 4-8 should be applied when NO_3-N levels exceed 0.12 ppm. In addition, NO_3-N concentrations greater than 0.2 ppm cause loss of sensitivity to the electrode, requiring reconditioning of the ISE module in an acidified blank and an acidified 100-2000 ppb perchlorate solution between every analysis to maintain adequate sensitivity to meet ±20% accuracy criteria during analytical runs in which such levels of nitrate are expected or encountered in field samples.

For matrices with levels less than 0.12 ppm NO_3-N, positive interference for perchlorate readings will not significantly exceed the ±20% accuracy criterion for this method, and correction of perchlorate readings may not be necessary. If nitrate concentrations are not available for field samples and nitrate levels are suspected to be causing false positives or other unacceptable interference, a nitrate ISE can be used to determine nitrate with the same ISE meter used for the perchlorate determinations. Alternatively, analysis by MSA may be used to compensate for unknown anion interference, especially for perchlorate readings less than 30 ppb, although further studies of the effectiveness of MSA to compensate for anion interferences are required (refer to Section 4.9). Definitive-level analyses should be performed whenever project objectives may be affected by indeterminate bias.

For a detailed discussion of the nitrate interference studies, refer to the Letter report of Finding for Task 4, Section 4.4.

1.3.2.9 Bromide Correction

A bromide interference study was performed on March 1, 2001 to determine the relationship between nitrate and bias for perchlorate readings. At pH 4.0, positive bias of 0-8 ppb perchlorate was noted for bromide concentrations of 0-5 ppm. The data indicate positive interference at all concentrations of bromide in all concentration standards of perchlorate, with potential interference less than 10 ppb unless bromide exceeds 5 ppm (refer to Table 4-4).

The suggested method for removal of bromide is the addition of 1.0 gram of silver sulfate per 200 mL sample to all standards and samples, which would generally impose unacceptable difficulties on the use of this method (refer to Section 1.3.2.7, above). For concentrations of bromide normally expected in environmental samples, bromide interference is not expected to significantly affect perchlorate results by this method. The application of correction factors to perchlorate readings according to Table 4-9 has been included for use if bromide concentrations greater than 1.2 ppm are determined to be present in samples.

For most matrices, bromide levels will be less than 1.2 ppm, and positive interference for perchlorate readings will not exceed the ±20% accuracy criterion for this method. If bromide concentrations are not available for field samples and bromide levels are suspected to be causing false positives or other unacceptable interference, a bromide ISE can be used to determine bromide with the same ISE meter used for the perchlorate determinations. Alternatively, analysis by MSA may be used to compensate for unknown anion interference, especially for perchlorate readings less than 30 ppb, although further studies of the effectiveness of MSA to compensate for anion interferences are required (refer to Section 4.9). Definitive-level perchlorate analyses should be performed whenever project objectives may be affected by indeterminate bias.

For a detailed discussion of the bromide interference studies, refer to the Letter report of Finding for Task 4, Section 4.5.

1.3.3 Split Sample Analyses

To help establish method accuracy and precision for environmental field samples, split samples from Edwards AFB were analyzed during method development. Definitive analyses were performed by E.S. Babcock & Sons, of Riverside, California according to EPA Method 314.0 (or CADOHS Modified EPA Method 300.0 for perchlorate). The known results of the definitive analyses for the first round of split sampling were used to investigate the effects of variations in the method to identify and mitigate matrix interferences and achieve results consistent with the definitive analyses. These split sampling results are included in Table 1-9. Results of all split sample analyses are discussed in detail in the Letter Report of Findings for Task 5, Section 5.0.

1.4 Method Development Conclusions

Method development studies for the *Low Concentration Method for the Determination of Perchlorate in Aqueous Samples Using Ion Selective Electrodes* indicate that the solid state perchlorate ISE with built-in reference electrode can be effectively used to determine if perchlorate is present in water at or above the project TDL and California action limit of 18 µg/L (ppb), and can be used to determine perchlorate in aqueous samples at concentrations from 15-100 ppb.

Perchlorate readings measured by the method at less than the 15 ppb RL can reliably be considered to be non-detected within 20% of the reported concentration (the method utilizes a ±20% accuracy criterion). Perchlorate readings above 15 ppb may be biased high due to anion interference. Such samples require knowledge or determination of the levels of chloride and NO_3-N, and correction of perchlorate readings according to Tables 4-7 and 4-8. Therefore, perchlorate readings between 15-30 ppb for samples with chloride concentrations of 30-500 ppm may be corrected to less than 15 ppb perchlorate. If NO_3-N exceeds 0.2 ppm, reconditioning of the electrode between every sample is necessary. Perchlorate readings greater than 15 ppb for samples with NO_3-N concentrations exceeding 0.12 ppm may be corrected to less than 15 ppb perchlorate. In matrices for which bromide exceeds 1.2 ppm, additional corrections may be required according to Table 4-9.

In cases where significant corrections lower results to below project action limits, the data user may decide that definitive-level analyses are required to confirm the presence or absence of perchlorate, or to confirm bias due to chloride, nitrate, or other interferents. For samples with unknown levels of interfering anions, analysis by MSA may have the potential to compensate for unknown anion interference, especially for perchlorate readings less than 30 ppb.

1.5 Method Development Recommendations

Further studies are recommended to reconfirm the accuracy of the chloride, nitrate, and bromide correction factors, and to study the effects of other potential interferents and mixtures of interfering anions. Possible methods to mitigate nitrate interference, including use of different type or concentrations of ISA should be explored to make the method more versatile. Further studies to determine and maximize the effectiveness of MSA are required.

2.0 Task 2 - Investigate Sample Concentration Methods

Task 2 specifies the investigation of the robustness and effectiveness of sample concentration methods for perchlorate in water analyses including sub-boiling point heating, heating to boiling point, and room temperature evaporation. Task 4 specifies the investigation of potential interferences for the low-level ISE screening method. Method development determined that in distilled water, the method detection limit (MDL) of 3 ug/L (parts per billion - ppb) allows for a reporting limit (RL) of 15 ppb, which meets the project target detection limit (TDL) and California action limit of 18 ppb with a 20% leeway for analytical accuracy. However, when the method was applied to sample matrices for groundwater split samples from Edwards AFB, problems with multiple interferences became apparent. Preconcentration of samples was therefore deemed counterproductive, as the detection limits are low enough and additional concentration of samples increases the matrix interference. Therefore, Task 2 was combined with Task 4 so additional work could be performed to resolve the matrix interferences in the split samples, and to determine what steps could be included in the method to effectively remove the interferences. For a complete discussion of the investigation of matrix interferences, please refer to Section 4.0.

3.0 Task 3 - Preparation of Revised Standard Operating Procedure

This section presents the Standard Operating Procedure (SOP) for the *Low Concentration Method for the Determination of Perchlorate in Aqueous Samples Using Ion Selective Electrodes*, d3.

A Preliminary Draft SOP for the Low Concentration Method for the Determination of Perchlorate in Aqueous Samples Using Ion Selective Electrodes was prepared prior to the analysis of split samples for this project. The revised SOP is presented as the result of method development (refer to Letter Report of Findings for Task 1, Section 1.0), including method-specific information determined from matrix interference studies (refer to Letter Report of Findings for Task 4, Section 4.0), and the first round of split sample analyses (refer to Letter Report of Findings for Task 5, Section 5.0). The SOP is presented as Attachment 1.

4.0 Task 4 – Investigation of Interference Using ISE Protocol

This section of the letter report of findings presents the results of matrix interference studies for the *Low Concentration Method for the Determination of Perchlorate in Aqueous Samples Using Ion Selective Electrodes*, as required for combined Tasks 2 and 4. Task 2 was combined with Task 4 so additional work could be performed to resolve complex matrix interferences after it was determined that the preconcentration of samples specified in Task 2 would result in increased matrix interference (refer to Section 2.0).

Task 4 specifies the investigation of potential interferences for the ions specified as interferents in the product literature for the perchlorate ISEs, and the recommendation of items for further study based on the findings. In addition to the investigation of six anions for matrix interference, the known results of definitive analyses for groundwater split samples from Edwards AFB were used to determine and resolve field sample matrix interferences.

Specific interferences due to carbonate/bicarbonate, bromide, chloride, fluoride, nitrate, and phosphate were identified and quantitated (refer to Tables 4.1 through 4.6). Although listed as primary interferents in the perchlorate ISE instrument documentation, thiocyanate and iodide were not investigated as these anions are not commonly identified in samples at Edwards AFB, where the study was based.

Carbonate and bicarbonate interferences were identified and removed by acidification of samples and standards to pH 4.0 with sulfuric acid. Chloride at the 50-500 ppm concentrations in the split samples was found to be an interferent requiring corrections to perchlorate readings according to Table 4.7. Nitrate was found to interfere significantly at concentrations greater than 0.12 ppm nitrate-as-nitrogen (NO_3-N). For samples with greater than 0.12 ppm NO_3-N, corrections to perchlorate readings according to Table 4.8 are required, and reconditioning of the ISE module between every sample is required when matrices with NO_3-N concentrations greater than 0.2 ppm are encountered. Bromide was found to interfere at concentrations greater than 1.2 ppm, which is higher than is typically found in environmental samples. For bromide, if sample concentrations exceed 1.2 ppm, corrections to perchlorate readings according to Table 4.9 are required. Fluoride and phosphate were found not to interfere in perchlorate quantitation. Dilution and reanalysis may be appropriate to confirm applied correction factors. Interference greater than 20% of the concentration in a perchlorate standard, or 20% of the 15 ppb RL for perchlorate standards less than the RL, was considered to be significant for the purposes of these studies.

The use of the method of standard additions (MSA) was found to have potential to compensate for unknown anion interference for samples with unknown levels of interfering anions, especially for perchlorate readings less than 30 ppb.

4.1 Field Sample Matrix Interferences

As method development progressed, split samples from Edwards AFB were analyzed by the low concentration ISE method to determine whether definitive analytical results for perchlorate by ion chromatography (IC) according to EPA Method 314.0 could be reproduced by ISE using the low concentration method. The ISE analyses immediately indicated both positive and negative matrix interferences with a strong correlation of false positives to conductivity, so potential matrix interferences were systematically evaluated by a review of historical results for the wells, where available (refer to Table 1.9).

The strongest correlations were between false positive perchlorate readings and carbonate/bicarbonate and chloride levels. In addition, significant loss of electrode sensitivity after analysis of some samples with false positive readings was noted. Several sequences of analyses allowed identification of possible samples causing loss of sensitivity, including samples P-7 and P-16, which had over 200 ppm alkalinity as CaCO3, and indicated the most likely cause to be carbonate/bicarbonate in the samples. Perchlorate readings for samples analyzed subsequent to sample P-7 were very low in spite of expected false positives due to known concentrations of positive interferents, and were associated with 69% and 34% recoveries of check standards after analysis of sample P-7 in data for two analytical runs on January 11, 2001. Sample P-16 demonstrated the same effect, causing a 46% recovery of the check standard on January 15, 2001 (see Table 4-10).

Adjustment of pH to 4.0 with sulfuric acid, which converts bicarbonate and carbonate to carbon dioxide, reduced the false positives significantly (for example, refer to Table 1-9, sample P-16) and removed the negative interference caused by loss of sensitivity, as demonstrated by acceptable recoveries of check samples during acidified reanalyses of samples previously associated with low recoveries in non-acidified analytical runs (see Table 4-10). Correction of chloride interference according to Table 4-7, with additional minor corrections for low concentrations of nitrate and bromide according to Tables 4-8 and 4-9, then produced excellent agreement between split sample results, with the exception of samples P-1 and P-11, which required significant corrections due to high levels of nitrate.

The results highlighted in bold in Table 1-9 for samples P-6 through P-9, P-16, and P-19 demonstrate the corrective effects of acidification and chloride, nitrate, and bromide correction factor subtraction; and the results for samples P-1 and P-11 (and samples P-102, P-103, and P-104, resampled for sample P-11) demonstrate additional significant corrections for high levels of nitrate.

Additional interferences due to other anions were not apparent in the split samples. Interference due to fluoride and phosphate were investigated with no effective interference demonstrated. Specific anion interference studies are discussed in the following sections.

Samples with high known concentrations of organic contaminants were not analyzed due to the potential for deterioration of the ISE module. In general, samples with high concentrations of organics are not recommended for analysis by ISE as organic solvents are known to deteriorate the ISE membranes.

4.2 Carbonate/Bicarbonate Interference Studies

Carbonate and bicarbonate are listed in ISE product literature as being primary interferents for perchlorate analysis by ISE. Acidification of samples using sulfuric acid is the suggested method for removal of the interference. Bicarbonate exists only in samples at pH greater than 8.3. Below pH 8.3, bicarbonate is converted to carbonate. Below pH 4.5, total conversion of carbonate to carbon dioxide is expected. As significant levels (greater than 100 ppm total alkalinity as calcium carbonate) of carbonate and/or bicarbonate are commonly found in environmental samples at Edwards AFB and other groundwater sample matrices, and as these ions were identified as causing interference for the low concentration perchlorate method, interference studies of these anions were performed during method development.

Bicarbonate spiking solutions were prepared from reagent grade sodium bicarbonate. On January 22, 2001, analysis of a 10 ppb perchlorate standard spiked with 50 ppm bicarbonate produced a perchlorate reading of 19.6 ppb, confirming suspected positive interference for bicarbonate. Subsequent analysis of this spiked standard acidified with sulfuric acid to pH 6.75 (bicarbonate converted to carbonate) and pH 4.0 (all carbonate removed by conversion to carbon dioxide) produced significantly increased millivolt readings indicative of sequential removal of positive bias for perchlorate (refer to Table 4-11). These millivolt readings for the acidified standards could not be specifically quantitated using the non-acidified calibration, as the millivolt readings for each level of perchlorate differ between acidified and non-acidified calibrations.

Analyses of a blank, 50 ppm, 100 ppm, and 300 ppm sodium bicarbonate solutions were then performed without pH adjustment. The 50 ppm bicarbonate solution produced a positive reading for perchlorate of 25.1 ppb. The 100 ppm and 300 ppm bicarbonate solutions produced readings for perchlorate of 31.3 ppb and 38.3 ppb, respectively, indicating increasing positive bias with increasing bicarbonate concentration (refer to Table 4-1A). However, due to loss of ISE sensitivity after analysis of each bicarbonate standard, as demonstrated by the 60% recovery of the subsequent check standard, the positive interference at these concentrations is expected to actually be higher. Again, acidification of the 300 ppm bicarbonate solution to pH 4.0 increased the millivolt readings significantly to levels that indicate complete removal of the interference.

To demonstrate the effectiveness of acidification of samples to pH 4.0 in removing carbonate/bicarbonate interference (both immediate positive bias and subsequent negative bias due to loss of sensitivity), on January 23, 2001 a calibration was performed using standards acidified to pH 4.0 with sulfuric acid (refer to Table 4-12). Initially, blanks with 50 ppm, 100 ppm, and 300 ppm of sodium bicarbonate were analyzed at pH 6.8 to demonstrate relative positive bias for the carbonate ion (specific bias could not be demonstrated as the millivolt readings for the non-acidified standards could not be quantitated using the acidified calibration). Blanks, 10 ppb, 20 ppb, and 50 ppb perchlorate standards with 50 ppm, 100 ppm, and 300 ppm of sodium bicarbonate were then analyzed at pH 4.0. All of the perchlorate readings were within the ±20% accuracy criterion, demonstrating effective removal of all interferences due to bicarbonate or carbonate, with no residual loss of sensitivity (refer to Table 4-1B).

Note that during analysis of the carbonate samples (pH 6.8), recoveries of the 20 ppb perchlorate check samples gradually decreased, and during analyses of the samples acidified to pH 4.0, the recoveries gradually increased (refer to Table 4-12). From this trend it was inferred that conditioning of the ISE module with acidified blanks helps counteract the loss of sensitivity caused by the carbonate/bicarbonate ions. This conditioning was later applied to nitrate interference, and has been incorporated as part of the recommended procedures in the method when loss-of-sensitivity interferences are expected or encountered.

To ensure complete removal of all carbonate and bicarbonate, the acidification of all samples and standards to pH 4.0 has been incorporated into the low concentration method. This acidification appears to increase linearity of calibrations as well as sensitivity, as demonstrated by consistent coefficients of determination greater than 0.9975.

4.3 Chloride Interference Studies

Chloride is listed in ISE product literature as being a minor interferent for perchlorate analysis by ISE. As significant levels of chloride (greater than 50 ppm) are commonly found in environmental samples at Edwards AFB and other groundwater sample matrices, and as an obvious correlation was apparent between chloride and false positives for perchlorate in the first round of split sample analyses, interference studies were performed for chloride during method development.

Chloride spiking solutions were prepared from reagent grade sodium chloride. On January 18, 2001, 10 ppb, 20 ppb, and 50 ppb perchlorate standards spiked with various combinations of 50 ppm, 100 ppm, 300 ppm, 400 ppm, and 500 ppm chloride were analyzed with no pH adjustment (refer to Table 4-13). On January 22, 2001, blanks spiked with 50 ppm, 100 ppm, 300 ppm, and 500 ppm chloride were analyzed with no pH adjustment (refer to Table 4-11). Minor positive interference was noted for the blank and 10 ppb perchlorate standards, and more pronounced negative interference was noted for the 20 and 50 ppb perchlorate standards, with greater interferences at higher chloride concentrations (refer to Table 4-2A).

On January 18 and 25, 2001, blanks, 20 ppb, 40 ppb, and 70 ppb perchlorate standards spiked with 50 ppm, 100 ppm, 300 ppm, and 500 ppm chloride were analyzed with pH adjustment to 4.0 (refer to Tables 4-14 and 4-15). Positive interference was noted for the blank, 20 ppb, and 40 ppb perchlorate standards, and negative interference was noted for the 70 ppb perchlorate standard (refer to Table 4-2B).

Additional analyses of a 50 ppb perchlorate standard spiked with 50 ppm, 60 ppm, 200 ppm, 1000 ppm, and 2000 ppm chloride; as well as 200 ppm, 1000 ppm, and 2000 ppm of chloride in blank, 20 ppb and 70 ppb perchlorate standards were performed on April 24, 2001 to verify the point of inflection between positive and negative bias, and extend the range of chloride concentrations studied (refer to Table 4-16). The additional analyses confirmed levels of bias found previously for the 50-500 ppm chloride standards, and defined bias in the 500-2000 ppm chloride range. The point of inflection between positive and negative bias was confirmed to be at or marginally above 50 ppb perchlorate (refer to Table 4-2C).

The potential for significant interference of 3.0 ppb false positive (20% of the 15 ppb RL) in samples with perchlorate concentrations less than 30 ppb commences at 50 ppm chloride, and rises to 12.5 ppb false positive at 500 ppm chloride. For samples with perchlorate concentrations between 30 ppb and 50 ppb, significant interference commences at 100 ppm chloride, and rises to 7.7 ppb false positive at 500 ppm chloride. The data indicate that for samples with perchlorate concentrations above 50 ppb, chloride interference becomes negligible then causes negative bias (refer to Table 4-2C). For samples with perchlorate readings above 50 ppb, sample dilutions should be performed to determine if interference is affecting results in such a way as to affect project objectives.

The suggested method for removal of chloride is the addition of 1.0 gram of silver sulfate per 200 mL sample to all standards and samples. The addition of silver sulfate would be costly, would result in additional waste disposal problems, would create solids in the solutions which would be difficult to remove and when stirred for analysis could potentially interfere, and would generally impose unacceptable difficulties on the use of this method. Therefore, the application of correction factors to perchlorate readings according to Table 4-7 has been implemented for the low concentration method. For samples with perchlorate readings above 30 ppb, dilution and reanalysis should be performed to help resolve the proportion of bias due to interference or actual perchlorate in the samples. This table is applicable to readings using adjustment of pH to 4.0, since pH adjustment is considered part of the low concentration method.

If chloride concentrations are not available for field samples and chloride levels are suspected to be causing false positives or other unacceptable interference, a chloride ISE can be used to determine chloride with the same ISE meter used for the perchlorate determinations. Alternatively, for samples with unknown levels of chloride, analysis by MSA may be possible to compensate for unknown anion interference, especially for perchlorate readings less than 30 ppb, although further studies of the effectiveness of MSA to compensate for anion interferences are required. The use of MSA for samples with high levels of chloride may not be effective (refer to Section 4.9). Definitive-level perchlorate analyses should be performed whenever project objectives may be affected by indeterminate bias.

4.4 Nitrate Interference Studies

Nitrate is listed in ISE product literature as being an interferent for perchlorate analysis by ISE. Levels of nitrate greater than 1.5 ppm NO_3-N are not generally found in environmental samples at Edwards AFB and in many surface and groundwater sample matrices, however, an historical nitrate level of 12.6 ppm was reported for sample P-1, which had a false positive reading for perchlorate of 70.6 ppb, indicating a possible correlation between nitrate and false positives for perchlorate. Therefore, interference studies were performed for nitrate.

Nitrate spiking solutions were prepared from reagent grade sodium nitrate and from a certified 100 ppm ion chromatography calibration standard. On February 28, 2001, blanks, 10 ppb, 20 ppb, and 50 ppb perchlorate standards spiked with 0.11 ppm, 0.23 ppm, and 0.45 ppm nitrate-as-nitrogen (NO_3-N), equivalent to 0.5 ppm, 1.0 ppm, and 2.0 ppm nitrate reported as nitrate, were analyzed with pH adjustment to 4.0. In addition, a blank spiked with 1.13 ppm and 2.26 ppm NO_3-N (5 ppm and 10 ppm nitrate) were analyzed to quantitate potential false positives for higher levels of nitrate (refer to Table 4-17). Positive interference was noted for all concentrations of nitrate in all levels of perchlorate standards (refer to Table 4-3A). Note that nitrate is most commonly measured and reported in mg/L (ppm) as nitrate-as-nitrogen (NO_3-N). The same results when reported as nitrate are 4.43 times the results reported as nitrogen. All subsequent references will be to nitrate reported as nitrogen, NO_3-N.

Additional nitrate interference studies were performed on April 30 and May 1, 2001, to verify the findings of the initial study and extend the range of concentrations studied (refer to Table 4-3B). Nitrate spiking solutions were prepared from a certified 100 ppm nitrate (NO3-N) standard prepared from potassium nitrate.

Blanks and 20 ppb perchlorate standards spiked with 0.05 ppm, 0.1 ppm, 0.2 ppm, 0.5 ppm, 1.0 ppm, 2.0 ppm, 5.0 ppm, and 10 ppm NO_3-N were analyzed with pH adjustment to 4.0 (refer to Tables 4-18A and 4-18B).

The potential for significant interference of 3.0 ppb false positive (20% of the 15 ppb RL) or greater than 20% of perchlorate concentration commences at 0.12 ppm NO_3-N, and the potential for a false positive reading greater than the 15 ppb RL commences at approximately 0.5 ppm NO_3-N. In the initial study, for 0.45 ppm NO_3-N in a blank, a positive reading for perchlorate of 14.1 ppb, which is below the 15 ppb RL, was reported; and in the extended study, for 1.0 ppm NO_3-N in a blank, a 19.0 ppb perchlorate reading was reported, marginally exceeding the 18 ppb TDL and California action limit.

Note that the curves for nitrate interference were steeper in the initial study than in the follow-up extended study at all concentrations of perchlorate and nitrate (refer to Table 4-3B). Interference values for low concentrations of nitrate were within the ±20% accuracy criteria for the method in standards with up to 0.5 ppm NO_3-N for both studies. However, the initial study curve for the blank spiked with nitrate diverges significantly above 0.5 ppm NO_3-N. This divergence is caused by the two high points on this curve, which appear to exceed the predicted curve from the low points and the other initial study perchlorate standard curves. The divergences may be due to nitrate solution precision, electrode condition, temperature, or other factors affecting sensitivity, especially since perchlorate readings become significantly more sensitive to changes in millivolt readings with increasing perchlorate concentration. However, all of the curves are generally parallel, and the data indicate positive interference at all concentrations of nitrate in all concentration standards of perchlorate, with potential interference of two to five times the RL in samples with 2-10 ppm NO_3-N (refer to Table 4-3B). Due to the consistency of the interference curves for the blank and 20 ppb perchlorate standard in the extended study, these curves were used to generate the correction factors presented in Table 4-8.

There is no suggested method for removal of nitrate interference in ISE product literature. Therefore, the application of correction factors to perchlorate readings according to Table 4-8 has been implemented for the low concentration method. In addition, nitrate at concentrations greater than 0.2 ppm NO_3-N causes loss of sensitivity to the electrode between every analysis to maintain adequate sensitivity to meet ±20% accuracy criteria. Reconditioning of the ISE module in an acidified blank followed by an acidified 100-2000 ppb perchlorate solution should be implemented during analytical runs in which such levels of nitrate are expected or encountered in field samples. The effectiveness of such reconditioning was demonstrated by the acceptable recoveries for check standards analyzed between each nitrate-spiked standard during the February 28, 2001 nitrate interference studies (refer to Table 4-17).

For matrices with nitrate levels less than 0.12 ppm, positive interference for perchlorate readings will not exceed the ±20% accuracy criterion for this method and reconditioning of the electrode will not be necessary. If nitrate concentrations are not available for field samples and nitrate levels are suspected to be causing false positives or other unacceptable interference, a nitrate ISE can be used to determine nitrate with the same ISE meter used for the perchlorate determinations. Alternatively, for samples with unknown levels of nitrate, analysis by MSA may be possible to compensate for unknown anion interference, especially for perchlorate readings less than 30 ppb, although further studies of the effectiveness of MSA to compensate for anion interferences are required. The use of MSA for samples with high levels of nitrate may not be effective (refer to Section 4.9). Definitive-level perchlorate analyses should be performed whenever project objectives may be affected by indeterminate bias.

Nitrate was found to be the strongest interferent studied, and use of the low concentration method on matrices with high concentrations of nitrate, especially if significant concentrations of other known interferents are present or suspected, may not be appropriate without significant dilutions and raised detection limits.

4.5 Bromide Interference Studies

Bromide is listed in ISE product literature as being a potential interferent for perchlorate analysis by ISE; therefore, interference studies were performed for bromide. Levels of bromide producing significant perchlorate interference (greater than 1.2 ppm bromide) are not commonly found in environmental samples at Edwards AFB or in most surface and groundwater sample matrices, so bromide interference is not expected to affect the usability of the low concentration method.

Bromide spiking solutions were prepared from reagent grade potassium bromide. On March 2, 2001, blanks, 10 ppb, 20 ppb, and 50 ppb perchlorate standards spiked with 0.5 ppm, 1.0 ppm, 2.0 ppm, and 5.0 ppm bromide were analyzed with pH adjustment to 4.0 (refer to Table 4-19). Positive interference was noted for all concentrations of bromide in all levels of perchlorate standards (refer to Table 4-4). Significant positive interference (greater than 20% of the perchlorate concentration, or 20% of the 15 ppb RL for perchlorate standards less than the RL) was noted for concentrations greater than 1.2 ppm bromide. For 2.0 ppm bromide in a blank, a reading of 7.5 ppb was noted (versus 4.6 for a blank), and for 5 ppm bromide in a blank, a positive reading for perchlorate of 10.5 ppb, which is below the 15 ppb RL, was noted. For 2.0 ppm bromide in a 10 ppb perchlorate standard, a reading of 14.1 ppb was noted, and for 5.0 ppm bromide in a 10 ppb perchlorate standard, a reading of 17.8 ppb was noted, which is below the 18 ppb TDL and California action limit. Thus, the potential for a false positive perchlorate reading greater than 18 ppb due to bromide interference is minimal.

The suggested method for removal of bromide is the addition of 1.0 gram of silver sulfate per 200 mL sample to all standards and samples, which would generally impose unacceptable difficulties on the use of this method (refer to Section 4.3, above). For concentrations of bromide normally expected in environmental samples, bromide interference is not expected to significantly affect perchlorate results by this method. However, the application of correction factors to perchlorate readings according to Table 4-9 has been included for use if bromide concentrations greater than 1.2 ppm are determined to be present in samples.

For most matrices, bromide levels will be less than 1.2 ppm, and positive interference for perchlorate readings will not exceed the ±20% accuracy criterion for this method. If bromide concentrations are not available for field samples and bromide levels are suspected to be causing false positives or other unacceptable interference, a bromide ISE can be used to determine bromide with the same ISE meter used for the perchlorate determinations. Alternatively, for samples with unknown levels of bromide, analysis by MSA may be possible to compensate for unknown anion interference, especially for perchlorate readings less than 30 ppb, although further studies of the effectiveness of MSA to compensate for anion interferences are required (refer to Section 4.9). Definitive-level perchlorate analyses should be performed whenever project objectives may be affected by indeterminate bias.

4.6 Fluoride Interference Studies

Fluoride is listed in ISE product literature as being a potential interferent for perchlorate analysis by ISE; therefore, interference studies were performed for fluoride. Fluoride was determined not to produce interference for the low concentration method.

Fluoride spiking solutions were prepared from reagent grade sodium fluoride. On April 23, 2001, blanks, 10 ppb, 20 ppb, and 50 ppb perchlorate standards spiked with 0.5 ppm, 1.0 ppm, 2.0 ppm, and 5.0 ppm bromide were analyzed with pH adjustment to 4.0 (refer to Table 4-20). No positive or negative interference was noted (refer to Table 4-5). Phosphate levels normally found in environmental samples are not expected to affect the usability of the low concentration method.

4.7 Phosphate Interference Studies

Phosphate is listed in ISE product literature as being a potential interferent for perchlorate analysis by ISE; therefore, interference studies were performed for phosphate. Phosphate was determined not to produce interference for the low concentration method.

Phosphate spiking solutions were prepared from a certified 1000 ppm ion chromatography calibration standard. On February 19, 2001, blanks, 10 ppb, 20 ppb, and 50 ppb perchlorate standards spiked with 5.0 ppm, 10 ppm, and 20 ppm phosphate were analyzed with pH adjustment to 4.0 (refer to Table 4-21). No positive or negative interference was noted (refer to Table 4-6). Phosphate levels normally found in environmental samples are not expected to affect the usability of the low concentration method.

4.8 Possible Organic Chemical Interference

Additional interference from organic chemicals is also considered possible. In the analyses of sample P-11 (well 422-MW01) and recollected samples P-102, P-103, and P-104 from well 422-MW01, which have high historical levels of organic contaminants, application of high correction factors due to high levels of nitrate and chloride resulted in corrected results with negative values for perchlorate. This over-correction may be the result of less interference for combined nitrate and chloride than the sums of the individual interferences. However, the possibility of response suppression due to organic compounds must be considered.

Additional studies of complex matrices with combinations of anions, and studies of the effects of organic compounds on response suppression are recommended.

Other split samples with high known concentrations of organic contaminants were not analyzed due to the potential for deterioration of the ISE module, including high concentrations of NDMA (refer to Table 1-9). In general, samples with high concentrations of organics are not recommended for analysis by ISE as organic solvents are known to deteriorate ISE membranes.

4.9 Method of Standard Additions

The method of standard additions (MSA) incorporates the sequential addition of three increments of a standard solution (spikes) to sample aliquots of the same size. Measurements are made on the original and after each addition. The slope, x-intercept and y-intercept are determined by least-squares analysis. The analyte concentration is determined by the absolute value of the x-intercept. Regression may be performed mathematically on a programmable calculator or on a computer; or the results for the three spiked additions of perchlorate may be graphed and the resulting line or curve extended through the y-axis until it intersects the x-axis. Ideally, the spike volume is low relative to the sample volume (approximately 10% of the volume). Standard addition may counteract matrix effects, especially if such effects are constant or linear.

Due to the low concentrations achieved by the low concentration method, significant interference from known and unknown interferents may result in the need to apply multiple correction factors for samples with complex matrices. In particular, high levels of nitrate may require the application of correction factors several times the method RL. In addition, specific anion concentrations necessary for the application of the appropriate correction factors may not be available. When detected perchlorate readings are expected or suspected of being due in part, or in entirety, due to anion interference, and correction factors to be applied are unknown, the use of MSA may be useful in mitigating matrix effects.

The MSA procedure is generally able to effectively compensate for interference and produce accurate results for many methods. However, initial cursory efforts to assess the use of MSA for the low concentration method indicates that due to complex curves in the interferences for different anions, MSA may not be effective for accurate correction of significant interferences due to high nitrate and chloride. MSA may, however, be useful in determining whether perchlorate readings not significantly greater than the RL or TDL are due to interference when anion concentrations are not available.

MSA was not included in the scope of work for method development for this project. However, MSA was performed on a 20 ppb perchlorate standard spiked with 2 ppm NO_3-N on May 1, 2001, by addition of sequential 10 ppb spikes (refer to Table 4-22A). The result of 36.5 ppb perchlorate by MSA was marginally lower than the 40.8 ppb reading without correction. Subtraction of the 22.5 ppb correction factor according to Table 4-8 provides a far more accurate final result.

To determine if MSA might be useful at other levels of interference, data from interference studies performed during method development that include sequences of analyses with levels of perchlorate approximating MSA sequences were examined. These data were plotted and assessed for effectiveness of regression analysis by MSA to provide more accurate results than those determined from direct readings.

MSA regression analysis results for blanks, 0.11 ppm, 0.23 ppm, and 0.45 ppm NO_3-N standards with 10 ppb, 20 ppb, and 50 ppb perchlorate additions are presented in Table 4-22B. The MSA results indicate acceptable performance in mitigating interference due to low concentrations of nitrate. For example, the 9 ppb perchlorate result for a blank with 0.45 ppm NO_3-N is lower than the 14.2 ppb perchlorate reading for this blank. However, all of the initial perchlorate readings were below the RL and TDL, and additional data for sequences equivalent to multiple additions at higher levels of nitrate, or for perchlorate with true values greater than the RL or TDL, were not available.

Although less accurate than multiple additions, double or single additions can be performed to determine analytical results by regression, so available data for higher concentrations of nitrate (2-10 ppm NO_3-N) were plotted as single additions to assess the slopes for potential effectiveness in mitigating more significant interference (refer to Table 4-22C). The slopes and intercepts of the graphs indicate poor ability of MSA to resolve more significant nitrate interference. Thus, the use of MSA appears to have good potential only for samples with less than 1 ppm NO_3-N.

Assessment of similar data sets for chloride interference indicate acceptable ability of MSA to resolve chloride interference at low concentrations, with poor ability to resolve more significant levels of interference (refer to Table 4-23A). This appears to be exacerbated by the non-linear nature of the chloride interference (refer to Table 4-23B). However, the available data include additions of 20, 40, and 70 ppb perchlorate instead of 10, 20, and 30 ppb, so to assess the potential for smaller additions of perchlorate to improve performance, data were plotted eliminating the high point on each curve, thus more closely approximating the slopes of 10 ppb perchlorate additions (refer to Table 4-23C). These data indicate improved potential for acceptable resolution by MSA, but again, all of the initial perchlorate readings were quite low (all were below the TDL), and no data were available for higher initial readings.

To simulate higher initial readings, the data were plotted eliminating the low point on each curve, approximating the slopes of 10 ppb perchlorate additions to samples with 20 ppb perchlorate true values (refer to Table 4-23D). The projected perchlorate results by MSA become higher than the initial direct perchlorate readings as the higher readings for more significant levels of chloride and perchlorate are associated with sections of the interference curves with flatter slopes. The 17.1-29.6 ppb initial perchlorate readings for the respective 20 ppb perchlorate standards with 0-500 ppm chloride are far more accurate than the projected 28-76 ppb perchlorate respective results for these standards. This again indicates poor MSA performance for significant interference.

Thus, initial cursory assessment of the ability of MSA to resolve anion interference indicates the potential for MSA to determine whether initial perchlorate readings between 15 ppb and 30 ppb are due to positive interference, but not to be effective in resolving significant interferences associated with readings higher than 30 ppb perchlorate. This may be useful for matrices with unknown amounts of chloride and nitrate when chloride is less than 500 ppm and nitrate is less than 1 ppm NO_3-N, which is expected to include most matrices. For samples with initial perchlorate readings greater than 30 ppb, dilutions may allow useful resolution by MSA.

As only a cursory study of MSA has been included in method development to date and no in-depth study of MSA was performed, a complete study of MSA, including complex interferences due to combinations of nitrate and chloride, is recommended. In addition, because of the complex interference curves and the logarithmic nature of the calibrations, additional study of alternative regression methods is recommended to determine if better results can be achieved.

4.10 ISE Conditioning

Due to the nature of the perchlorate ISE, recharging perchlorate sites in the perchlorate ISE membrane is a routine requirement to maintain sensitivity. The perchlorate ISE requires special preconditioning prior to first use, then daily before calibration. Some anions, notably nitrate, and possibly some organic chemicals, were found to cause loss of sensitivity between analyses. During method development, sample matrices with nitrate concentrations greater than 0.2 ppm NO_3-N were found to require implementation of reconditioning between every sample. When long periods of time became necessary for millivolt readings to stabilize, or if low recoveries for check standard recoveries were encountered after analysis of field samples, reconditioning of the ISE was found to be effective in maintaining sensitivity and accuracy.

Extended exposure of perchlorate ISEs to field sample matrices will gradually diminish ISE sensitivity. When sensitivity for a specific ISE module is found to decline with extended use, Sentek recommends using an abrasive such as fine emery paper to renew the exposed PVC surface of the electrode. See manufacturer directions for this procedure. Note that exposure to samples containing organic solvents may permanently degrade the electrode membrane. Refer to Section 1.3.2.1 for details.

4.11 Interference Study Conclusions

Interference studies for the *Low Concentration Method for the Determination of Perchlorate in Aqueous Samples Using Ion Selective Electrodes* indicate that the solid state perchlorate ISE with built-in reference electrode can be used effectively to determine if perchlorate is present in waters at or above the project TDL and California action limit of 18 µg/L (ppb) in aqueous samples with low concentrations of interfering anions. Use of the method for samples with high levels of interfering anions, especially nitrate, may not be appropriate.

The method is especially useful for matrices with less than 1000 mg/L chloride and 1.5 mg/L nitrate as nitrogen (NO3-N). Correction factors must be applied for concentrations in excess of 50 mg/L chloride, 0.12 mg/L NO3-N, or 1.2 mg/L bromide, for which significant positive interference (greater than 20% of perchlorate concentration, or 20% of the 15 µg/L RL for perchlorate results less than the RL) was demonstrated. If nitrate exceeds 0.2 ppm NO_3-N, reconditioning of the electrode between every sample is necessary. Samples with uncorrected perchlorate readings less than action limits can be considered to effectively indicate lack of perchlorate if subsequent QC sample recoveries are within specified accuracy criteria. Interference due to carbonate and bicarbonate is eliminated by the acidification of all standards and samples to pH 4.0 (± 0.1) with sulfuric acid.

Samples with nitrate concentrations of 1.1 to 5.5 mg/L NO3-N cause positive bias of 15-45 µg/L perchlorate (one-to-three times the RL). The user may need to determine the maximum level of nitrate correction acceptable for project objectives if samples include high-nitrate matrices.

Analysis by the method of standard additions (MSA) was found to have the potential to compensate for anion interference, especially for perchlorate readings less than 30 µg/L. Further studies of the effectiveness of MSA to compensate for anion interferences are required.

Due to the potential for positive bias due to matrix interference, ten percent of samples analyzed by this method should generally be confirmed by definitive-level analysis, especially to confirm when application of anion-specific correction factors lower perchlorate readings to below project action limits.

4.12 Interference Study Recommendations

Further studies are recommended to reconfirm the accuracy of the chloride, nitrate, and bromide correction factors, and to study the effects of mixtures of interfering anions. Interference studies for iodide, other anions, and organic compounds are also recommended. Possible methods to mitigate nitrate interference, including use of different type or concentrations of ISA should be explored to make the method more versatile. Further studies to determine and maximize the effectiveness of MSA are required.

5.0 Task 5 – Analyses of Split Samples

This section presents the data report for the analyses of split samples according to USEPA Method 314.0 for definitive level analyses, and the *Low Concentration Method for the Determination of Perchlorate in Aqueous Samples Using Ion Selective Electrodes* for the ISE analyses.

Twenty-nine samples were collected at Edwards AFB for split sample analysis during the first semi-annual groundwater (SAGW) sampling event used for this study in December 2000, of which four samples were not analyzed due to known high concentrations of organic contaminants and one sample was not successfully analyzed as the sample was expended in method development. Thirty-five samples were collected for split sample analysis during a second SAGW sampling event in July and August 2001 and successfully analyzed. In addition, five duplicate samples were analyzed by ISE in the first SAGW event, and seven duplicate samples were analyzed by ISE in the second SAGW event.

Results for a total of 72 ISE analyses were available for split sample comparison to the definitive level results (refer to Table 5-1). Additional samples useful for split sample analyses by the low concentration ISE method were not available during regularly scheduled sampling events at Edwards AFB during the period of performance for this project. Split samples were not collected for ten percent of the samples for EPA perchlorate analysis as specified in the statement of work for this project, per instructions by EPA.

5.1 Split Sample Results

Definitive level analyses were performed by E.S. Babcock & Sons (Babcock), of Riverside, California according to EPA Method 314.0 (or CADOHS Modified EPA Method 300.0 for perchlorate). ISE analyses were performed according to the *Low Concentration Method for the Determination of Perchlorate in Aqueous Samples Using Ion Selective Electrodes* (the low concentration ISE method) developed during this project, per the Standard Operating Procedure (SOP) presented as Attachment 1of Section 3.0, above, by Earth Tech chemists in San Jose, California.

Perchlorate ISE readings were corrected for anion interference according to Tables 1-3 of the SOP (Tables 4-7 through 4-9 of this report) using historical data, where available, as specified in the method. When historical anion data were not available, anion analyses were performed by Babcock, unless the uncorrected perchlorate reading was already less than the RL, in which case anion correction was considered unnecessary. Sample location information, historical anion concentrations and correction factors, raw ISE readings and anion-corrected perchlorate ISE results, and definitive perchlorate results are presented in Table 5-1. Analytical results, including calibrations, field and QC sample ISE readings, and raw perchlorate concentrations for all ISE analytical runs for split samples, are presented in Tables 5-2 and 5-3.

5.1.1 Non-Detected Result Confirmations

Of the 72 split sample analyses, ISE results for 66 analyses were reported as non-detected at the reporting limit (RL) of 0.015 mg/L (15 µg/L, or 15 parts per billion [ppb]). All of these ISE results were confirmed as non-detected at 4 ppb or 16 ppb by the definitive level analyses (refer to Table 5-1); with the exception of one sample, its duplicate, and three additional samples subsequently collected at the well (samples P-11, P-11D, P102, P-103, and P-104) for which the definitive result was reported at 6 ppb; and one sample (sample S-4) with a reported definitive result of 18 ppb, which is at the ±20% accuracy limit specified for this method (refer to Section 1.3.1.3, above) and within the <30 RPD field precision criterion specified in Section 8.3.5 of the SOP (refer to Table 5-4). Thus, 100% of the non-detected ISE results were confirmed as non-detected within 20% of the ISE RL by definitive level split sample analysis.

Note that the anion-corrected ISE result of 10.1 ppb for sample S-4 was the only result reported as non-detected that was greater than the 10 ppb low-concentration standard for this method. In addition, sample P-1 for the well at this site-location (ED-189-MW03) was not analyzed by ISE during the first SAGW event due to high historical concentrations of organic contaminants (chloromethane at 1200 ppb, other compounds to 140 ppb). Organic contaminants are considered potentially damaging to the ISE membrane, and may be responsible for low bias in perchlorate ISE results. Although this was not investigated during method development due to the potential damage to the instruments and difficulties associated with handling such samples, several samples with high historical concentrations of organic contaminants were successfully analyzed at the end of this project, with some unusual interferences noted (refer to Section 5.2.1).

5.1.2 Detected Result Confirmations

Split sample precision is measured for detected results by the relative percent difference (RPD) between the low concentration ISE and definitive method results. Confirmation of detected results is considered excellent when split sample results meet the less-than 30 RPD criterion specified in Section 8.3.6 of the low concentration ISE method SOP.

Detected results were reported by both ISE and definitive analyses for the samples from the wells at two site-locations during both SAGW events, and at one well sampled only during the second SAGW event (refer to

Tables 5-1 and 5-4). Anion corrections were not applied to any of the ISE results for these samples due to sample dilutions.

At well ED-188-MW01, the ISE result of 126.5 ppb was confirmed by the definitive level result of 140 ppb for the second SAGW event, for an RPD of 10.1. This location was not sampled during the first SAGW event.

At well ED-196-MW01, the ISE result of 24,423 ppb was confirmed by definitive level result of 20,000 ppb for the first SAGW event, for an RPD of 19.9. For the second SAGW event, the 13,270 ppb ISE result was confirmed by field duplicate definitive level results of 36,000 ppb and 27,000 ppb, for RPDs of.92.3 and 68.2 for the split sample analyses (and an RPD of 28.6 for the definitive level field duplicate sample results).

At well ED-286-MW01, the 4336 ppb ISE result for the first SAGW event was confirmed by a definitive level result of 5900 ppb, for an RPD of 30.5. For the second SAGW event, the field duplicate ISE results of 612 ppb and 731 ppb were confirmed by field duplicate definitive level results of 920 ppb and 1100 ppb. RPDs of 22.9, 40.2, 40.3, and 57.0 can be calculated for the four possible combinations of split sample results, with RPDs of 17.7 and 17.8 for the ISE and definitive field duplicate results, respectively.

The precision for the detected split sample results noted above (refer to Table 5-4) indicates excellent confirmation of ISE detected results by the definitive method for approximately half of the samples, with lower precision for the remaining sample pairs, and confirmation of all ISE detections by definitive analysis. Changes in results at some wells may be attributable to changes in groundwater concentrations with time, or to differences in sampling techniques or screening levels used for the samples.

The results indicate acceptable overall ability of the ISE method to quantitate perchlorate at concentrations greater than 100 ppb, even at high dilutions.

5.1.3 Split Sample Result Interpretation

In general, split sample results for this project indicate acceptable reproducibility of perchlorate results by the low concentration ISE and definitive methods for the samples analyzed for this project. However, the samples available for this study were notably lacking in detectable concentrations near the target detection limit (TDL) and California action limit of 18 µg/L (18 ppb). Most of the samples were reported as non-detected at the ISE RL of 15 ppb and the definitive method RL of 4 ppb or 16 ppb (for samples diluted 4 times due to interference), or detected above 100 ppb.

The low concentration ISE method is demonstrated by the split sample analyses to be effective at determining whether perchlorate is not present at or above the 18 ppb TDL, especially when perchlorate readings are less than the TDL before anion correction factors are applied. Only one false negative was reported for anion-corrected ISE results, and the definitive result for that sample was at the 18 ppb TDL. The 37 ISE readings less than the 15 ppb RL before anion-correction indicate the potential for the method to successfully assess the lack of perchlorate in matrices free of significant anion interferences. For example, the method successfully determined lack of perchlorate in all of the samples from USGS locations (samples P-18 through P-25 and S-18 through S-25) for which no anion information was available.

However, low matrix spike recoveries indicate the possibility that low concentrations of perchlorate in environmental matrices may produce false negatives by this method (refer to Section 5-2.2, below). Therefore, for samples with uncorrected perchlorate ISE readings greater than 18 ppb with final results reported as non-detected at 15 ppb after anion correction, additional steps should be taken to determine the potential for matrix interference. This includes matrix spike analyses of the samples in question and definitive confirmation analyses, especially if the corrected readings exceed 10 ppb. For samples with uncorrected perchlorate readings above 50 ppb, sample dilutions may be appropriate to determine if interference is affecting results in such a way as to affect project objectives.

Application of the anion correction factors overcompensates for positive interference in some samples, resulting in corrected readings with negative values (refer to Table 5-1). Of the 29 non-detected anion-corrected perchlorate results with original readings greater than 18 ppb, 11 final anion-corrected readings were less than zero. All of these samples had high historical levels of multiple interfering anions, especially nitrate. This overcompensation may be due to the use of historical concentrations of anions instead of current concentrations (which were not generally available), or it may be due to the subtraction of individual correction factors for each interfering anion, whereas interference for multiple anions may be less than the sum of the interference for each anion studied separately. Additional study of the effects and ways to compensate for the presence of multiple interfering anions is recommended.

In addition to effective determination of lack of perchlorate at the 18 ppb TDL in low nitrate matrices, the low concentration ISE method was demonstrated by the split sample analyses to be effective at determining perchlorate concentrations significantly above 18 ppb, especially for concentrations above 100 ppb, for which minimal dilutions of five times can be used to eliminate interference.

5.2 Quality Control Results for ISE Analyses

Overall, the low concentration ISE method demonstrates the ability to perform within the QC limits specified in the SOP for laboratory accuracy and precision. Results for matrix precision were acceptable; however significant variations in matrix-specific accuracy indicate the sensitivity of the method to matrix interferences.

5.2.1 Calibration Verification

Initial and continuing calibration verifications (ICVs and CCVs) and laboratory control samples (LCS) were analyzed before, during, and after sample analyses, as specified in the low concentration ISE method SOP. Recoveries were generally maintained within the ±20% accuracy criterion for the method (refer to Tables 5-2 and 5-3). When verifications exceeded the specified criteria, reconditioning or recalibration and reanalysis of affected samples was generally performed.

Low recoveries tended to occur with continuing use during long analytical runs, especially during the analysis of samples with more complex matrices, including samples with high concentrations of nitrate or organic compounds. This effect is most likely due to perchlorate site-blocking in the ISE membrane (refer to Section 1.3.2.1, above), which was mitigated by the implementation of ISE module reconditioning, as specified in Section 10.2 of the low concentration ISE method SOP.

5.2.2 Matrix Spike Recoveries

Matrix spike analyses were performed at an approximate frequency of one-per 20 field samples for the ISE analyses. Results generally indicate appropriate increases in perchlorate readings for samples with low levels of anion and organic interferents (samples P-5 and P-7), whereas for samples with high levels of nitrate (sample P-11), matrix spike recoveries were inconsistent (refer to Table 5-5). The anion corrected results for these samples do not indicate detectable recoveries of spikes after anion-correction, except when anion concentrations are extremely low, such as in sample P-5 for well ED-196-MW01.

For the MS analyses of samples S-2 (diluted five-fold) and S-29 from wells ED-188-MW01 and ED-286-MW03, respectively, unusual interferences were noted. Matrix spike recoveries varied from over 1000%

recovery to non-detection at different times for the same spiked samples. The samples were respiked and reanalyzed from different spiking solutions with similar results (refer to Table 5-3C). In addition, the pH for samples S-2 and S-2MS from ED-188-MW01 increased back to pH 8 after initial acidification, indicating complex matrix effects possibly related to chemical reaction balances between organic compounds and carbonate/bicarbonate species in this sample. Sample S-2 is known to contain Freon 113 at 21 ppb, whereas sample S-29 does not contain known concentrations of volatile organic compounds (VOCs). Concentrations of interfering anions or non-VOC organic compounds are unknown for both samples. Additional study of these matrices is recommended.

The MS analyses confirm the usability of the low concentration ISE method for samples with low levels of interfering anions and organic compounds, while reinforcing the understanding that the method may not be appropriate for complex matrices due to interference at the extreme sensitivity required to accurately determine perchlorate at the 18 ppb TDL.

5.2.3 Field and Laboratory Duplicate Precision

Field and laboratory precision for the low concentration ISE method was acceptable for all analyses. Field duplicate samples prepared from separate sample containers collected in the field, and for laboratory replicate reanalyses of samples prepared from the same sample container indicate excellent precision for the low concentration ISE method. All field and laboratory duplicate and replicate analyses were within the ≤20 RPD criterion for laboratory precision and the ≤30 RPD criterion for field precision specified in Sections 8.3.4 and 8.3.5, respectively, of the low concentration ISE method SOP (refer to Table 5-6).

5.2.4 Method and Equipment Blanks

Equipment blanks were analyzed by the low concentration ISE method for both SAGW events (refer to samples P-13 and S-3 in Table 5-1), and method blanks were analyzed before, during, and after sample analyses as initial and continuing calibration blanks (ICBs and CCBs). All raw perchlorate readings for blanks were less than one-half the 15 ppb RL, and were generally below 5 ppb.

Method and equipment blank results indicate that false positives due to carry-over contamination are not likely for the low concentration ISE method.

5.2.5 ISE Module Reconditioning

The use of ISE conditioning, as described in Section 10.2 of the low concentration ISE method SOP was found to be an effective aid to maintaining precision and accuracy. For samples with low concentrations of nitrate and organic contamination, only preconditioning was required. For samples with high concentrations of nitrate and for samples with organic contamination, successful analyses were performed using more rigorous reconditioning of the perchlorate module in 500 ppb perchlorate solutions and acidified blanks between every field and QC sample analysis.

5.3 Split Sample Study Conclusions

Analyses performed according to the *Low Concentration Method for the Determination of Perchlorate in Aqueous Samples Using Ion Selective Electrodes* according to the SOP presented in Attachment 1 of Section 3.0, above, are in general agreement with definitive analyses performed by a fixed based laboratory using EPA Method 314.0.

Uncorrected perchlorate readings measured by the low concentration ISE method at less than the 15 ppb RL can reliably be considered to indicate non-detection within 20% of the reported concentration. For perchlorate readings above 15 ppb, correction according to Tables 1-3 of the SOP (Tables 4-7, 4-8, and 4-9 of this document) for positive interference due to interfering anions appears to be an effective method for accurately compensating for such interference in samples with low-to-moderate concentrations of anions. However, in samples with complex matrices, including samples with chloride above 500 ppm, bromide above 3.0 ppm, and especially nitrate-as-nitrogen (NO_3-N) above 1.0 ppm, or combinations thereof, anion-correction loses accuracy, and overcompensation may result in false negatives for such matrices. In addition, the presence of organic contaminants may cause interference.

The use of reconditioning routines reduces some forms of matrix interference. Matrix spike analyses may be used to resolve the potential for false negatives in specific samples or matrices. Otherwise, to mitigate such effects in samples with complex matrices, dilutions of five-times or more is recommended, effectively raising the useful detection limit to 50-75 ppb perchlorate. In cases where significant corrections to uncorrected readings lower final results to below project action limits, the data user may decide that definitive-level analyses are required to confirm the presence or absence of perchlorate, or to confirm bias due to chloride, nitrate, or other interferents.

The low concentration ISE method appears to be useful for determining the presence of perchlorate at concentrations above 100 ppb. Such results are best quantitated at dilutions of five-times or more, which effectively reduces potential interference, although accuracy may vary with matrix and dilution technique. For samples with perchlorate concentrations above 700 ppb, the low concentration method was found to be acceptable, but is not required, as such concentrations are within the manufacturer-specified detection range for perchlorate ISEs, and the standard ISE techniques described in ISE product literature become applicable.

In general, the low concentration ISE method can be effectively used to determine the presence or absence of perchlorate at the 18 ppb TDL and California action limit in samples with low concentrations of the interfering anions chloride, nitrate, and, to a lesser extent, bromide. Samples with high concentrations of these anions require more specific knowledge of anion concentrations, should be analyzed with more frequent matrix spike analyses, may require additional dilutions, and should be confirmed by definitive analysis at a higher frequency. Samples with confirmed presence of organic contaminants may be subject to additional interferences and may damage the ISE membrane.

5.4 Split Sample Study Recommendations

Further studies are recommended to determine more accurate compensation for samples with mixtures of interfering anions. Additional methods to mitigate nitrate interference should be explored to make the method more versatile. More study of samples with confirmed presence of organic contaminants is also recommended, although ISE membrane deterioration may occur.

SECTION 1 Tables

TABLES 1-1 THROUGH 1-9

Table 1-1 Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

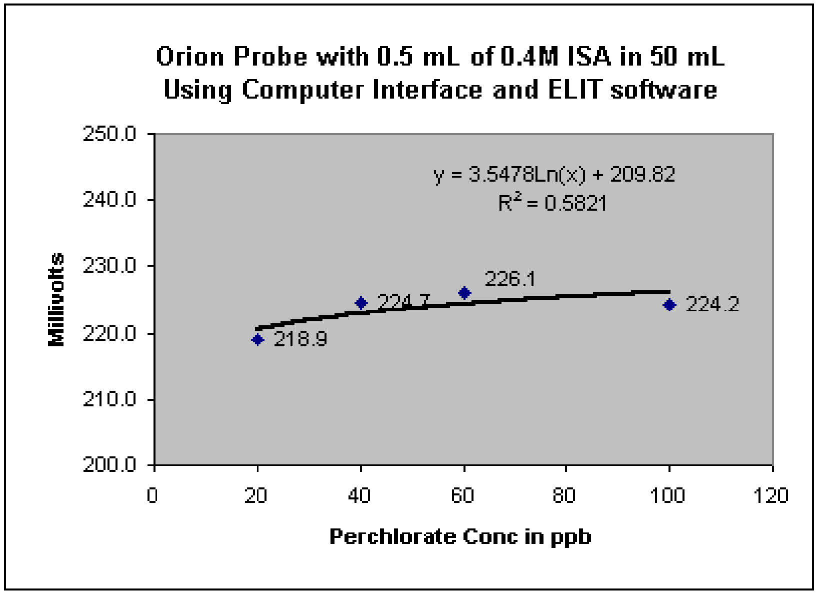
Matrix: Water Units: ug/L (ppb) Extraction/Digestion: None

Analyst: Earth Tech, Inc. Date: January 2, 2001

Computer Interface: LAVAL ELIT 8804

Instrument:

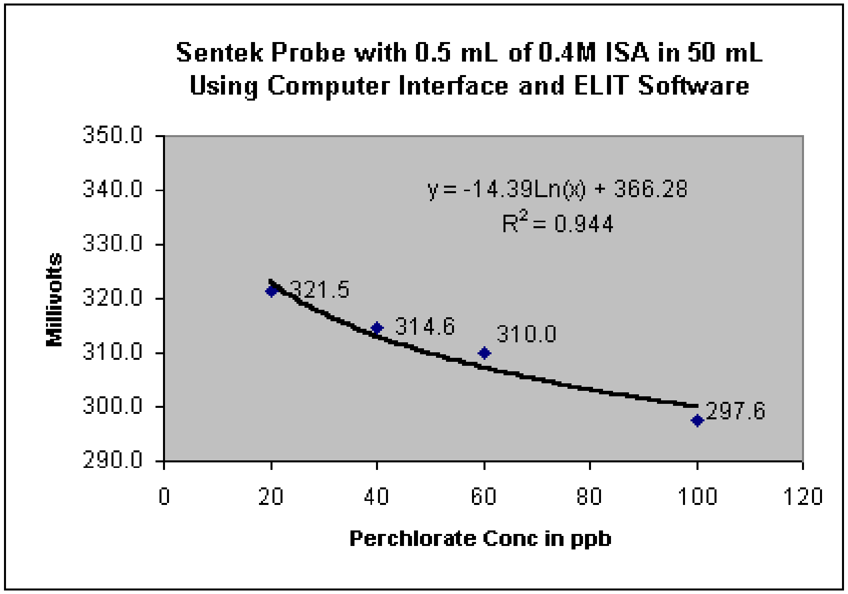
Orion 938101 Plastic Membrane Half-Cell Perchlorate ISE with Double Junction Reference Electrode



Sample/Calibration ID	Sample Volume	Millivolts Reading	Concentration in ppb
20	200 mL	218.9	Not Calculated
40	200 mL	224.7	Not Calculated
60	200 mL	226.1	Not Calculated
100	200 mL	224.2	Not Calculated
Calibration Date		**1/2/2001**	

Instrument:

Sentek 367-75 Solid State Perchlorate Combination ISE with Built-in Reference Electrode



Sample/Calibration ID	Sample Volume	Millivolts Reading	Concentration in ppb
20	200 mL	321.5	22.4
40	200 mL	314.6	36.3
60	200 mL	310.0	50.1
100	200 mL	297.6	118.0
Calibration Date		**1/2/2001**	

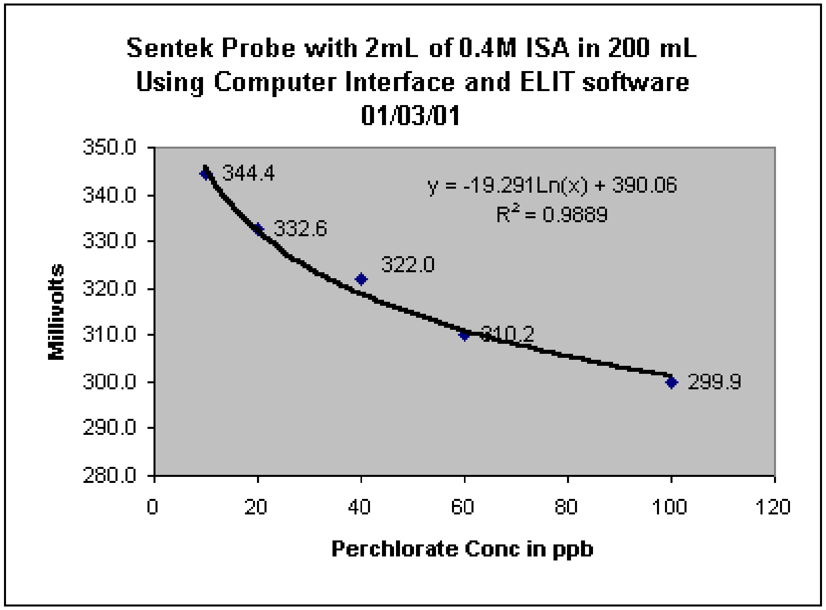
Table 1-2 Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water Units: ug/L (ppb) Extraction/Digestion: None

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

Analyst: Earth Tech, Inc. Date: January 3, 2001

Laval ELIT 8804 Computer Interface

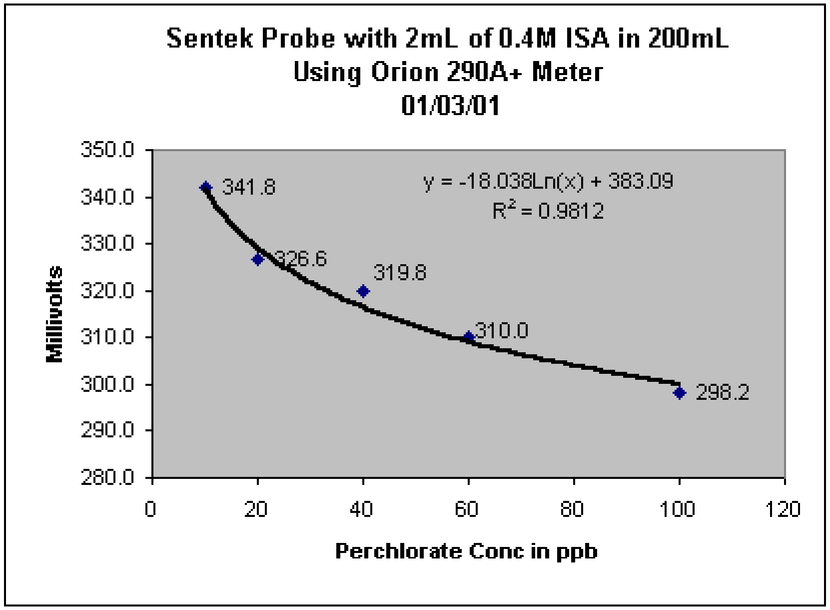


Sentek Probe with 2mL of 0.4M ISA in 200 mL
Using Computer Interface and ELIT software
01/03/01

Sample/Calibration ID	Sample Volume	Millivolts Reading	Concentration in ppb
10	200 mL	344.4	10.7
20	200 mL	332.6	19.7
40	200 mL	322.0	34.0
60	200 mL	310.2	62.7
100	200 mL	299.9	107.0

Calibration Date & Time **01/04/01 2:25pm**

Orion 290A Advanced Portable Meter



Sentek Probe with 2mL of 0.4M ISA in 200mL
Using Orion 290A+ Meter
01/03/01

Sample/Calibration ID	Sample Volume	Millivolts Reading	Concentration in ppb
10	200 mL	341.8	9.9
20	200 mL	326.6	22.9
40	200 mL	319.8	33.4
60	200 mL	310.0	57.5
100	200 mL	298.2	110.6

Calibration Date & Time **01/04/01 2:25pm**

Table 1-3 Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

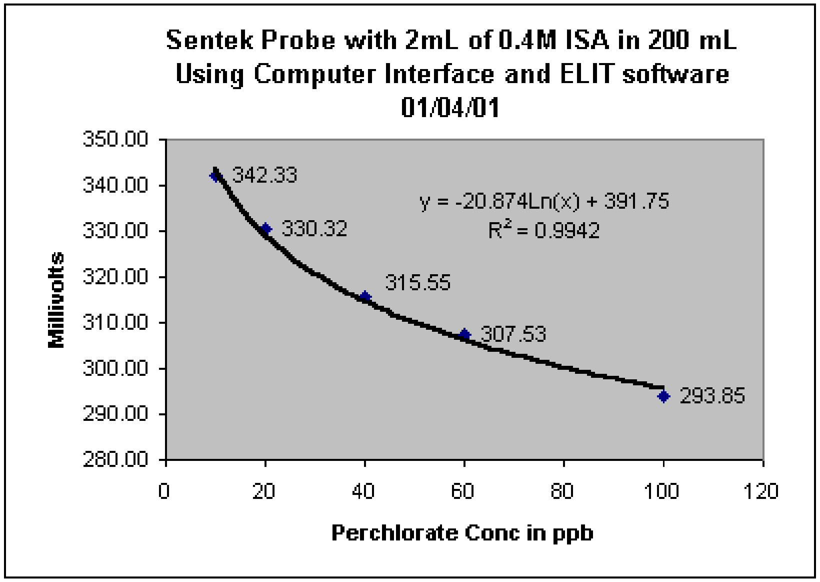
Matrix: Water Units: ug/L (ppb) Extraction/Digestion: None

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

ISA: 2 mL of 0.4M Ammonium Sulfate ISA in 200 mL of Standard, No pH Adjustment

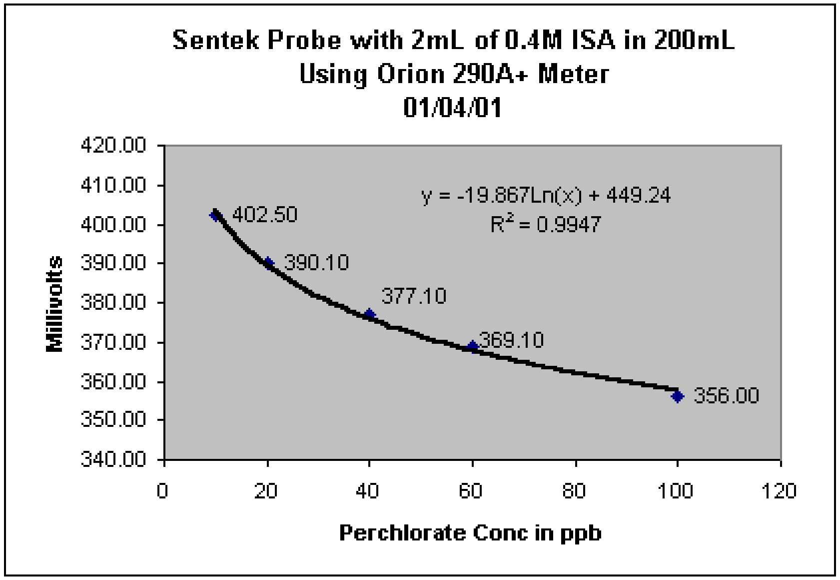
Analyst: Earth Tech, Inc. Date: January 4, 2001

Laval ELIT 8804 Computer Interface


Sentek Probe with 2mL of 0.4M ISA in 200 mL
Using Computer Interface and ELIT software
01/04/01

Sample/Calibration ID	Sample Volume	Millivolts Reading	Concentration in ppb
10	200 mL	342.33	10.67
20	200 mL	330.32	18.97
40	200 mL	315.55	38.49
60	200 mL	307.53	56.53
100	200 mL	293.85	108.86

Orion 290A Advanced Portable Meter


Sentek Probe with 2mL of 0.4M ISA in 200mL
Using Orion 290A+ Meter
01/04/01

Sample/Calibration ID	Sample Volume	Millivolts Reading	Concentration in ppb
10	200 mL	402.50	10.51
20	200 mL	390.10	19.62
40	200 mL	377.10	37.76
60	200 mL	369.10	56.48
100	200 mL	356.00	109.20

Calibration Date & Time		01/04/01 2:25pm	
Sample ID	**Sample Volume**	**Millivolts Reading**	**Concentration in ppb**
LCS/ICV	200 mL	308.39	54.60
MB/ICB	200 mL	388.12	1.19
MDL1	200 mL	328.05	**21.26**
MDL2	200 mL	326.55	**22.84**
MDL3	200 mL	327.02	**22.33**
MDL4	200 mL	328.54	**20.76**
MDL5	200 mL	326.65	**22.73**
MDL6	200 mL	328.09	**21.21**
MDL7	200 mL	327.74	**21.57**
MDL8	200 mL	326.94	**22.42**
MDL9	200 mL	328.53	**20.77**
MDL10	200 mL	327.75	**21.56**
CCV	200 mL	328.52	20.78
CCB	200 mL	392.13	0.98

Calibration Date & Time		01/04/01 2:25pm	
Sample ID	**Sample Volume**	**Millivolts Reading**	**Concentration in ppb**
LCS/ICV	200 mL	370.23	53.35
MB/ICB	200 mL	439.37	1.64
MDL1	200 mL	387.78	**22.06**
MDL2	200 mL	386.99	**22.95**
MDL3	200 mL	387.23	**22.67**
MDL4	200 mL	389.06	**20.68**
MDL5	200 mL	388.76	**20.99**
MDL6	200 mL	389.12	**20.62**
MDL7	200 mL	388.54	**21.23**
MDL8	200 mL	388.26	**21.53**
MDL9	200 mL	388.99	**20.75**
MDL10	200 mL	388.51	**21.26**
CCV	200 mL	388.76	20.99
CCB	200 mL	444.37	1.28

Data highlighted in bold used for MDL calculations

Perchlorate MDL Study: Sentek ISE with 1 mL of 0.4M ISA in 200mL, No pH Adjustment

Mean	**21.75**
Std Dev.	**0.780**
T-Value	**2.821**
Calculated MDL*	**2.2**
Reported MDL	**3**
%RSD	**0.0359**
MDL Qualifier notes	**Valid MDL Data**

Mean	**21.47**
Std Dev.	**0.829**
T-Value	**2.821**
Calculated MDL*	**2.3**
Reported MDL	**3**
%RSD	**0.0386**
MDL Qualifier notes	**Valid MDL Data**

* According to 40 CFR Part 136, Appendix B

Table 1-4 Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water Units: ug/L (ppb) Extraction/Digestion: None

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

ISA: 1 mL of 0.1M Sodium Acetate ISA in 200 mL of Standard, pH Adjustment to 4.0 with Sulfuric Acid

Analyst: Earth Tech, Inc. Dates: January 24-29, 2001

Perchlorate MDL Study: Sentek ISE with 1 mL of 0.1M ISAB in 200mL Using Orion 290A+ Meter, pH 4.0

Sample ID	Date Analyzed	Result (ppb)
MDL-1	01/24/01	18.80
MDL-2	01/24/01	18.47
MDL-3	01/25/01	20.42
MDL-4	01/25/01	20.66
MDL-5	01/25/01	19.73
MDL-6	01/25/01	19.28
MDL-7	01/26/01	21.23
MDL-8	01/26/01	20.00
MDL-9	01/26/01	20.94
MDL-10	01/26/01	21.04
MDL-11	01/26/01	20.56
MDL-12	01/29/01	20.57
MDL-13	01/29/01	18.97
MDL-14	01/29/01	21.37
MDL-15	01/29/01	19.90

Mean	20.13
Std Dev.	0.918
T-Value	2.624
Calculated MDL*	2.4
Reported MDL	3
% RSD	0.0456
MDL Qualifier notes	Valid MDL Data

* According to 40 CFR Part 136, Appendix B

Table 1-5 Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water Units: ug/L (ppb) Extraction/Digestion: None

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

Analyst: Earth Tech, Inc. Date: January 29, 2001

Standard Used: 20 ppb with 1 mL ISAB in 200 mL, pH 4.0

Temperature	Millivolts	Concentration (ppb)
10.0	292.2	99.3
10.5	293.4	93.8
11.0	295.3	85.7
11.5	296.5	80.9
12.0	297.6	76.8
12.5	298.9	72.2
13.0	300.6	66.5
13.5	301.7	63.1
14.0	302.7	60.2
14.5	303.6	57.7
15.0	304.6	55.0
15.5	305.9	51.7
16.0	306.8	49.5
16.5	307.9	47.0
17.0	308.9	44.8
17.5	310.1	42.3
18.0	310.9	40.7
18.5	311.8	39.0
19.0	312.9	37.0
19.5	314.2	34.8
20.0	315.5	32.7
20.5	316.4	31.3
21.0	317.2	30.1
21.5	318.9	27.8
22.0	320.1	26.2
22.5	321.0	25.1
23.0	321.8	24.2
23.5	322.5	23.4
24.0	323.5	22.3
24.5	324.3	21.5
25.5	325.9	19.9
27.5	329.6	16.7
30.5	338.9	10.7
32.5	340.9	9.7

Change in Perchlorate Concentration with change in Temperature

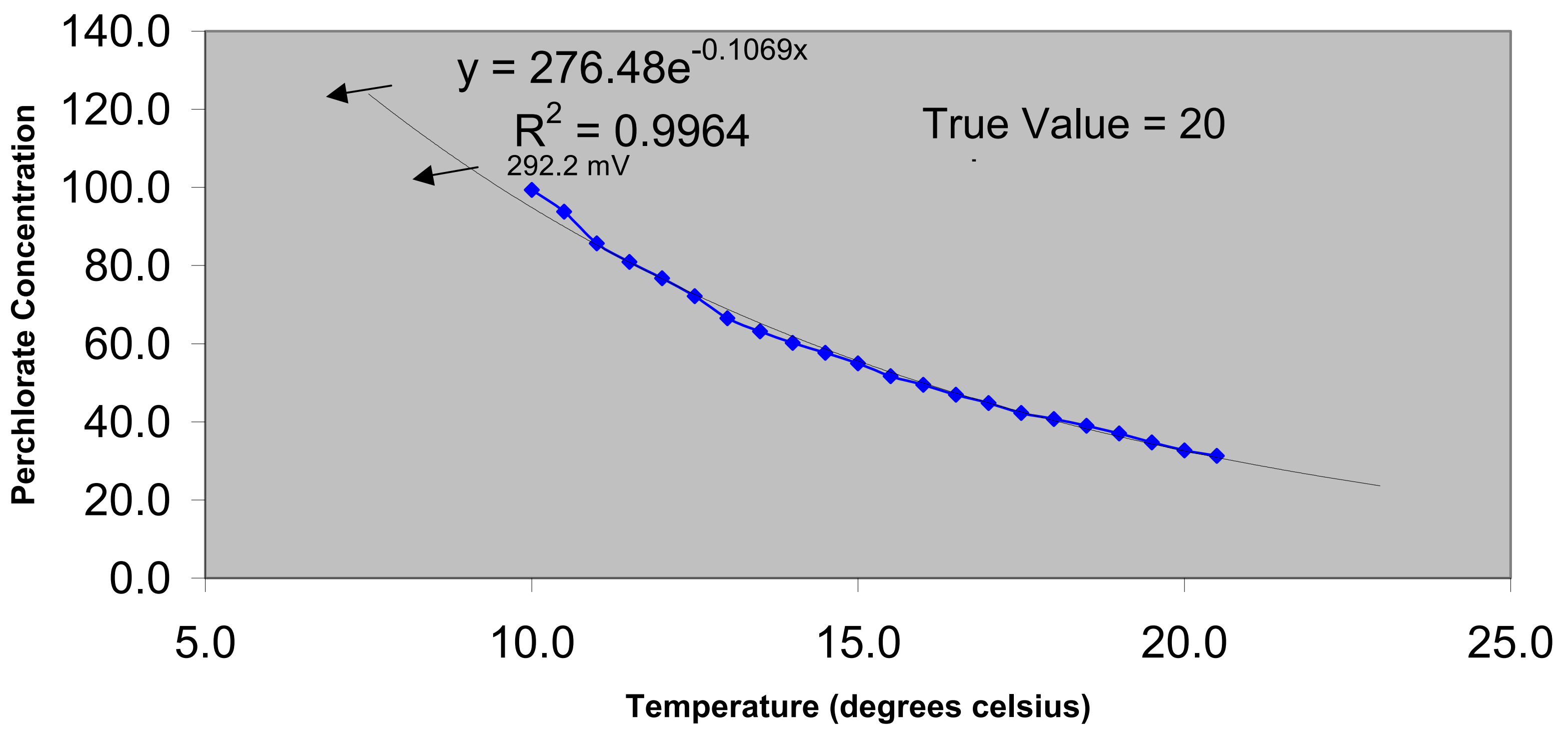


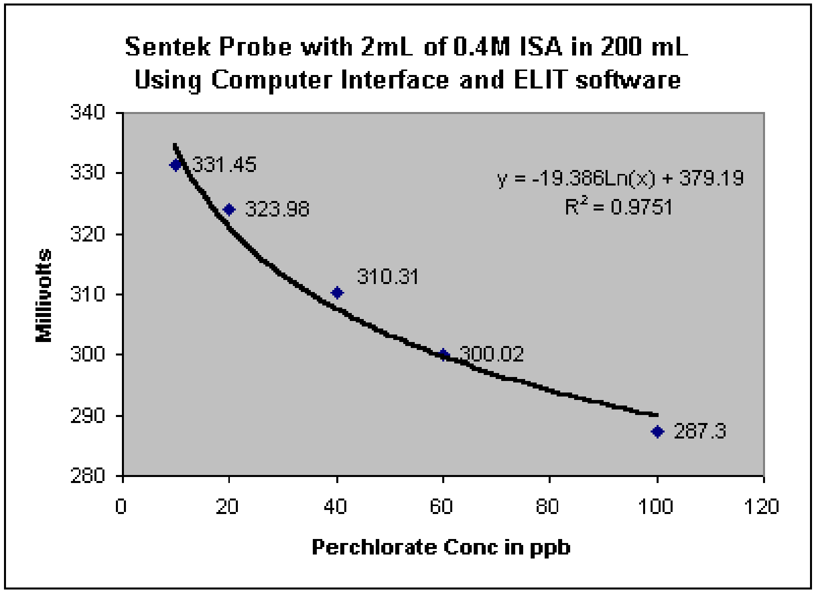
Table 1-6 Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water Units: ug/L (ppb) Extraction/Digestion: None

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

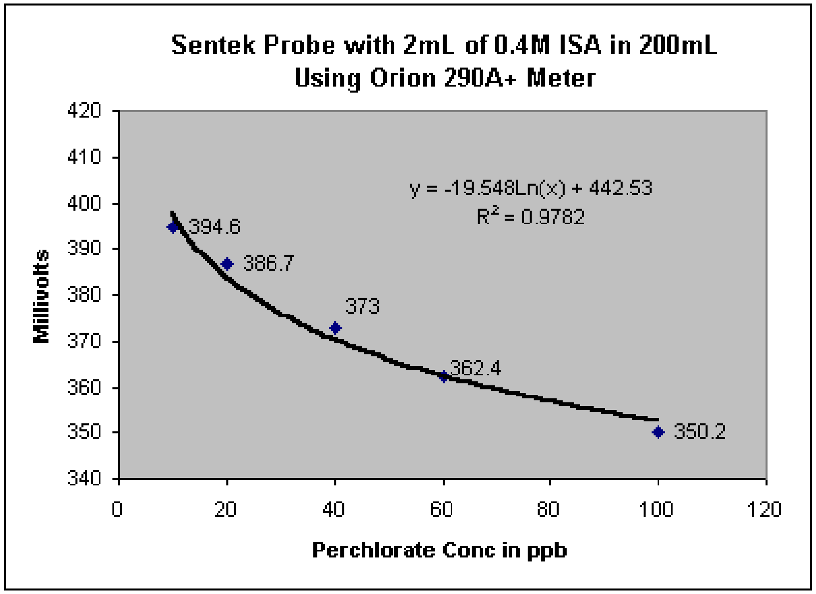
Analyst: Earth Tech, Inc. Date: January 9, 2001

Laval ELIT 8804 Computer Interface



Sample ID/ Calibration	Sample Volume	Millivolts Reading	Concentration in ppb
10	200 mL	331.45	11.7
20	200 mL	323.98	17.3
40	200 mL	310.31	34.9
60	200 mL	300.02	59.4
100	200 mL	287.3	114.4
Calibration Date & Time		**1/9/2000**	5:15pm
Temperature	**16^{0}C**		

Orion 290A Advanced Portable Meter



Sample ID/ Calibration	Sample Volume	Millivolts Reading	Concentration in ppb
10	200 mL	394.6	11.6
20	200 mL	386.7	17.4
40	200 mL	373	35.1
60	200 mL	362.4	60.3
100	200 mL	350.2	112.5
Calibration Date & Time		**1/9/2000**	5:15pm
Temperature	**16^{0}C**		

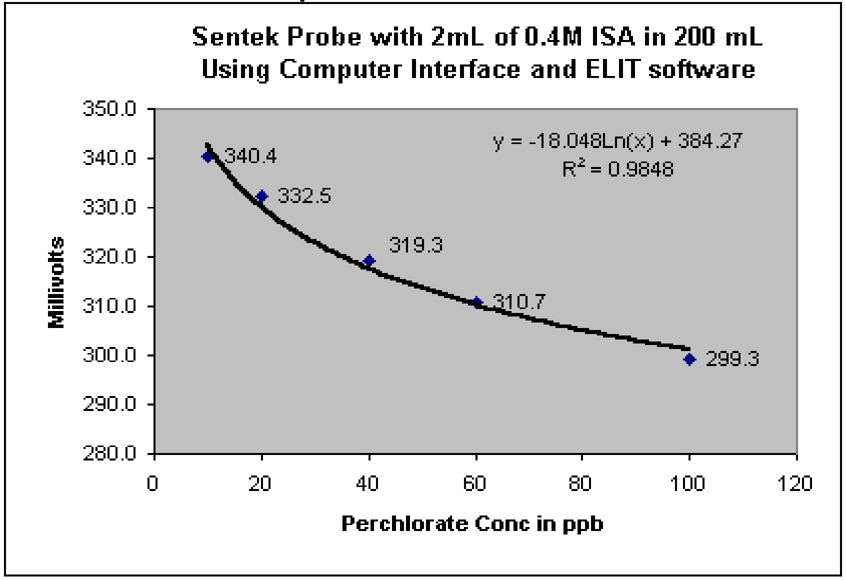
Table 1-7 Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water Units: ug/L (ppb) Extraction/Digestion: None

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

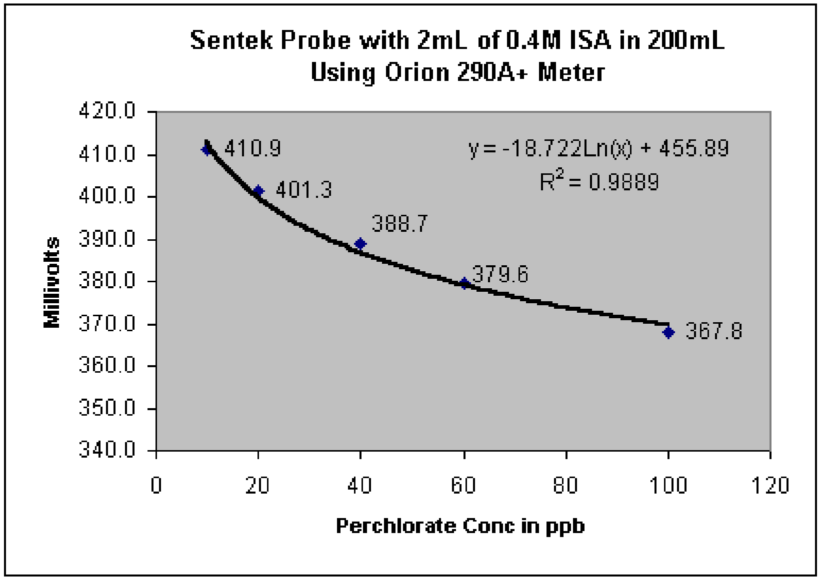
Analyst: Earth Tech, Inc. Date: January 10, 2001

Laval ELIT 8804 Computer Interface



Sample/Calibration ID	Sample Volume	Millivolts Reading	Concentration in ppb
10	200 mL	340.4	11.3
20	200 mL	332.5	17.6
40	200 mL	319.3	36.7
60	200 mL	310.7	58.8
100	200 mL	299.3	111.1
Calibration Date & Time		**1/10/2001**	2:32pm
Temperature	**21^0C**		
Slope	**18.048**	**Intercept**	384.27

Orion 290A Advanced Portable Meter



Sample/Calibration ID	Sample Volume	Millivolts Reading	Concentration in ppb
10	200 mL	410.9	11.1
20	200 mL	401.3	18.5
40	200 mL	388.7	36.2
60	200 mL	379.6	58.8
100	200 mL	367.8	110.5
Calibration Date & Time		**1/10/2001**	2:32pm
Temperature	**21^0C**		
Slope	**18.722**	**Intercept**	455.89

Sample ID	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV	200 mL	315.4	**45.5**
MB/ICB	200 mL	357.8	**4.3**
5 ppb	200 mL	353.9	**5.4**
MDL 1 (20 ppb)	200 mL	332.8	17.3
P-1	200 mL	307.9	68.8
MDL2	200 mL	332.1	18.0
P-6	200 mL	322.1	31.3
P-21	200 mL	326.4	**24.7**
P-10 (1:200)	200 mL	339.9	11.7
P-10 (1:200)+20ppb ms	200 mL	328.3	22.2
MDL 3 (20 ppb)	200 mL	336.2	14.4
100ppb	200 mL	298.26	117.4

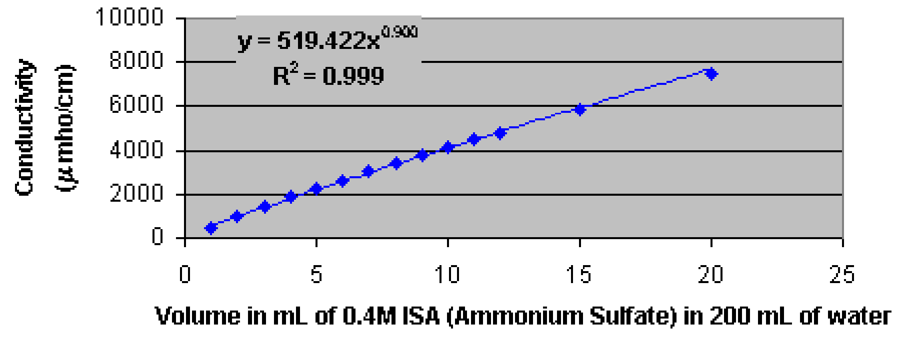
Sample ID	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV	200 mL	384.1	**46.3**
MB/ICB	200 mL	425.4	**5.1**
5 ppb	200 mL	420.8	**6.5**
MDL 1 (20 ppb)	200 mL	400.8	19.0
P-1	200 mL	376.2	70.6
MDL2	200 mL	400.7	19.1
P-6	200 mL	395.0	25.9
P-21	200 mL	393.7	**27.7**
P-10 (1:200)	200 mL	408.8	12.4
P-10 (1:200)+20ppb ms	200 mL	397.5	22.6
MDL 3 (20 ppb)	200 mL	403.9	16.1
100ppb	200 mL	365.9	122.3

Highlighted data are referenced in Section 1.3.2.4 of the report.

Table 1-8 Conductivity Levels for Ionic Strength Adjustor Solutions for Low-Level Perchlorate Analysis

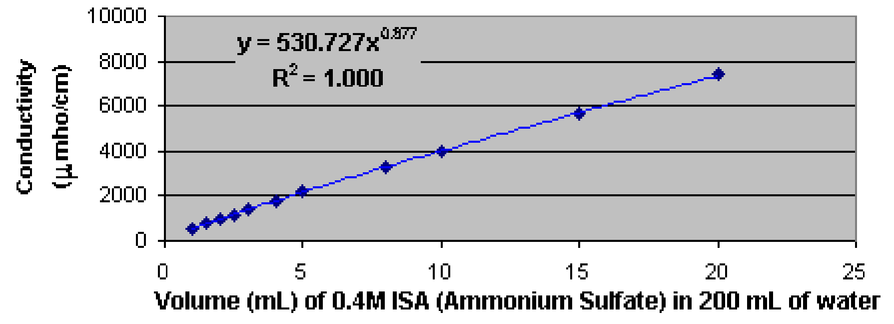
mL 0.4M ISA per 200 mL Sample, No pH Adjustment	Conductivity in µS/cm
1	493
2	980
3	1423
4	1849
5	2250
6	2650
7	3030
8	3400
9	3760
10	4120
11	4460
12	4800
15	5870
20	7450

Table 1-8A: Conductivity/ISA Relationships
No pH Adjustment 01/08/01



mL ISA per 200 mL Sample, Sulfuric Acid to pH 4.0	Conductivity in µS/cm
1	529
1.5	759
2	974
2.5	1193
3	1398
4	1795
5	2180
8	3260
10	3940
15	5700
20	7460

Table 1-8B: Conductivity/ISA Relationships
pH Adjusted to 4 with Sulfuric Acid 05/01/01



Conductivity Levels for Ionic Strength Adjustor Solutions for Low-Level Perchlorate Analysis

mL 1.0M ISAB per 200 mL Sample, No pH Adjustment	Conductivity in µS/cm
0.5	84
1	164
1.5	242
2	319
2.5	394
3	469
4	615
5	756
6	894
8	1163
10	1420
15	2020
20	2590

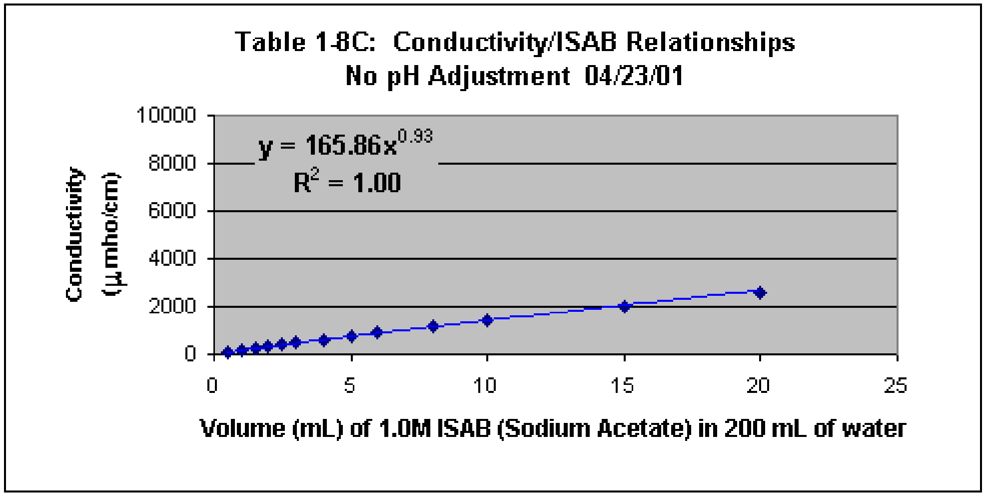


Table 1-8C: Conductivity/ISAB Relationships
No pH Adjustment 04/23/01

mL ISAB per 200 mL Sample, Sulfuric Acid to pH 4.0	Conductivity in µS/cm
1	280
1.5	371
2	471
2.5	574
3	683
4	844
5	1023
8	1496
10	1800
15	2580
20	3360

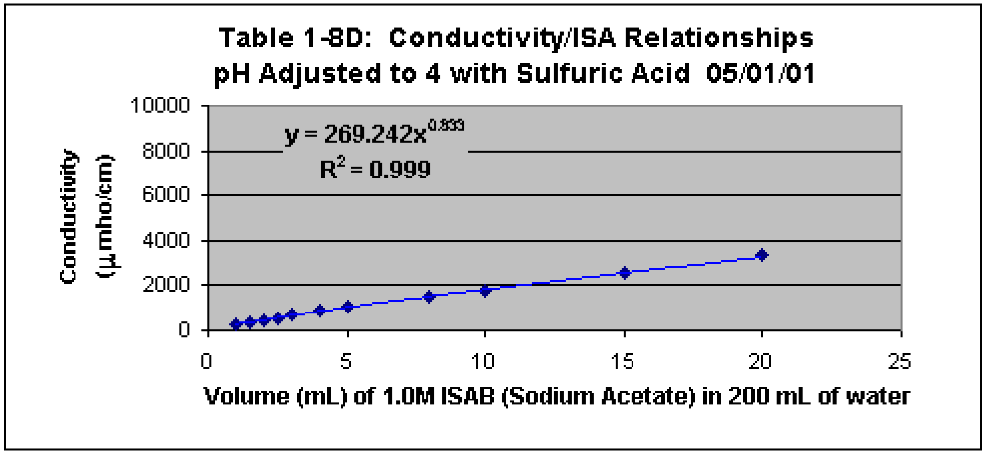


Table 1-8D: Conductivity/ISA Relationships
pH Adjusted to 4 with Sulfuric Acid 05/01/01

Table 1-9

Definitive Result RL (ppb)	Field ID	ID	Conductivity (uMhos/cm)	Other Known Interferents** Anions and TOC in (ppm); Organic compounds in ppb
4	ED-NM-MW01A-W11	P-13	1.47	EB
4	ED-NM-MW03A-W07	P-15	417	F = 0.82, PO4 = 3.1, NO3-N = 0.4, TOC = 0.47
4	ED-NM-MW02A-W11	P-14	430	F = 1, PO4 = 1.2
4	ED-USGS-W1AE4-W05	P-21	432	Not Available
4	ED-USGS-W1AE2-W06	P-20	433	Not Available
4	ED-NM-MW06-W06	P-18	435	TOC = 0.5
4	ED-USGS-W1C4-W09	P-25	482	Not Available
4	ED-USGS-W1C2-W08	P-23	728	Not Available
4	ED-199-MW01-W14	**P-8**	**796**	
4	ED-NM-MW04B-W13	**P-16**	**805**	Br = 0.4, F = 0.9, PO4 = 5.4, TOC = 0.29
4	ED-USGS-W1C3-W08	P-24	823	Not Available
4	ED-USGS-W1C1-W07	P-22	955	Not Available
4	ED-NM-MW01A-W10	P-12	1012	B r= 0.36, F = 0.98, PO4 = 15, TOC = 1.2, NO3-N = 0.1
16	ED-NM-MW05-W14	P-17	1031	Contains high levels of organic contaminants
400	ED-286-MW01-W08	P-10	1201	Br <1, F <1
4	ED-285-MW02-W06	**P-9**	**1337**	NO3-N = 0.18, Br = 0.76, F <1
16	ED-196-MW06-W15	**P-7**	**1345**	Br = 1.4, F = 0.64, NO3-N = 1.4, PO4 <0.1
4	ED-NM-MW07-W11	**P-19**	**1363**	Br = 1.4, NO3-N = 0.14, PO4 = 0.13, TOC = 12.4
4000	ED-196-MW01-W09	P-5	1426	Br = 1.2, F = 0.8, PO4, NO3-N < 0.2
4	ED-196-MW03-W11	**P-6**	**1671**	Br =1.1, F = 0.7, PO4 = 0.14, NO3-N = 0.17; toluene=44 ppb
16	ED-189-MW03-W08	P-4	1813	Contains high levels of organic contaminants
16	ED-189-MW02-W13	P-3	1948	Contains high levels of organic contaminants
16	ED-189-MW01-W25	P-2	2100	Contains high levels of organic contaminants
16	ED-189-MW01-W24	P-1	2100	NO3-N = 12.6, Br = 1.0, F = 0.8; high levels of organic contaminants
4	ED-422-MW01-W07	P-11	2190	Br = 1.3, F<1, NO3-N = 6.3, Cl = 500 Contains high levels of organic contaminants: 11DCA@1.1, FC113@ 9.4, cis12DCE@8.4,TCE@11,TIC@16 (ppb)
	ED-422-MW01-W07-RE1	P-102	NA	
	ED-422-MW01-W07-RE2	P-103	NA	
4	ED-422-MW01-W07-RE3	P-104	NA	

**Known intrferents determined from historical data for specified wells from previous sampling events. Not all methods and analytes were performed at each location.

EB=Equipment Bank
Br=Bromide
Cl=Chloride
F=Fluoride

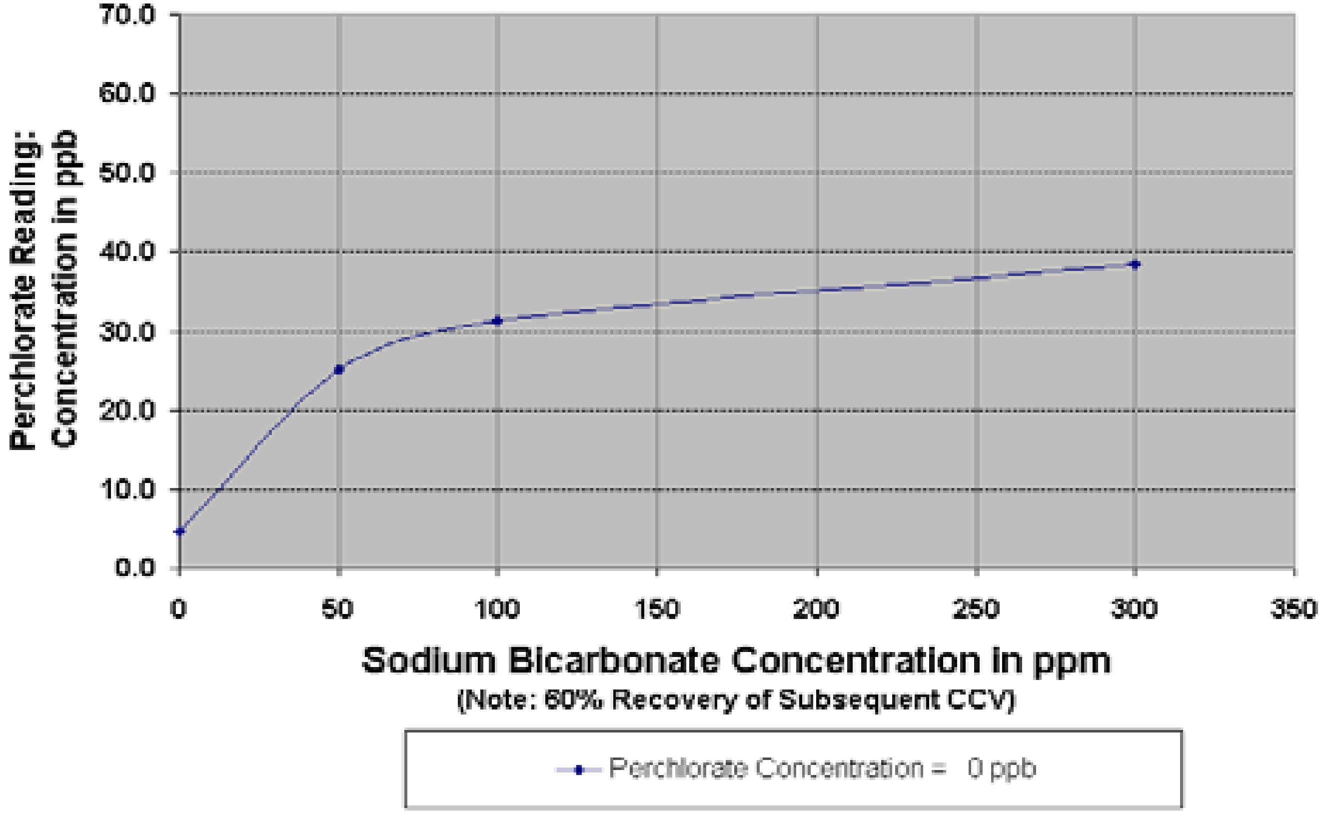
NO3=Nitrate as nitrogen
PO4=Phosphate
TOC=Total Organic Carbon
ppb=parts per billion (µg/L)
ppm=parts per million (mg/L)

11DCA=1,1-Dichloroethane
cis 12DCE= *cis*-1,2-Dichloroethene
FC113=Freon 113
TCE=Trichloroethene
TIC=Tentatively Identified Compound

SECTION 4 TABLES

TABLES 4-1 THROUGH 4-23

Table 4-1A: Effect of Carbonate/Bicarbonate Interference on Perchlorate ISE Readings: 50/100/300 ppm Bicarbonate (pH=8.0/8.4/8.7)



ISE = Ion Selective Electrode ppb = parts per billion (µg/L) ppm = parts per million (mg/L) CCV = Continuing Calibration Verification

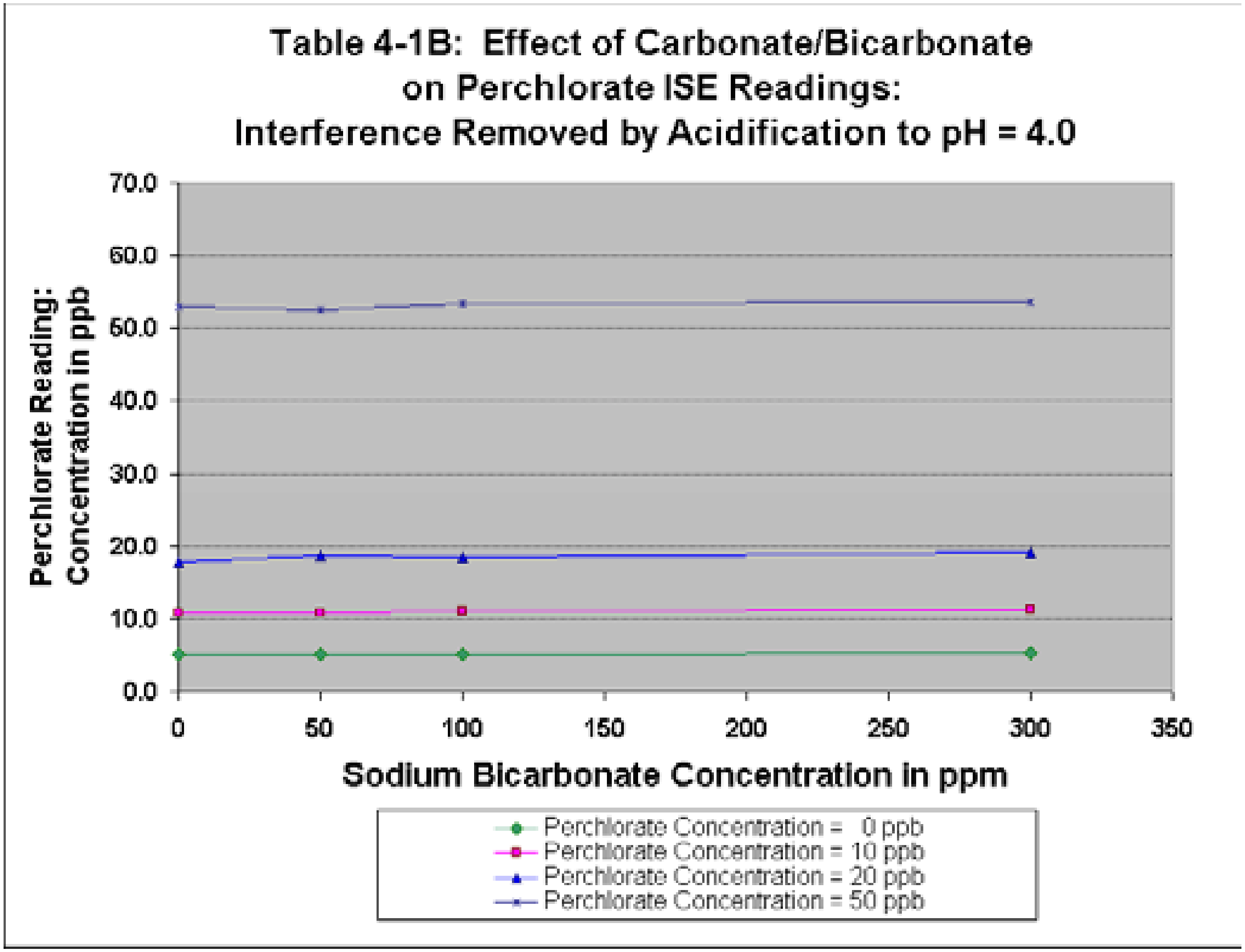
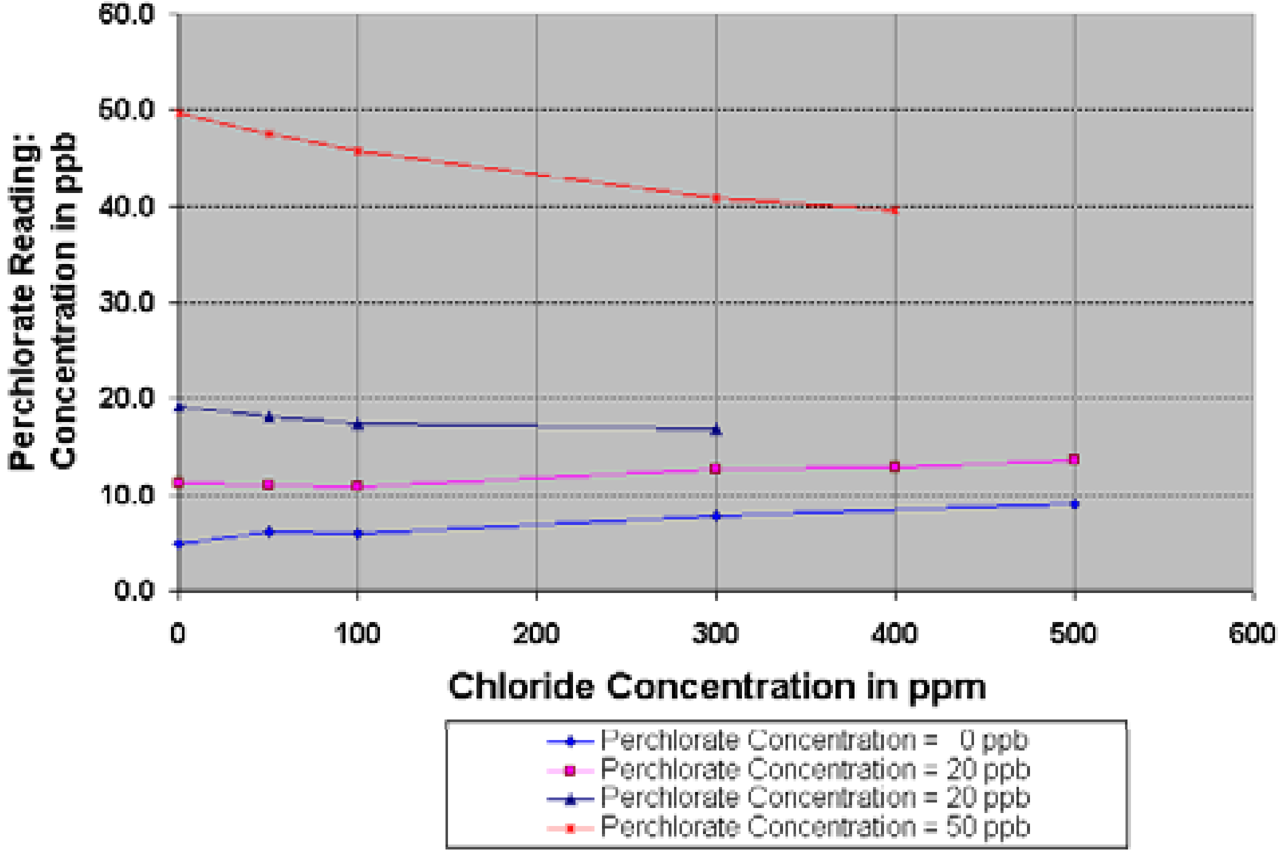


Table 4-1B: Effect of Carbonate/Bicarbonate on Perchlorate ISE Readings: Interference Removed by Acidification to pH = 4.0

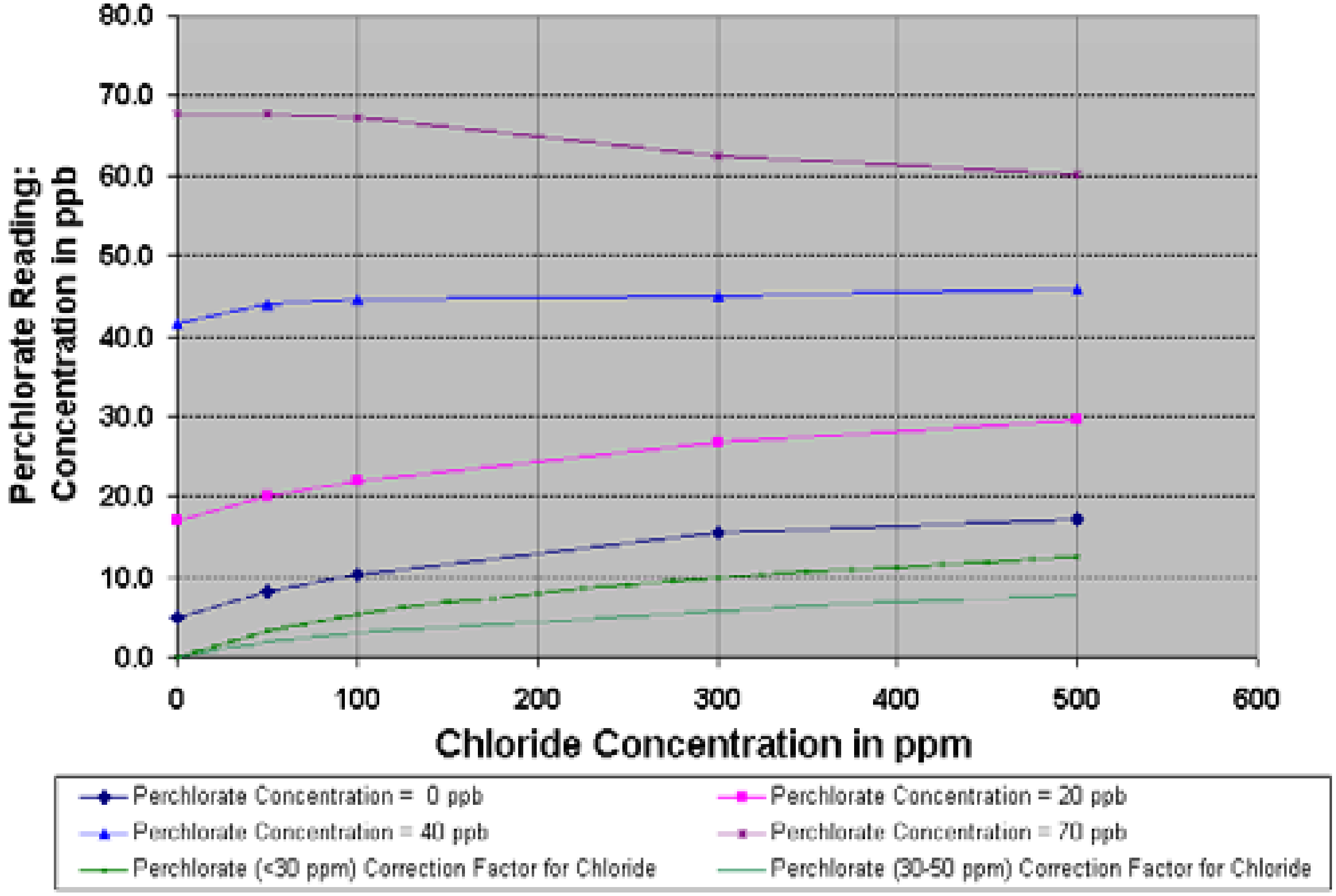
ISE = Ion Selective Electrode ppb = parts per billion (µg/L) ppm = parts per million (mg/L)

Table 4-2A: Effect of Chloride Interference on Perchlorate ISE Readings: 0-500 ppm Chloride; Approximate pH = 7.0



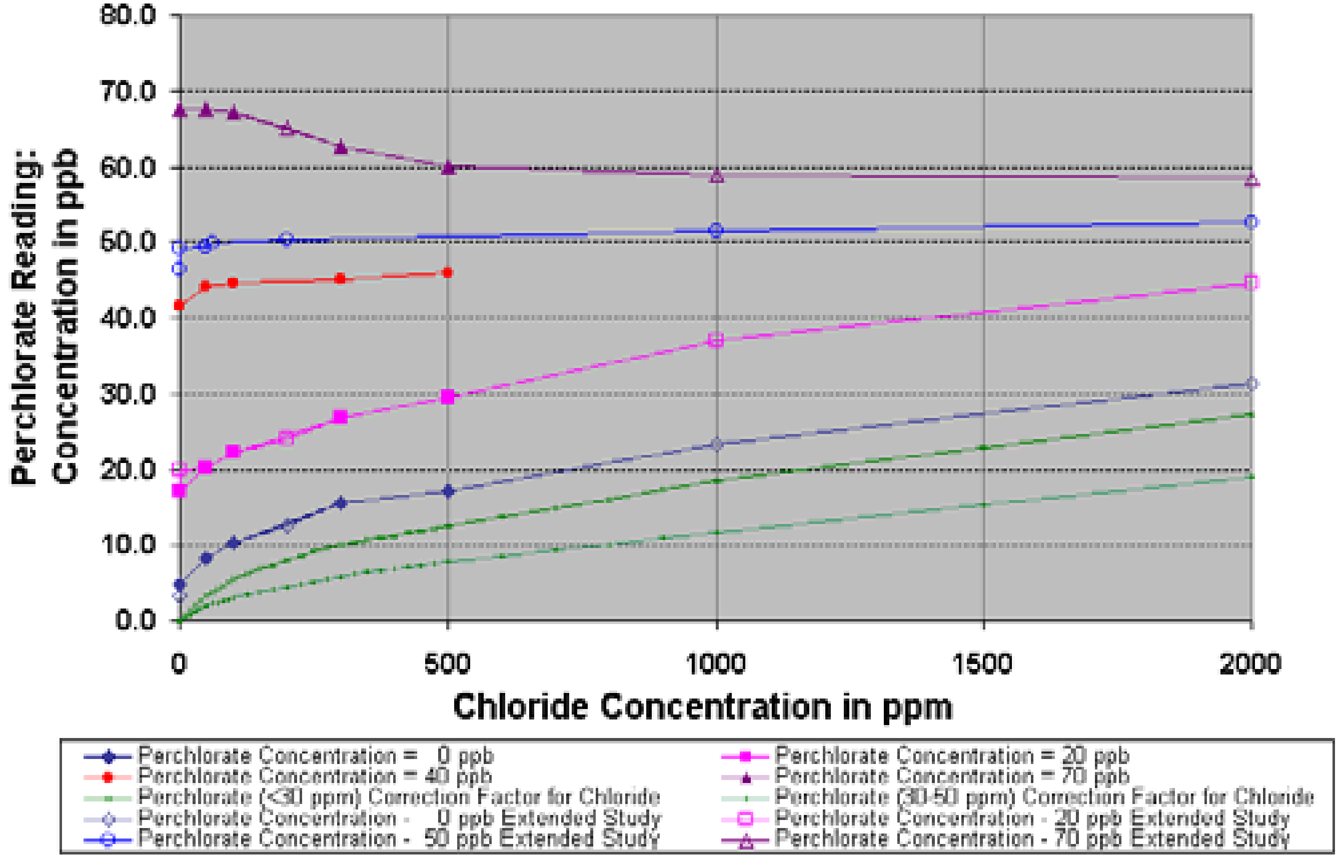
ISE = Ion Selective Electrode ppb = parts per billion (µg/L) ppm = parts per million (mg/L)

Table 4-2B: Effect of Chloride Interference on Perchlorate ISE Readings: 0-500 ppm Chloride; pH = 4.0



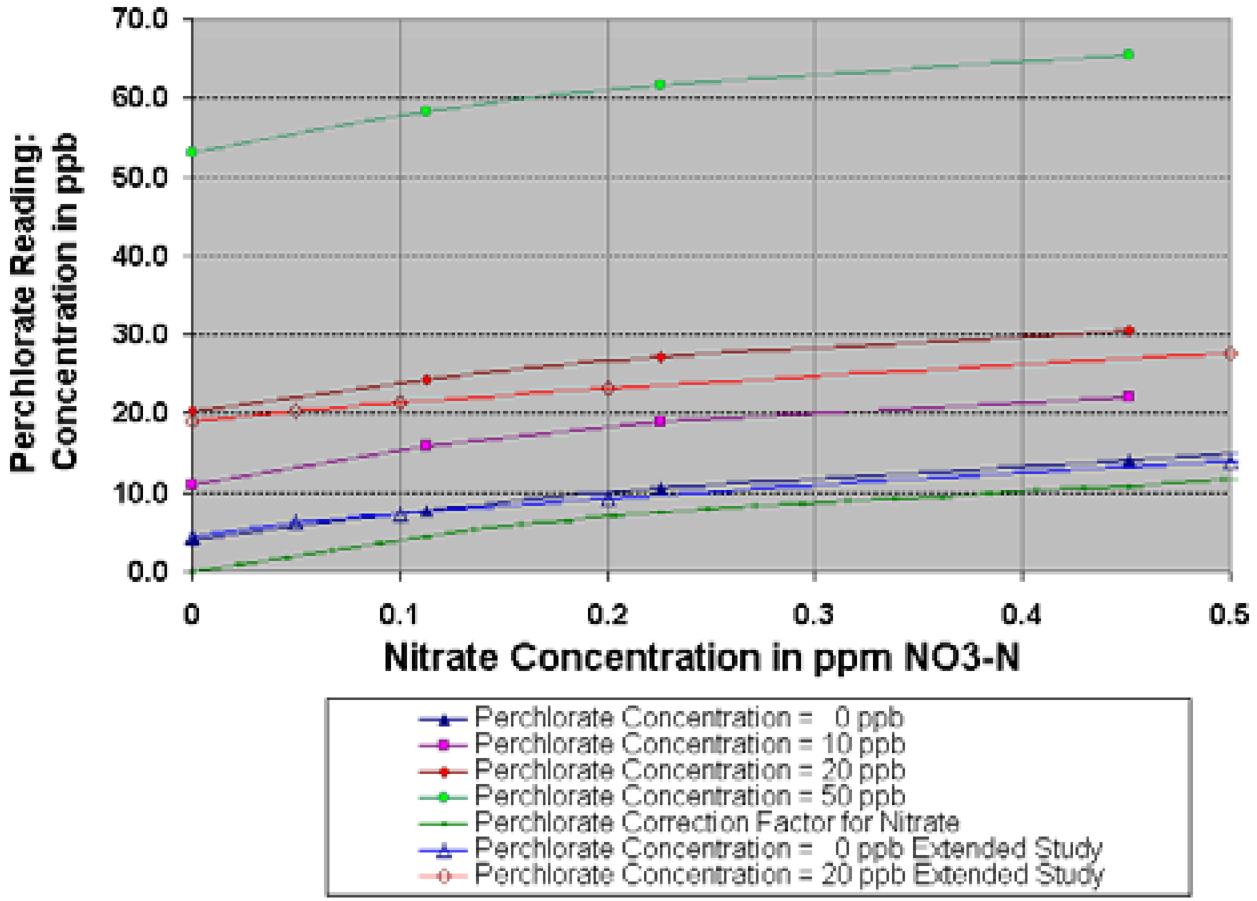
ISE = Ion Selective Electrode ppb = parts per billion (µg/L) ppm = parts per million (mg/L)

Table 4-2C: Effect of Choride Interference on Perchlorate ISE Readings, Extended Study: 0-2000 ppm Chloride; pH = 4.0



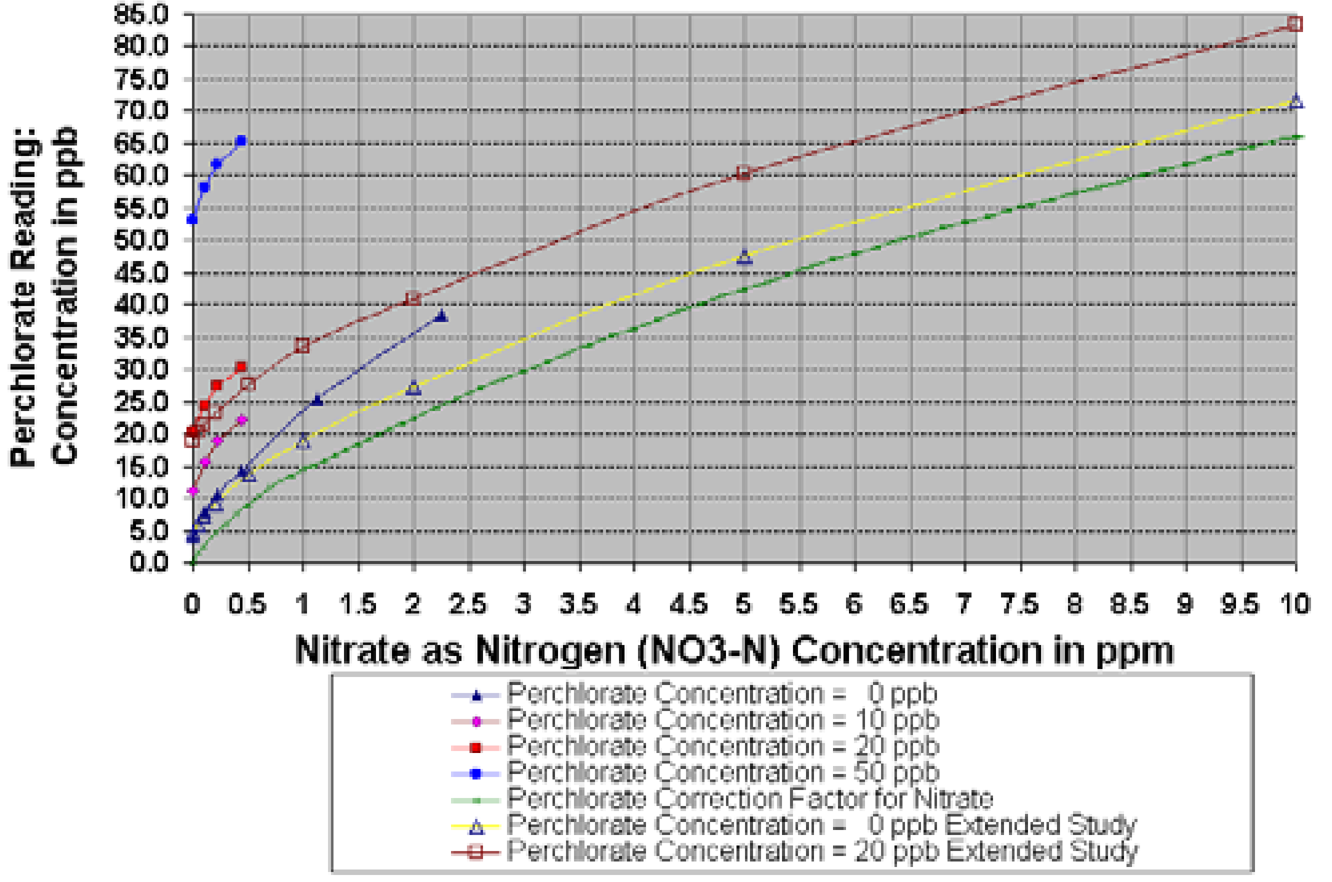
ISE = Ion Selective Electrode   ppb = parts per billion (µg/L)   ppm = parts per million (mg/L)

Table 4-3A: Effect of Nitrate Interference on Perchlorate ISE Readings: 0-0.45 ppm NO3-N; pH = 4.0



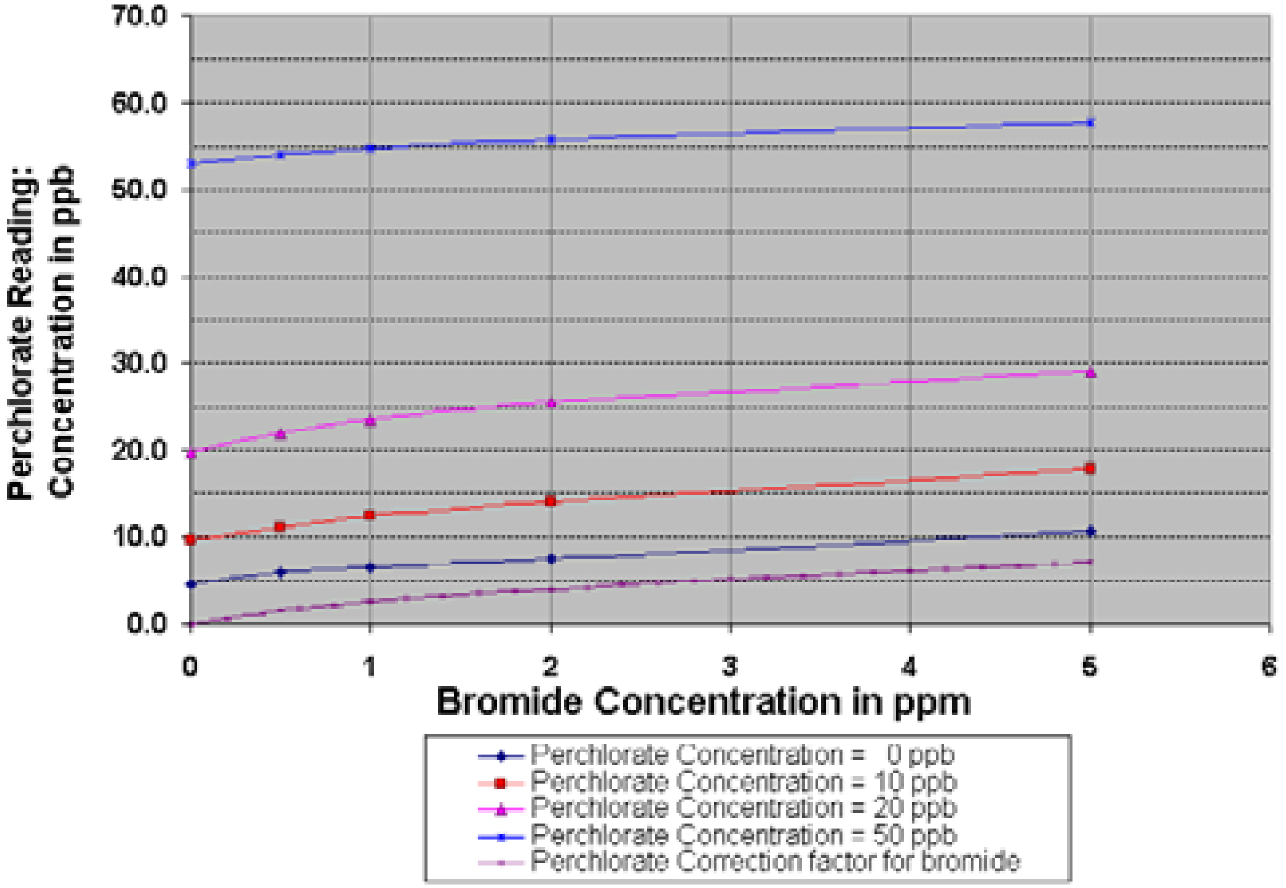
ISE = Ion Selective Electrode ppb = parts per billion (μg/L) ppm = parts per million (mg/L)

Table 4-3B: Effect of Nitrate Interference on Perchlorate ISE Readings, Extended Study: 0-10 ppm NO3-N; pH = 4.0



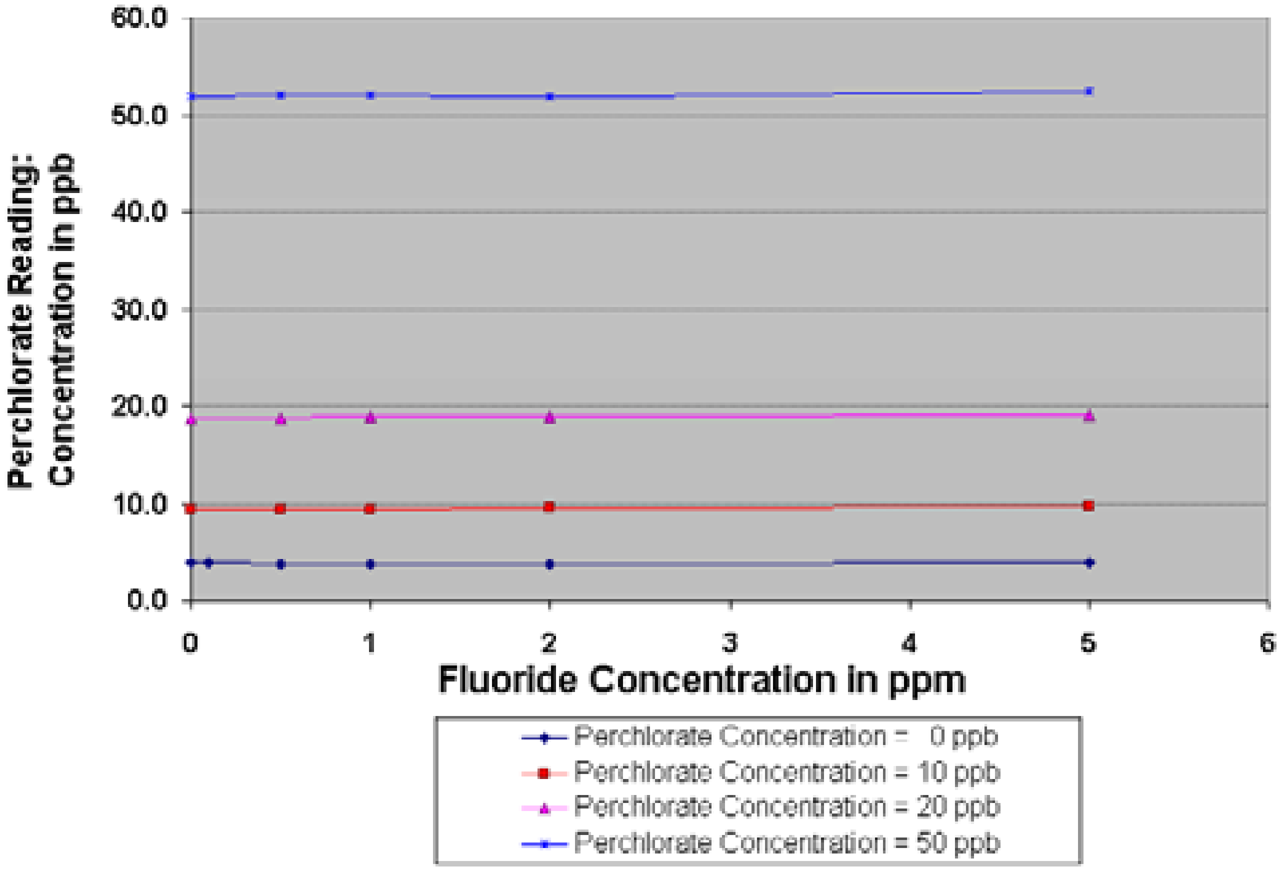
ISE = Ion Selective Electrode ppb = parts per billion (µg/L) ppm = parts per million (mg/L)

Table 4-4: Effect of Bromide Interference on Perchlorate ISE Readings: 0-5 ppm Bromide; pH = 4.0



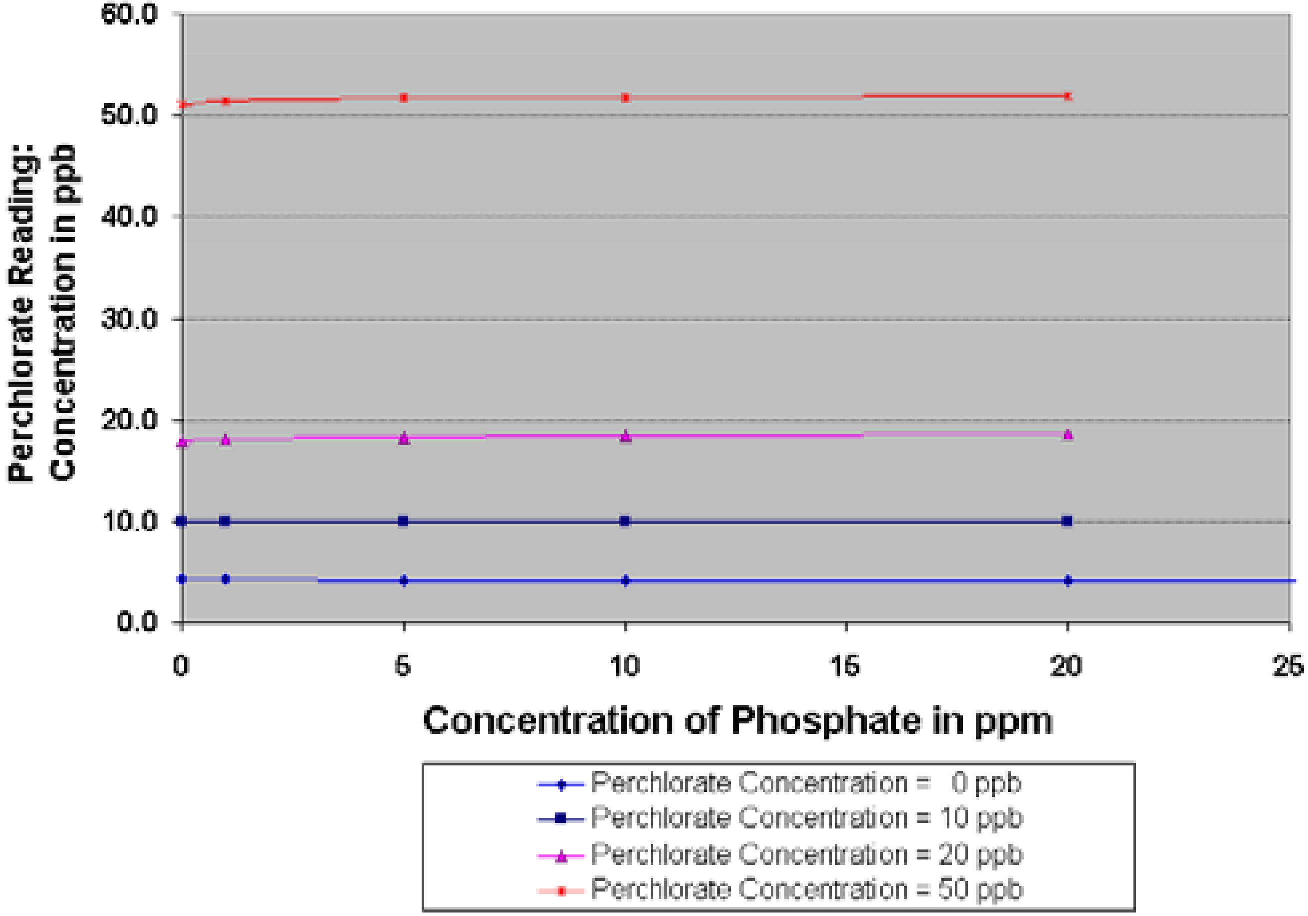
ISE = Ion Selective Electrode ppb = parts per billion (µg/L) ppm = parts per million (mg/L)

Table 4-5: Effect of Fluoride Interference on Perchlorate ISE Readings: 0-5 ppm Fluoride; pH = 4.0



ISE = Ion Selective Electrode   ppb = parts per billion (µg/L)   ppm = parts per million (mg/L)

Table 4-6: Effect of Phosphate Interference on Perchlorate ISE Readings: 0-20 ppm Phosphate; pH = 4



ISE = Ion Selective Electrode ppb = parts per billion (µg/L) ppm = parts per million (mg/L)

Table 4-7 Correction Factors: Subtract from Initial Perchlorate Reading Due to Chloride Interference

For Perchlorate Reading <30 ug/L (ppb)

Chloride Concentration in mg/L (ppm)	Correction Factor to Perchlorate in ug/L (ppb)
0	0.0
10	0.6
20	1.3
30	2.0
40	2.6
50	3.2
60	3.7
70	4.1
80	4.6
90	5.0
100	5.4
125	6.2
150	6.8
175	7.4
200	8.0
225	8.6
250	9.1
275	9.6
300	10.0
325	10.4
350	10.7
375	11.0
400	11.3
425	11.6
450	11.9
475	12.2
500	12.5
600	13.7
700	14.9
800	16.1
900	17.3
1000	18.5
1500	22.9
2000	27.2

For Perchlorate Reading 30-45 ug/L (ppb)*

Chloride Concentration in mg/L (ppm)	Correction Factor to Perchlorate in ug/L (ppb)
0	0.0
10	0.4
20	0.8
30	1.2
40	1.6
50	1.9
60	2.2
70	2.4
80	2.6
90	2.8
100	3.0
125	3.4
150	3.7
175	4.1
200	4.4
225	4.8
250	5.1
275	5.5
300	5.8
325	6.1
350	6.4
375	6.7
400	6.9
425	7.1
450	7.3
475	7.5
500	7.7
600	8.5
700	9.3
800	10.1
900	10.9
1000	11.7
1500	15.4
2000	19.0

* For perchlorate results greater than 50 ppb, chloride interference is negligible or negative. Dilution and reanalysis os recommended.

Table 4-8 Correction Factors: Subtract from Initial Perchlorate Reading Due to Nitrate Interference

For Nitrate-as-Nitrogen Concentration 0.05 - 4.4 ppm

Nitrate as Nitrate (NO3) in mg/L (ppm)	Nitrate as Nitrogen (NO3-N) in mg/L (ppm)	Correction Factor to Perchlorate in ug/L (ppb)
0.22	0.05	1.5
0.44	0.1	2.5
0.89	0.2	4.5
1.33	0.3	6.0
1.77	0.4	7.5
2.22	0.5	9.0
2.66	0.6	10.4
3.10	0.7	11.6
3.54	0.8	12.6
3.99	0.9	13.6
4.43	1.0	14.5
4.87	1.1	15.3
5.32	1.2	16.0
5.76	1.3	16.9
6.20	1.4	17.7
6.65	1.5	18.5
7.09	1.6	19.3
7.53	1.7	20.1
7.97	1.8	20.9
8.42	1.9	21.7
8.86	2.0	22.5
9.75	2.2	24.0
10.63	2.4	25.5
11.52	2.6	27.0
12.40	2.8	28.4
13.29	3.0	29.8
14.18	3.2	31.2
15.06	3.4	32.5
15.95	3.6	33.8
16.83	3.8	35.1
17.72	4.0	36.4
18.61	4.2	37.7
19.49	4.4	38.9

For Nitrate-as-Nitrogen Concentration 4.6 - 15 ppm

Nitrate as Nitrate (NO3) in mg/L (ppm)	Nitrate as Nitrogen (NO3-N) in mg/L (ppm)	Correction Factor to Perchlorate in ug/L (ppb)
20.38	4.6	40.1
21.26	4.8	41.3
22.15	5.0	42.5
23.04	5.2	43.7
23.92	5.4	44.8
24.81	5.6	45.9
25.69	5.8	47.0
26.58	6.0	48.0
27.47	6.2	49.0
28.35	6.4	50.0
29.24	6.6	51.0
30.12	6.8	51.9
31.01	7.0	52.8
31.90	7.2	53.7
32.78	7.4	54.6
33.67	7.6	55.5
34.55	7.8	56.4
35.44	8.0	57.3
36.33	8.2	58.2
37.21	8.4	59.1
38.10	8.6	60.0
38.98	8.8	60.9
39.87	9.0	61.8
40.76	9.2	62.7
41.64	9.4	63.6
42.53	9.6	64.4
43.41	9.8	65.2
44.30	10.0	66.0
48.73	11.0	66.8
53.16	12.0	67.6
57.59	13.0	68.4
62.02	14.0	69.2
66.45	15.0	70.0

Table 4-9 Correction Factors: Subtract from Initial Perchlorate Reading Due to Bromide Interference For Bromide Concentration 0.2 - 5.0 mg/L (ppm)

Bromide Concentration in mg/L (ppm)	Correction Factor to Perchlorate in ug/L (ppb)
0	0
0.2	0.6
0.4	1.2
0.5	1.5
0.6	1.75
0.8	2.2
1.0	2.6
1.2	2.9
1.4	3.2
1.6	3.5
1.8	3.75
2.0	4.0
2.2	4.25
2.4	4.5
2.6	4.7
2.8	4.9
3.0	5.1
3.2	5.3
3.4	5.5
3.6	5.7
3.8	5.9
4.0	6.1
4.2	6.3
4.4	6.5
4.6	6.7
4.8	6.9
5.0	7.1

Table 4-10

Sample ID	pH	mL Sample	milli- volts	Conc. (ppb) Reading	Date Analyzed	Sample ISA/ISAB per 200 mL	ICAL ISA/ISAB per 200 mL	Assoc. Check Standard %R	pH of Calibration / Comments
P-1	Not Adj	200 mL	376.20	70.6	1/10/2001	2mL of 0.4M ISA	2mL of 0.4M ISA	20 ppb 95%R	pH Not Adjusted
P-1	4.02	200 mL	281.00	79.7	3/02/2001	2mL of 0.4M ISA	2mL of 0.4M ISA	100 ppb 117%R	pH 4.0
P-2	Not analyzed; Contains high levels of organics								
P-3	Not analyzed; Contains high levels of organics								
P-4	Not analyzed; Contains high levels of organics								
P-5 (400x dilution)	3.99	200 mL	302.40	61.1	1/29/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	20 ppb 100%R	pH 4.0 24423 ppb
P-5 (400x dil) + 20ppb	3.98	200 mL	297.10	78.6	1/29/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	20 ppb 100%R	pH 4.0 MS 87.8%R
P-6	Not Adj	140 mL	395.00	25.9	1/10/2001	2mL of 0.4M ISA	2mL of 0.4M ISA	20 ppb 80%R	pH Not Adjusted
P-6	Not Adj	140 mL	389.50	20.9	1/11/2001	2mL of 0.4M ISA	2mL of 0.4M ISA	100 ppb 68.7%R	pH Not Adjusted
P-6	Not Adj	140 mL	398.50	12.5	1/11/2001RE	2mL of 0.4M ISA	2mL of 0.4M ISA	40 ppb 34%R	pH Not Adjusted
P-6	3.95	140 mL	330.20	14.0	1/25/2001	2mL of 0.4M ISA	1mL of Sentek ISAB	20 ppb 96%R	pH 4.0
P-7	Not Adj*	135mL	378.50	34.1	1/11/2001	2mL of 0.4M ISA	2mL of 0.4M ISA	100 ppb 68.7%R	pH Not Adjusted
P-7	Not Adj*	135mL	382.80	26.3	1/11/2001RE	2mL of 0.4M ISA	2mL of 0.4M ISA	40 ppb 34%R	pH Not Adjusted
P-7	3.99	140 mL	323.10	23.4	1/26/2001	2mL of 0.4M ISA	1mL of Sentek ISAB	20 ppb 100%R	pH 4.0
P-7 (dil fac=2) + 20 ppb	3.98	200 mL	316.60	31.6	1/26/2001	2mL of 0.4M ISA	1mL of Sentek ISAB	2- ppb 110%R	pH 4.0 MS 75.8%R
P-7 dilution factor = 2	3.99	100 mL	330.80	16.4	1/26/2001	2mL of 0.4M ISA	1mL of Sentek ISAB	20 ppb 100%R	pH 4.0
	*Likely caused loss of sensitivity								
P-8	Not Adj	140 mL	407.30	8.2	36902.00	2mL of 0.4M ISA	2mL of 0.4M ISA	40 ppb 34%R	pH Not Adjusted
P-8	Not Adj	140 mL	385.30	33.6	1/12/2001	5mL of 0.4M ISA	5mL of 0.4M ISA	50 ppb 89%R	pH Not Adjusted
P-8	Not Adj	140 mL	385.30	33.0	1/12/2001	10mL of 0.4M ISA	10mL of 0.4M ISA	50 ppb 87%R	pH Not Adjusted
P-8	3.99	140 mL	321.90	19.3	1/25/2001	10mL of 0.4M ISA	1mL of Sentek ISAB	20 ppb 99%R	pH 4.0
P-9	Not Adj	180 mL	326.49	8.5	1/15/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	50 ppb 70%R	pH Not Adjusted

P-9	8.27	180 mL	309.00	31.2	1/17/2001	1mL of Sentek ISAB	1mL of Sentek ISAB		pH Not Adjusted
P-9	4.42	180 mL	362.00	7.0	1/17/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	50 ppb 80%R	pH 4.0
P-9	3.97	180 mL	343.90	14.6	1/24/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	20 ppb 94%R	pH 4.0
P-10 (1:200)	Not Adj	200 mL	408.80	12.4	1/10/2001	2mL of 0.4M ISA	2mL of 0.4M ISA	20 ppb 80%R	pH Not Adjusted
P-10 (1:200)+20ppb ms	Not Adj	200 mL	397.50	22.6	1/10/2001	2mL of 0.4M ISA	2mL of 0.4M ISA	20 ppb 80%R	pH Not Adjusted
P-10 (200x dilution)	3.96	200 mL	324.10	21.7	1/29/2001	2mL of 0.4M ISA	1mL of Sentek ISAB	20 ppb 100%R	pH 4.0 4336 ppb
MS = Matrix Spike									
P-11	4.02	140 mL	301.50	63.7	1/29/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	20 ppb 95%R	pH 4.0
P-11	3.91	200 mL	285.80	45.3	2/23/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	20 ppb 83%R	pH 4.0
P-102 (P-11 resampled)	3.98	200 mL	278.80	60.1	2/23/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	20 ppb 94%R	pH 4.0
P-103 (P-11 resampled)	4.01	200 mL	287.60	42.2	2/23/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	100 ppb 87%R	pH 4.0
P-104 (P-11 resampled)	4.04	200 mL	288.50	40.7	2/23/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	20 ppb 83%R	pH 4.0
P-102 + 20 ppb	4.02	200 mL	275.90	67.6	2/23/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	20 ppb 94%R	pH 4.0 MS 111%R
P-102 + 20 ppb	4.03	200 mL	281.10	54.8	2/23/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	20 ppb 94%R	pH 4.0 MS 47.4%R
P-12	Not Adj	140 mL	394.10	15.4	36902.00	2mL of 0.4M ISA	2mL of 0.4M ISA	40 ppb 34%R	pH Not Adjusted
P-12	3.97	140 mL	332.10	15.4	1/26/2001	2mL of 0.4M ISA	1mL of Sentek ISAB	2- ppb 110%R	pH 4.0
P-13 (EB)		140 mL	442.30	1.6	36902.00	2mL of 0.4M ISA	2mL of 0.4M ISA	40 ppb 34%R	pH Not Adjusted
P-13 (EB)	3.95	140 mL	361.40	4.0	1/26/2001	2mL of 0.4M ISA	1mL of Sentek ISAB	20 ppb 103%R	pH 4.0
P-14	Not Adj	140 mL	415.20	5.6	36902.00	2mL of 0.4M ISA	2mL of 0.4M ISA	40 ppb 34%R	pH Not Adjusted
P-14	Not Adj	140 mL	386.90	31.0	1/12/2001	5mL of 0.4M ISA	5mL of 0.4M ISA	50 ppb 89%R	pH Not Adjusted
P-14	Not Adj	140 mL	386.90	30.5	1/12/2001	10mL of 0.4M ISA	10mL of 0.4M ISA	50 ppb 87%R	pH Not Adjusted
P-14	3.97	140 mL	337.20	10.7	1/25/2001	10mL of 0.4M ISA	1mL of Sentek ISAB	20 ppb 99%R	pH 4.0
P-15	Not Adj	140 mL	418.90	4.7	36902.00	2mL of 0.4M ISA	2mL of 0.4M ISA	40 ppb 34%R	pH Not Adjusted
P-15	3.98	140 mL	344.10	8.9	1/26/2001	2mL of 0.4M ISA	1mL of Sentek ISAB	20 ppb 103%R	pH 4.0
P-16	Not Adj	200 mL	303.00	47.0	1/15/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	50 ppb 46%R	pH Not Adjusted

P-16	6.50	200 mL	322.90	29.0	1/17/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	50 ppb 80%R?	pH 4.0
P-16/H2SO4 pH 6	6.00	200 mL	341.40	17.9	1/15/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	50 ppb 78%R	pH 4.0
P-16 H2SO4	4.00	200 mL	341.70	14.6	1/17/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	50 ppb 80%R?	pH 4.0
P-16 H2SO4	4.40	200 mL	341.10	15.0	1/17/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	50 ppb 80%R?	pH 4.0
P-16	3.96	200 mL	337.80	18.0	1/24/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	20 ppb 92%R	pH 4.0
P-17	Not analyzed; Contains high levels of organics								
P-18	Not Adj	140 mL	418.50	4.8	36902.00	2mL of 0.4M ISA	2mL of 0.4M ISA	40 ppb 34%R	pH Not Adjusted
P-18	3.96	140 mL	345.60	8.3	1/26/2001	2mL of 0.4M ISA	1mL of Sentek ISAB	20 ppb 103%R	pH 4.0
MS = Matrix Spike									
P-19	Not Adj	140 mL	409.10	7.5	36902.00	2mL of 0.4M ISA	2mL of 0.4M ISA	40 ppb 34%R	Not Adj
P-19	Not Adj	140 mL	384.60	34.8	1/12/2001	5mL of 0.4M ISA	5mL of 0.4M ISA	50 ppb 89%R	Not Adj
P-19	Not Adj	140 mL	384.60	34.1	1/12/2001	10mL of 0.4M ISA	10mL of 0.4M ISA	50 ppb 87%R	Not Adj
P-19	4.03	140 mL	328.10	15.2	1/25/2001	10mL of 0.4M ISA	1mL of Sentek ISAB	20 ppb 107%R	pH 4.0
P-20	Not Adj	135mL	399.60	11.8	1/11/2001RE	2mL of 0.4M ISA	2mL of 0.4M ISA	40 ppb 34%R	Not Adj
P-20	3.95	140 mL	345.20	8.4	1/26/2001	2mL of 0.4M ISA	1mL of Sentek ISAB	20 ppb 103%R	pH 4.0
P-21	Not Adj	200 mL	393.70	27.7	1/10/2001	2mL of 0.4M ISA	2mL of 0.4M ISA	20 ppb 80%R	Not Adj
P-21	Not Adj	200 mL	388.30	26.8	1/10/2001RE	5mL of 0.4M ISA	5mL of 0.4M ISA	60 ppb 97%R	Not Adj
P-21 (1:2)	Not Adj	200 mL	398.00	15.5	1/10/2001RE	5mL of 0.4M ISA	5mL of 0.4M ISA	60 ppb 97%R	Not Adj
P-21 (1:4)	Not Adj	200 mL	409.90	7.9	1/10/2001RE	5mL of 0.4M ISA	5mL of 0.4M ISA	60 ppb 97%R	Not Adj
P-21 (1:5)	Not Adj	200 mL	416.60	5.4	1/10/2001RE	5mL of 0.4M ISA	5mL of 0.4M ISA	60 ppb 97%R	Not Adj
P-21	Not Reanalyzed at pH 4; No more sample for reanalysis after original sample used for serial dilution								
P-22	3.99	140 mL	348.50	6.8	1/29/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	20 ppb 100%R	pH 4.0
P-23	Not Adj	200 mL	328.66	7.3	1/15/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	50 ppb 70%R	Not Adj

P-23	4.01	200 mL	354.20	10.1	1/24/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	20 ppb 94%R	pH 4.0
P-24	3.99	140 mL	338.50	10.9	1/29/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	20 ppb 107%R	pH 4.0
P-25	3.99	140 mL	351.80	5.8	1/29/2001	1mL of Sentek ISAB	1mL of Sentek ISAB	20 ppb 100%R	pH 4.0
tap water	Not Adj	200 mL	305.10	40.3	1/15/2001	1mL of Sentek ISAB	1mL of Sentek ISAB		Not Adj
tap water	pH 4.0	200 mL	364.70	6.8	1/15/2001	1mL of Sentek ISAB	1mL of Sentek ISAB		pH 4.0

Assoc. = associated
dil fac =dilution factor
EB = equipment blank
ISA and ISAB = ionic strength adjustor solutions

m = molar
mL = milliliter
ms = matrix spike
not adj = not adjusted

ppb = parts per billion (µg/L)
%R = percent recovery
RE = reanalysis

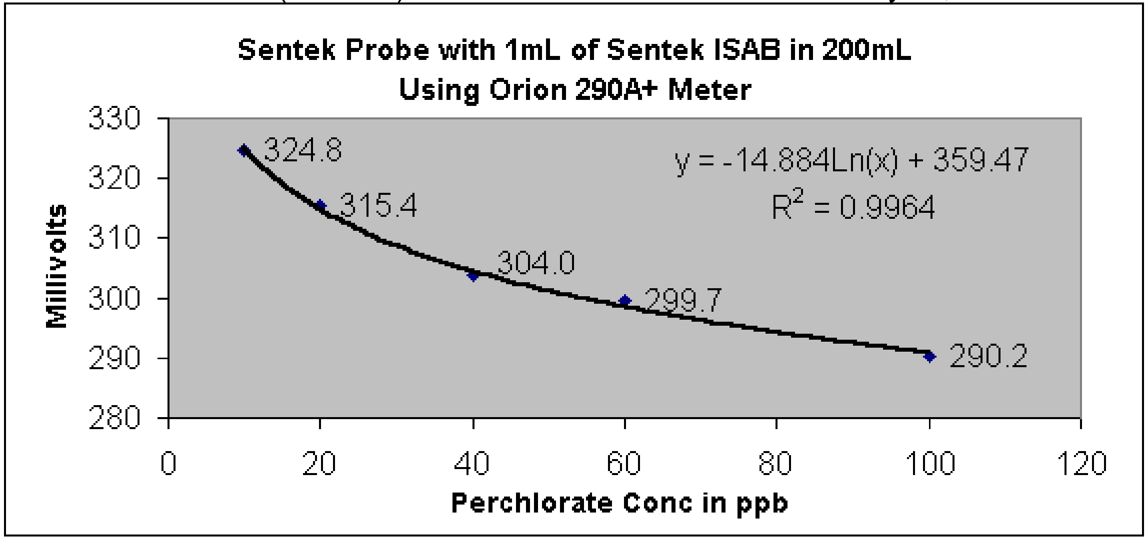
Table 4-11 Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water Units: ug/L (ppb) Extraction/Digestion: None

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

Analyst: Earth Tech, Inc.

Meter: ORION 290A (Portable) Date: January 22, 2001


Sentek Probe with 1mL of Sentek ISAB in 200mL Using Orion 290A+ Meter

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	6.7	200 mL	324.8	10.3
20	6.69	200 mL	315.4	19.3
40	6.68	200 mL	304.0	41.5
60	6.7	200 mL	299.7	55.5
100	6.67	200 mL	290.2	105.0
Calibration Date	**1/22/2001**		**Time**	**12:00pm**
Temperature		**21^0C**		

Slope	**14.884**		**Intercept**	**359.5**
Sample/Calibration ID	**pH**	**Sample Volume**	**Millivolts Reading**	**Concentration in ppb**
LCS/ICV	6.72	200 mL	302.7	45.3
MB/ICB	6.74	200 mL	335.7	4.9
blank + 0ppm Cl	6.73	200 mL	335.8	**4.9**
blank + 50ppm Cl	6.72	200 mL	332.6	**6.1**
blank + 100ppm Cl	6.69	200 mL	332.9	**6.0**
blank + 300ppm Cl	6.67	200 mL	328.8	**7.9**
blank + 500ppm Cl	6.65	200 mL	326.8	**9.0**
ccv	6.7	200 mL	305.6	37.3
ccb	6.53	200 mL	337.7	4.3
10ppb std +0ppm HCO3	6.85	200 mL	325.3	**9.9**
10ppb std +50ppm HCO3	8.05	200 mL	315.2	**19.6**
10ppb std +50ppm HCO3*	6.74*	200 mL	338.8	4.0*
10ppb std +50ppm HCO3*	4.02*	200 mL	382.5	0.2*
60 ppb standard	6.67	200 mL	299.0	58.1
blank	6.92	200 mL	336.7	4.6
blank + 50ppm HCO3	8.02	200 mL	311.5	**25.1**
blank + 100ppm HCO3	8.38	200 mL	308.2	**31.3**
blank + 300ppm HCO3	8.68	200 mL	305.2	**38.3**
blank + 300ppm HCO3*	3.93*	200 mL	442.1	0.0*
60 ppb standard	6.65	200 mL	306.2	35.8

Data in bold used for graphs in Tables 4-1 and 4-2

* pH adjusted with sulfuric acid. As the calibration curve uses standards not pH adjusted with acid, the perchlorate concentrations reported for pH adjusted samples indicate relative changes in perchlorate readings but are quantitatively inaccurate as the referenced calibration curve is not applicable to these samples.

Table 4-12

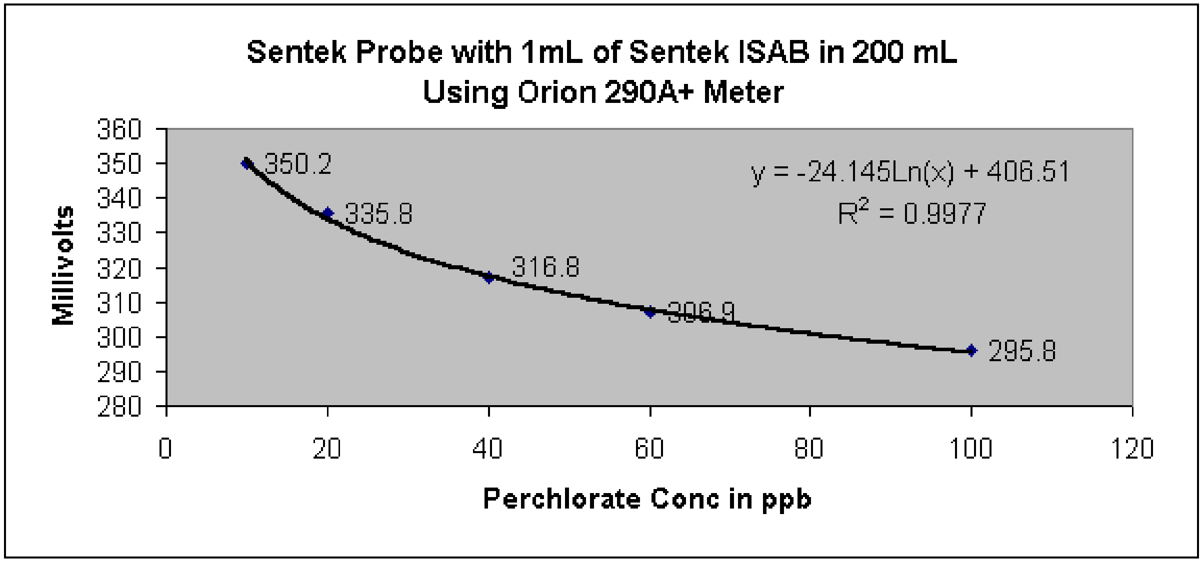
Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water Units: ug/L (ppb) Extraction/Digestion: Acidification to pH 4 with Sulfuric Acid

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

Analyst: Earth Tech, Inc.

Meter: ORION 290A (Portable) Date: January 23, 2001



Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	4.03	200 mL	350.2	10.3
20	4.00	200 mL	335.8	18.7
40	4.02	200 mL	316.8	41.1
60	3.95	200 mL	306.9	61.9
100	4.03	200 mL	295.8	98.0
Calibration Date	**1/23/2001**		**Time**	**2:30**
Temperature		**22^{0}C**		
Slope	**24.145**		**Intercept**	**406.51**

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb (pH 4.0 CAL Curve)	* Adjusted Concentration in ppb (Non-Acidified pH Curve)
LCS/ICV	3.98	200 mL	311.1	52.0	
MB/ICB	3.98	200 mL	369.9	4.6	
Blank	6.84	200 mL	348.7	11.0**	6.4***
20 ppb std	6.83	200 mL	325.9	28.2**	18.5*** (92.5%R)
Blank + 50ppm bicarb*	6.78*	200 mL	343.6	13.5**	8.1***
20 ppb std	6.82	200 mL	328.7	25.1**	16.2*** (81.0%R)
Blank + 100ppm bicarb*	6.80*	200 mL	334.8	19.5**	12.2***
20 ppb std	6.79	200 mL	329.3	24.5**	15.8*** (79.0%R)
Blank + 300ppm bicarb*	6.82*	200 mL	335.3	19.1**	12.0***
20 ppb std	6.78	200 mL	330.6	23.2**	14.9*** (74.5 %R)
20 ppb std	4.04	200 mL	338.6	16.7	
Blank	4.03	200 mL	367.6	5.0	
Blank + 50ppm bicarb	3.97	200 mL	367.1	**5.0**	
20 ppb std	4.02	200 mL	338.4	16.8	
Blank + 100ppm bicarb	3.98	200 mL	367.2	**5.1**	
20 ppb std	4.02	200 mL	337.9	17.1	
Blank + 300ppm bicarb	4.03	200 mL	366.3	**5.3**	
20 ppb std	4.00	200 mL	337.2	17.6	
50 ppb std	3.97	200 mL	310.6	53.1	
50 ppb std +50ppm bicarb	3.97	200 mL	310.8	**52.7**	
50 ppb std +100ppm bicarb	4.02	200 mL	310.4	**53.5**	
50 ppb std +300ppm bicarb	4.02	200 mL	310.3	**53.8**	
20 ppb std	4.00	200 mL	336.9	17.9	
20 ppb std +50ppm bicarb	3.96	200 mL	335.9	**18.6**	
20 ppb std +100ppm bicarb	3.97	200 mL	336.2	**18.4**	
20 ppb std +300ppm bicarb	3.99	200 mL	335.4	**19.0**	
10 ppb std	4.01	200 mL	349.2	10.7	
10 ppb std +50ppm bicarb	4.03	200 mL	349.1	**10.8**	
10 ppb std +100ppm bicarb	4.01	200 mL	348.6	**11.0**	
10 ppb std +300ppm bicarb	3.99	200 mL	348.1	**11.2**	
CCV (60 ppb)	4.02	200 mL	308.4	58.2	
CCB	4.03	200 mL	372.4	4.1	

* pH adjusted to approximately pH 6.7 using sulfuric acid so bicarbonate is converted to carbonate.

** As the calibration curve uses standards adjusted to pH 4.0 with acid, the perchlorate concentrations reported for samples pH adjusted to 6.8 or for non-pH adjusted check standards indicate relative changes in perchlorate readings but are quantitatively inaccurate.

*** Modified results were quantitated with calibration data from 1/11/01 to simulate calibration at pH 6.75 and demonstrate relative effect of carbonate interference. Note loss of sensitivity in check standards due to carbonate interference.

Data in bold used for graphs in Table 4-1

Table 4-13

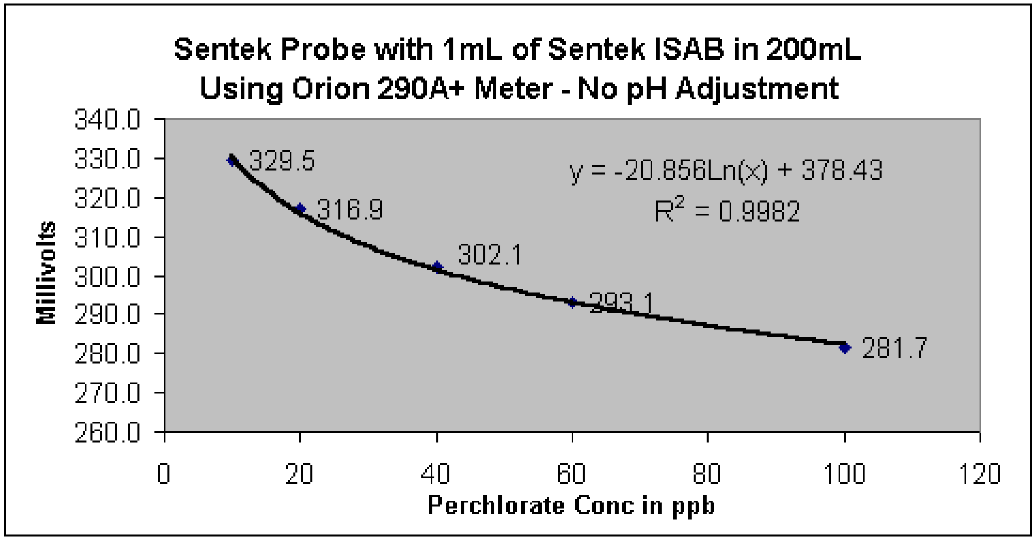
Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water   Units: ug/L (ppb)   Extraction/Digestion: None

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

Analyst: Earth Tech, Inc.

Meter: ORION 290A (Portable)   Date: January 18, 2001



Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	6.80	200 mL	329.5	10.4
20	6.81	200 mL	316.9	19.1
40	6.80	200 mL	302.1	38.9
60	6.80	200 mL	293.1	59.8
100	6.82	200 mL	281.7	103.3
Calibration Date	**1/18/2001**		**Time**	**12:30pm**
Temperature		**20.5^{0}C**		
Slope	**20.856**		**Intercept**	**378.43**

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV	6.79	200 mL	297.2	49.1
MB/ICB	6.74	200 mL	342.2	5.7
20 ppb std	6.72	200 mL	316.8	**19.2**
20 ppb std + 50ppm Cl	6.69	200 mL	318.1	**18.0**
20 ppb std + 100ppm Cl	6.68	200 mL	318.9	**17.4**
20 ppb std + 300ppm Cl	6.65	200 mL	319.5	**16.9**
10 ppb std	6.65	200 mL	328.0	**11.2**
10 ppb std + 50ppm Cl	6.63	200 mL	328.4	**11.0**
10 ppb std + 100ppm Cl	6.61	200 mL	328.6	**10.9**
10 ppb std + 300ppm Cl	6.6	200 mL	325.5	**12.7**
10 ppb std + 400ppm Cl	6.58	200 mL	325.1	**12.9**
10 ppb std + 500ppm Cl	6.58	200 mL	324.1	**13.5**
50 ppb std	6.74	200 mL	297.0	**49.6**
50ppb std + 50ppm Cl	6.7	200 mL	297.9	**47.5**
50ppb std + 100ppm Cl	6.68	200 mL	298.7	**45.7**
50ppb std + 300ppm Cl	6.64	200 mL	301.1	**40.8**
50ppb std + 400ppm Cl	6.63	200 mL	301.7	**39.6**
CCV (100ppb)	6.88	200 mL	283.7	93.9
CCB	6.64	200 mL	356.8	2.8

Data in bold used for graphs in Table 4-2

Table 4-14

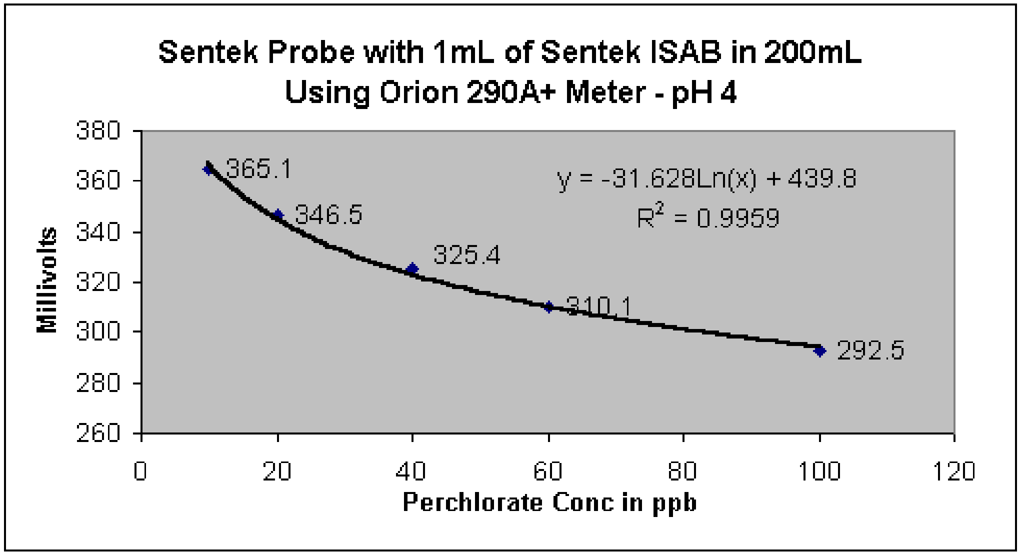
Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water   Units: ug/L (ppb)   Extraction/Digestion: Acidification to pH 4 with Sulfuric Acid

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

Analyst: Earth Tech, Inc.

Meter: ORION 290A (Portable)   Date: January 18, 2001



Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	3.98	200 mL	365.1	10.6
20	3.99	200 mL	346.5	19.1
40	3.98	200 mL	325.4	37.2
60	3.96	200 mL	310.1	60.4
100	3.97	200 mL	292.5	105.3
Calibration Date	**1/18/2001**		**Time**	**2:45pm**
Temperature		**20.5^{0}C**		
Slope	**31.628**		**Intercept**	**439.8**

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV	3.98	200 mL	315.3	51.3
MB/ICB	3.97	200 mL	385.4	5.6
20 ppb std	3.99	200 mL	350.0	**17.1**
20ppb std + 50ppm Cl	3.97	200 mL	344.9	**20.1**
20ppb std + 100ppm Cl	3.95	200 mL	341.9	**22.1**
20ppb std + 300ppm Cl	3.93	200 mL	335.9	**26.7**
20ppb std + 500ppm Cl	3.91	200 mL	332.7	**29.6**
40 ppb std	3.98	200 mL	321.9	**41.6**
40ppb std + 50ppm Cl	3.96	200 mL	320.1	**44.0**
40ppb std + 100ppm Cl	3.94	200 mL	319.7	**44.6**
40ppb std + 300ppm Cl	3.93	200 mL	319.4	**45.0**
40ppb std + 500ppm Cl	3.91	200 mL	318.8	**45.9**
70ppb std	3.97	200 mL	306.5	**67.7**
70ppb std + 50ppm Cl	3.95	200 mL	306.5	**67.7**
70ppb std + 100ppm Cl	3.93	200 mL	306.7	**67.2**
70ppb std + 300ppm Cl	3.91	200 mL	309.0	**62.5**
70ppb std + 500ppm Cl	3.89	200 mL	310.2	**60.2**
CCV	3.91	200 mL	348.5	17.9
CCB	3.99	200 mL	387.3	5.3

Data in bold used for graphs in Table 4-2

Table 4-15

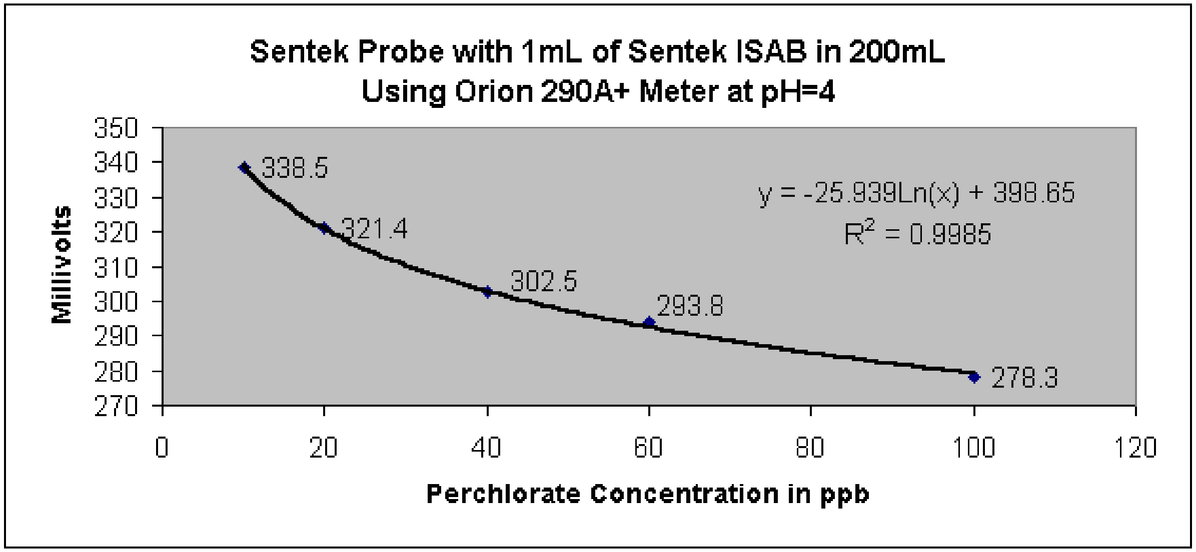
Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water Units: ug/L (ppb) Extraction/Digestion: Acidification to pH 4 with Sulfuric Acid

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

Analyst: Earth Tech, Inc.

Meter: ORION 290A (Portable) Date: January 25, 2001



Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	4.01	200 mL	338.5	10.2
20	3.98	200 mL	321.4	19.7
40	4.02	200 mL	302.5	40.7
60	4.00	200 mL	293.8	57.0
100	4.03	200 mL	278.3	103.5
Calibration Date	**1/25/2001**		**Time**	**11:20am**
Temperature		**21^0C**		
Slope	**25.939**		**Intercept**	**398.65**

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV	3.98	200 mL	292.8	59.2
MB/ICB	3.96	200 mL	357.3	4.9
20 ppb std	3.99	200 mL	320.4	20.4
P-19	4.03	140 mL	328.1	15.2
20 ppb std	4.00	100 mL	319.1	21.5
80 ppb	3.98	200 mL	284.7	80.9
80 ppb	3.98	100 mL	283.6	84.4
Blank	3.97	200 mL	357.5	**4.9**
Blank + 50ppm Cl	3.95	200 mL	344.1	**8.2**
Blank + 100ppm Cl	3.93	200 mL	338.1	**10.3**
Blank + 300ppm Cl	3.91	200 mL	327.4	**15.6**
Blank + 500ppm Cl	3.91	200 mL	324.8	**17.2**
CCV (20 ppb std)	3.98	200 mL	320.1	20.7
CCB	3.99	200 mL	362.5	4.0
P-8	3.99	140 mL	321.9	19.3
P-14	3.97	140 mL	337.2	10.7
20 ppb std	3.95	200 mL	321.3	19.7
P-6	3.95	140 mL	330.2	14.0
20 ppb std	3.97	200 mL	321.9	19.3
ccv (60 ppb std)	3.98	200 mL	292.5	59.9
ccb	4.01	200 mL	358.2	4.8

Data in bold used for graphs in Table 4-2

Table 4-16

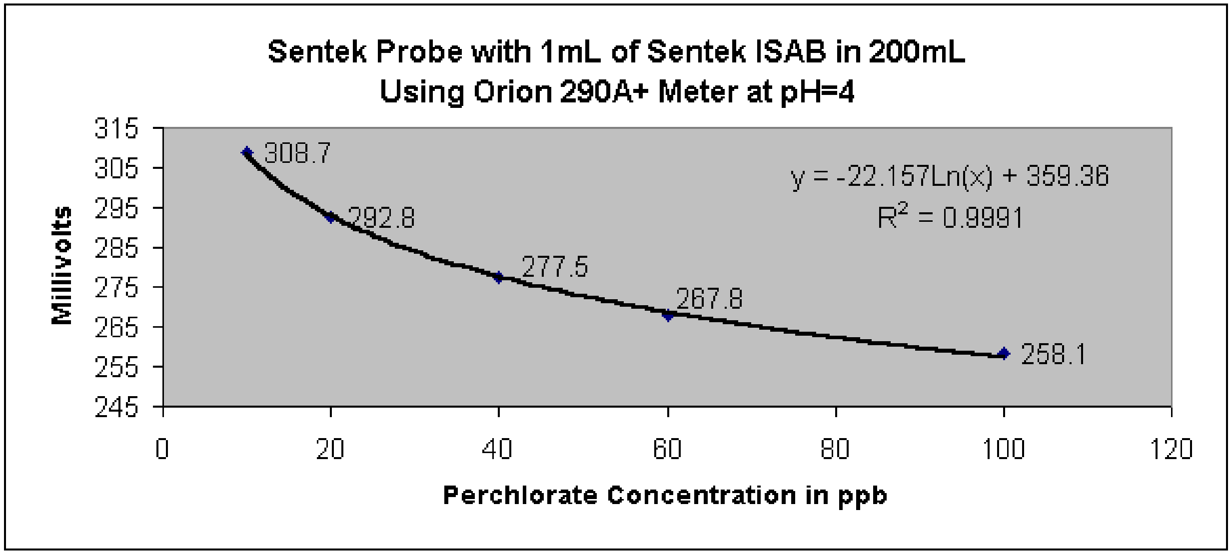
Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water Units: ug/L (ppb) Extraction/Digestion: Acidification to pH 4 with Sulfuric Acid

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

Analyst: Earth Tech, Inc.

Meter: ORION 290A (Portable) Date: January 25, 2001



Sentek Probe with 1mL of Sentek ISAB in 200mL
Using Orion 290A+ Meter at pH=4

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	4.01	200 mL	308.7	9.8
20	3.98	200 mL	292.8	20.2
40	4.02	200 mL	277.5	40.2
60	4.00	200 mL	267.8	62.3
100	4.03	200 mL	258.1	96.6
Calibration Date	**4/24/2001**		**Time**	**11:55am**
Temperature		**25.5^{0}C**		
Slope	**22.157**		**Intercept**	**359.36**

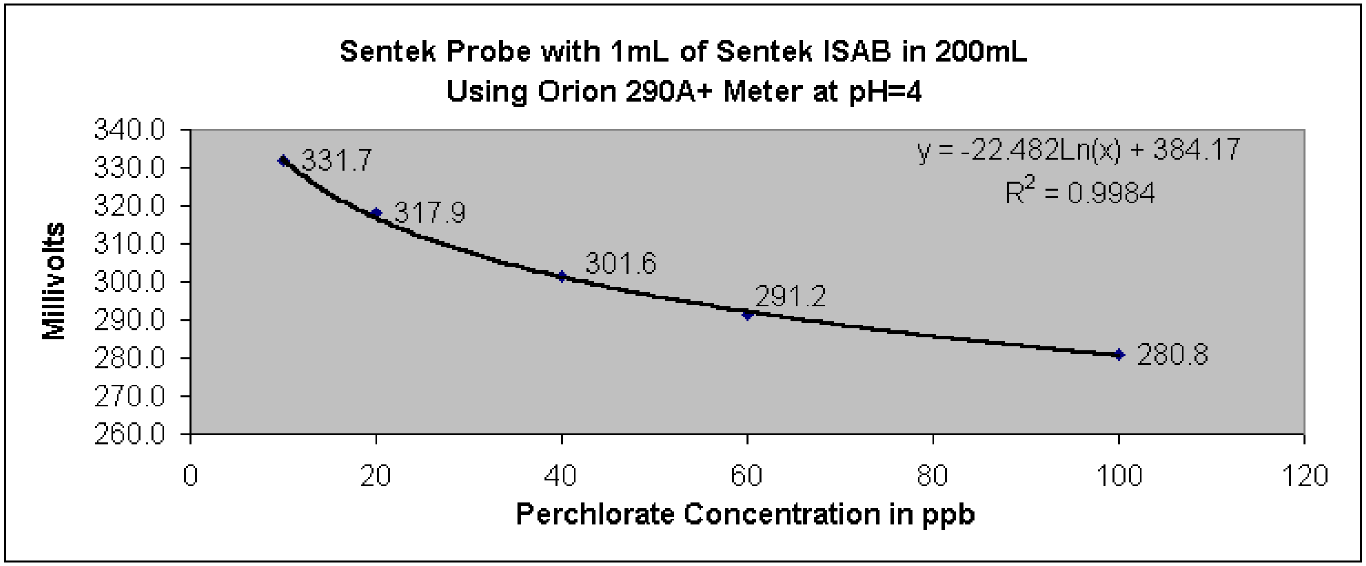
Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV		200 mL	274.4	46.3
Blank		200 mL	328.6	4.0
50 ppb std		200 mL	274.3	**46.5**
50 ppb std + 50ppm chloride		200 mL	273.0	**49.3**
50 ppb std + 60ppm chloride		200 mL	272.8	**49.7**
20 ppb std		200 mL	295.4	**17.9**
Blank		200 mL	333.1	**3.3**
Blank + 200 ppm chloride		200 mL	303.1	**12.7**
Blank + 1000 ppm chloride		200 mL	289.5	**23.4**
Blank + 2000 ppm chloride		200 mL	283.1	**31.2**
40 ppb std		200 mL	279.2	37.3
20 ppb std		200 mL	293.2	**19.8**
20 ppb + 200 ppm chloride		200 mL	288.9	**24.0**
20 ppb + 1000 ppm chloride		200 mL	279.4	**36.9**
20 ppb + 2000 ppm chloride		200 mL	275.2	**44.6**
70 ppb std		200 mL	265.9	**67.9**
70 ppb + 200 ppm chloride		200 mL	266.8	**65.2**
70 ppb + 1000 ppm chloride		200 mL	269.0	**59.0**
70 ppb + 2000 ppm chloride		200 mL	269.2	**58.5**
50 ppb std		200 mL	273.1	**49.1**
50 ppb + 200 ppm chloride		200 mL	272.6	**50.2**
50 ppb + 1000 ppm chloride		200 mL	272.1	**51.3**
50 ppb + 2000 ppm chloride		200 mL	271.6	**52.5**
20 ppb		200 mL	293.5	19.5
Blank		200 mL	332.6	3.3

Data in bold used for graphs in Table 4-2

Table 4-17

Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode
Matrix: Water Units: ug/L (ppb) Extraction/Digestion: Acidification to pH 4 with Sulfuric Acid
Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE
Analyst: Earth Tech, Inc.

Meter: ORION 290A (Portable) Date: February 28, 2001



Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	3.95	200 mL	331.7	10.3
20	3.96	200 mL	317.9	19.1
40	3.98	200 mL	301.6	39.4
60	3.96	200 mL	291.2	62.5
100	4.01	200 mL	280.8	99.3
Calibration Date: 2/28/01	**2/28/2001**		**Time**	**11:00am**
Temperature		**23.5^{0}C**		
Slope: 22.482	**22.482**		**Intercept**	**384.17**

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV	3.95	200 mL	296.2	50.0
Blank	3.99	200 mL	352.9	4.0
Blank + 0.5 ppm nitrate (0.11 ppm NO3-N)	3.99	200 mL	338.1	**7.8**
20 ppb std	3.98	200 mL	318.4	18.6
Blank + 1 ppm nitrate (0.23 ppm NO3-N)	3.98	200 mL	331.1	**10.6**
20 ppb std	3.97	200 mL	317.9	19.1
Blank + 2ppm nitrate (0.45 ppm NO3-N)	3.98	200 mL	324.5	**14.2**
20 ppb std	3.97	200 mL	317.4	19.5
Blank + 5ppm nitrate (1.13 ppm NO3-N)	3.99	200 mL	311.3	**25.6**
20 ppb std	3.97	200 mL	317.1	19.8
Blank + 10ppm nitrate 2.26 ppm NO3-N)	3.99	200 mL	302.2	**38.3**
10 ppb std	4.02	200 mL	330.1	11.1
10 ppb std + 0.5 ppm nitrate (0.11 ppm NO3-N)	4.01	200 mL	322.1	**15.8**
20 ppb std	3.97	200 mL	316.4	20.4
10 ppb std + 1 ppm nitrate (0.23 ppm NO3-N)	4.01	200 mL	318.1	**18.9**
20 ppb std	3.98	200 mL	316.1	20.7
10 ppb std + 2 ppm nitrate (0.45 ppm NO3-N)	4.01	200 mL	314.5	**22.2**
50 ppb std	4.01	200 mL	294.9	53.0
50 ppb std + 0.5 ppm nitrate (0.11 ppm NO3-N)	4.01	200 mL	292.8	**58.2**
50 ppb std +1 ppm nitrate (0.23 ppm NO3-N)	4.01	200 mL	291.5	**61.7**
50 ppb std + 2 ppm nitrate (0.45 ppm NO3-N)	4.01	200 mL	290.2	**65.4**
20 ppb std	3.98	200 mL	316.5	20.3
20 ppb std + 0.5 ppm nitrate (0.11 ppm NO3-N)	3.98	200 mL	312.5	**24.2**
20 ppb std + 1ppm nitrate (0.23 ppm NO3-N)	3.98	200 mL	309.9	**27.2**
20 ppb std + 2 ppm nitrate (0.45 ppm NO3-N)	3.98	200 mL	307.4	**30.4**
ccv (20 ppb std)	3.97	200 mL	316.1	20.7
ccb	3.99	200 mL	353.6	3.9

Note: ISE probe reconditioned between every analysis with acidified 100 ppb perchlorate standard.

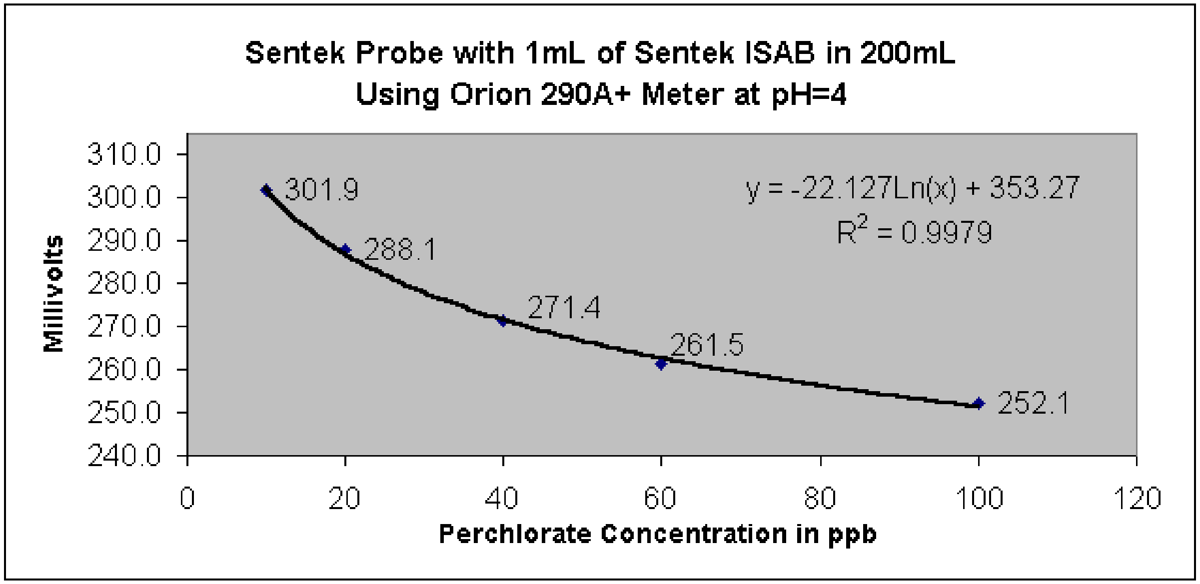
To convert nitrate to nitrate as nitrogen (NO3-N), divide by 4.43

Data in bold used for graphs in Table 4-3

Table 4-18A

Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode
Matrix: Water Units: ug/L (ppb) Extraction/Digestion: Acidification to pH 4 with Sulfuric Acid
Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE
Analyst: Earth Tech, Inc.

Meter: ORION 290A (Portable) Date: April 30, 2001



Sentek Probe with 1mL of Sentek ISAB in 200mL
Using Orion 290A+ Meter at pH=4

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	3.95	200 mL	301.9	10.2
20	3.96	200 mL	288.1	19.0
40	3.98	200 mL	271.4	40.4
60	3.96	200 mL	261.5	63.3
100	4.01	200 mL	252.1	96.8
Calibration Date	**4/30/2001**		**Time**	**12:00pm**
Temperature		**23.5^{0}C**		
Slope	**22.127**		**Intercept**	**353.27**

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV	4	200 mL	268.1	47.0
Blank	4	200 mL	320.0	**4.5**
Blank + 0.05 ppm Nitrate as N	4	200 mL	313.3	**6.1**
Blank + 0.1 ppm Nitrate as N	4	200 mL	309.5	**7.2**
Blank + 0.2 ppm Nitrate as N	4	200 mL	304.1	**9.2**
Blank + 0.5 ppm Nitrate as N	4	200 mL	295.0	**13.9**
Blank + 1.0 ppm Nitrate as N	4	200 mL	288.1	**19.0**
Blank + 2 ppm Nitrate as N	4	200 mL	280.0	**27.4**
Blank + 5 ppm Nitrate as N	4	200 mL	267.8	**47.6**
Blank + 10 ppm Nitrate as N	4	200 mL	258.7	**71.8**
ccv (20 ppb)	4	200 mL	288.2	18.9
ccb	4	200 mL	321.2	4.3
20ppb	4	200 mL	288.1	**19.0**
20 ppb + 5 ppm Nitrate as N	4	200 mL	262.5	**60.5**
20 ppb + 10 ppm Nitrate as N	4	200 mL	255.4	**83.4**
ccv (20 ppb)	4	200 mL	288.5	18.7
ccb	4	200 mL	319.5	4.6

Data in bold used for graphs in Table 4-3

Note: ISE probe reconditioned between every analysis with acidified 100 ppb perchlorate standard.

To convert nitrate as nitrogen (NO3-N) to nitrate as nitrate, multiply by 4.43

Table 4-18B

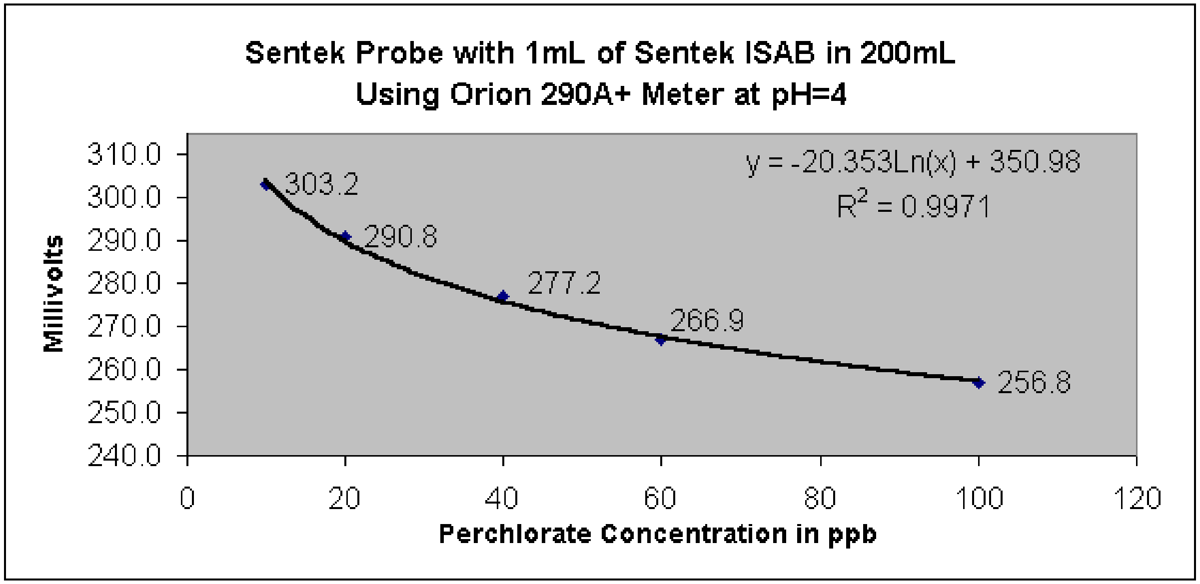
Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water Units: ug/L (ppb) Extraction/Digestion: Acidification to pH 4 with Sulfuric Acid

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

Analyst: Earth Tech, Inc.

Meter: ORION 290A (Portable) Date: May 1, 2001



Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	3.95	200 mL	303.2	10.5
20	3.96	200 mL	290.8	19.2
40	3.98	200 mL	277.2	37.5
60	3.96	200 mL	266.9	62.2
100	4.01	200 mL	256.8	102.2
Calibration Date	**5/1/2001**		**Time**	**1:15pm**
Temperature		**25.5^0C**		
Slope	**20.353**		**Intercept**	**350.98**

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV		200 mL	272.5	47.3
Blank		200 mL	321.2	**4.3**
20 ppb std		200 mL	291.1	**19.0**
20 ppb + 0.05ppm NO3 as N		200 mL	289.7	**20.3**
20 ppb + 0.1 ppm NO3 as N		200 mL	288.7	**21.3**
20 ppb + 0.2 ppm NO3 as N		200 mL	287.0	**23.2**
20 ppb + 0.5 ppm NO3 as N		200 mL	283.5	**27.5**
20 ppb + 1 ppm NO3 as N		200 mL	279.5	**33.5**
100 ppb check std		200 mL	256.7	**102.7**
ccb		200 mL	320.5	4.5
20 ppb std		200 mL	291.5	**18.6**
20 ppb std + 2 ppm NO3 as N*		200 mL	275.5	**40.8**
* + 10 ppb ClO4		200 mL	271.3	50.1
* + 20 ppb ClO4		200 mL	267.9	59.3
* + 30 ppb ClO4		200 mL	264.1	71.4
ccv (20 ppb)		200 mL	292.2	18.0
ccb		200 mL	322.5	4.1

Data in bold used for graphs in Table 4-3

Note: ISE probe reconditioned between every analysis with acidified 100 ppb perchlorate standard.

To convert nitrate as nitrogen (NO3-N) to nitrate as nitrate, multiply by 4.43

* Determination by the method of standard additions (MSA); See Table 4-22

Table 4-19

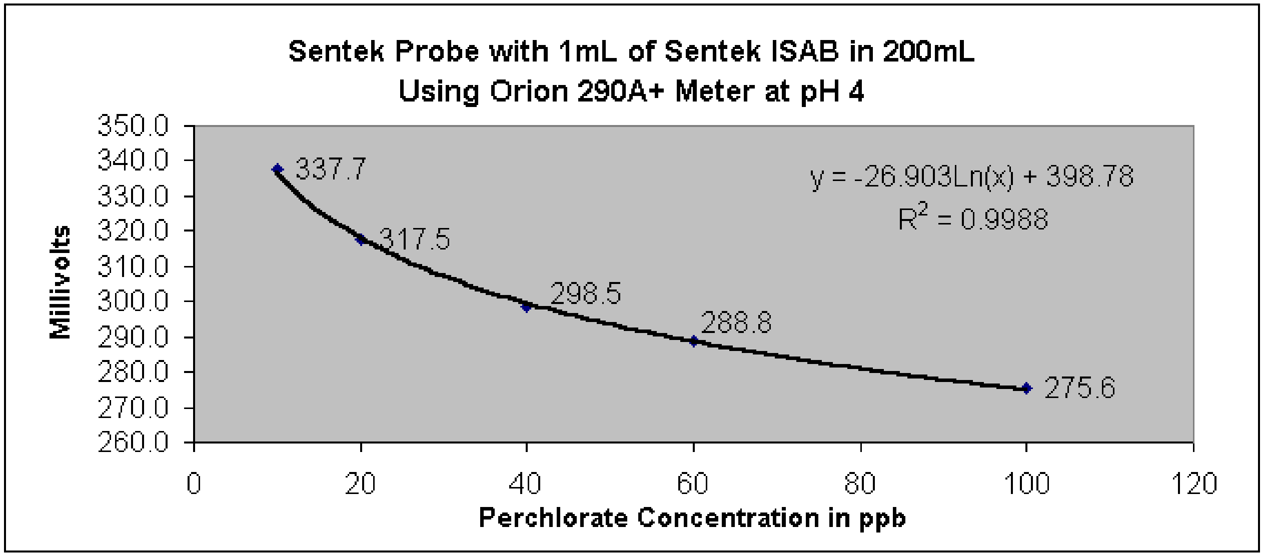
Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water Units: ug/L (ppb) Extraction/Digestion: Acidification to pH 4 with Sulfuric Acid

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

Analyst: Earth Tech, Inc.

Meter: ORION 290A (Portable) Date: March 2, 2001



Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	3.96	200 mL	337.7	9.7
20	4.01	200 mL	317.5	20.5
40	4.01	200 mL	298.5	41.6
60	4.02	200 mL	288.8	59.6
100	3.98	200 mL	275.6	97.4
Calibration Date	**3/2/2001**		**Time**	**12:00pm**
Temperature		**23.5^{0}C**		
Slope	**26.903**		**Intercept**	**398.8**

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV	3.96	200 mL	293.2	50.6
Blank	3.97	200 mL	357.7	4.6
Blank + 0.5 ppm Bromide	3.97	200 mL	351.1	**5.9**
Blank + 1 ppm Bromide	3.97	200 mL	348.2	**6.6**
Blank + 2 ppm Bromide	3.97	200 mL	344.5	**7.5**
Blank + 5 ppm Bromide	3.97	200 mL	335.2	**10.6**
20 ppb	4.01	200 mL	319.5	19.0
10 ppb std	3.96	200 mL	337.8	9.6
10 ppb std+ 0.5 ppm bromide	3.96	200 mL	334.1	**11.1**
10 ppb std+ 1 ppm bromide	3.96	200 mL	331.1	**12.4**
10 ppb std+ 2 ppm bromide	3.96	200 mL	327.6	**14.1**
10 ppb std+ 5 ppm bromide	3.96	200 mL	321.3	**17.8**
20 ppb	4.01	200 mL	318.6	19.7
20 ppb std+ 0.5 ppm bromide	4.01	200 mL	315.8	**21.9**
20 ppb std+ 1 ppm bromide	4.01	200 mL	313.7	**23.6**
20 ppb std+ 2 ppm bromide	4.01	200 mL	311.6	**25.5**
20 ppb std+ 5 ppm bromide	4.01	200 mL	308.1	**29.1**
50 ppb	3.95	200 mL	292.0	52.9
50 ppb std+ 0.5 ppm bromide	3.95	200 mL	291.5	**53.9**
50 ppb std+ 1 ppm bromide	3.95	200 mL	291.1	**54.7**
50 ppb std+ 2 ppm bromide	3.95	200 mL	290.6	**55.8**
50 ppb std+ 5 ppm bromide	3.95	200 mL	289.7	**57.7**
20 ppb	3.98	200 mL	318.5	19.8
Blank	4.01	200 mL	354.2	5.2
P-1	4.02	200 mL	281.0	79.7
100 ppb std	4.01	200 mL	270.6	117.3
ccb	4.01	200 mL	355.1	5.1

Data in bold used for graph in Table 4-4

Table 4-20

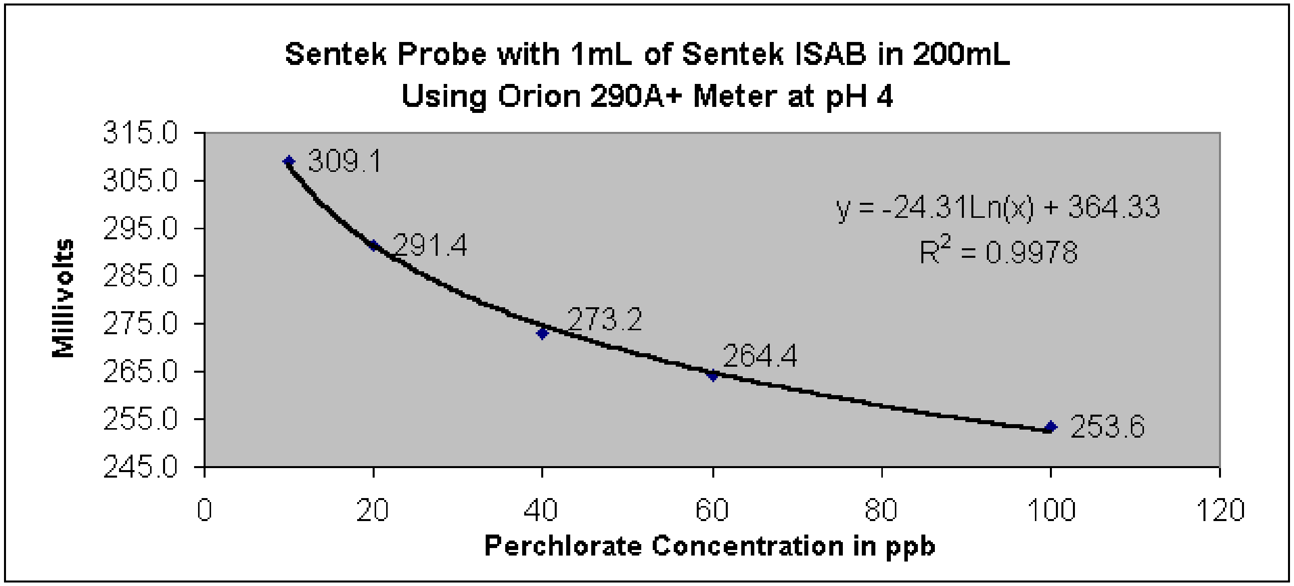
Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water   Units: ug/L (ppb)   Extraction/Digestion: Acidification to pH 4 with Sulfuric Acid

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

Analyst: Earth Tech, Inc.

Meter: ORION 290A (Portable)   Date: April 23, 2001



Sentek Probe with 1mL of Sentek ISAB in 200mL
Using Orion 290A+ Meter at pH 4

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	3.96	200 mL	309.1	9.3
20	4.01	200 mL	291.4	19.5
40	4.01	200 mL	273.2	41.7
60	4.02	200 mL	264.4	60.3
100	3.98	200 mL	253.6	94.8
Calibration Date	**4/23/2001**		**Time**	**12:45pm**
Temperature		**24.5^{0}C**		
Slope	**24.31**		**Intercept**	**364.3**

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV		200 mL	269.1	49.6
Blank		200 mL	330.3	**3.8**
Blank + 0.1 ppm Fluoride		200 mL	330.1	**3.9**
Blank + 0.5 ppm Fluoride		200 mL	330.5	**3.8**
Blank + 1 ppm Fluoride		200 mL	331.5	**3.6**
Blank + 2 ppm Fluoride		200 mL	330.5	**3.8**
Blank + 5 ppm Fluoride		200 mL	329.8	**3.9**
20 ppb		200 mL	290.4	20.3
10 ppb std		200 mL	309.1	**9.3**
10 ppb std+ 0.5 ppm Fluoride		200 mL	308.9	**9.4**
10 ppb std+ 1 ppm Fluoride		200 mL	308.7	**9.5**
10 ppb std+ 2 ppm Fluoride		200 mL	308.5	**9.5**
10 ppb std+ 5 ppm Fluoride		200 mL	308.0	**9.7**
20 ppb		200 mL	292.4	**18.7**
20 ppb std+ 0.5 ppm Fluoride		200 mL	292.3	**18.8**
20 ppb std+ 1 ppm Fluoride		200 mL	292.2	**18.9**
20 ppb std+ 2 ppm Fluoride		200 mL	292.1	**18.9**
20 ppb std+ 5 ppm Fluoride		200 mL	291.9	**19.1**
50 ppb		200 mL	268.0	**51.9**
50 ppb std+ 0.5 ppm Fluoride		200 mL	267.9	**52.1**
50 ppb std+ 1 ppm Fluoride		200 mL	267.9	**52.1**
50 ppb std+ 2 ppm Fluoride		200 mL	268.0	**51.9**
50 ppb std+ 5 ppm Fluoride		200 mL	267.8	**52.3**
20 ppb		200 mL	289.5	21.1
Blank		200 mL	330.5	3.8

Data in bold used for graph in Table 4-5

Table 4-21

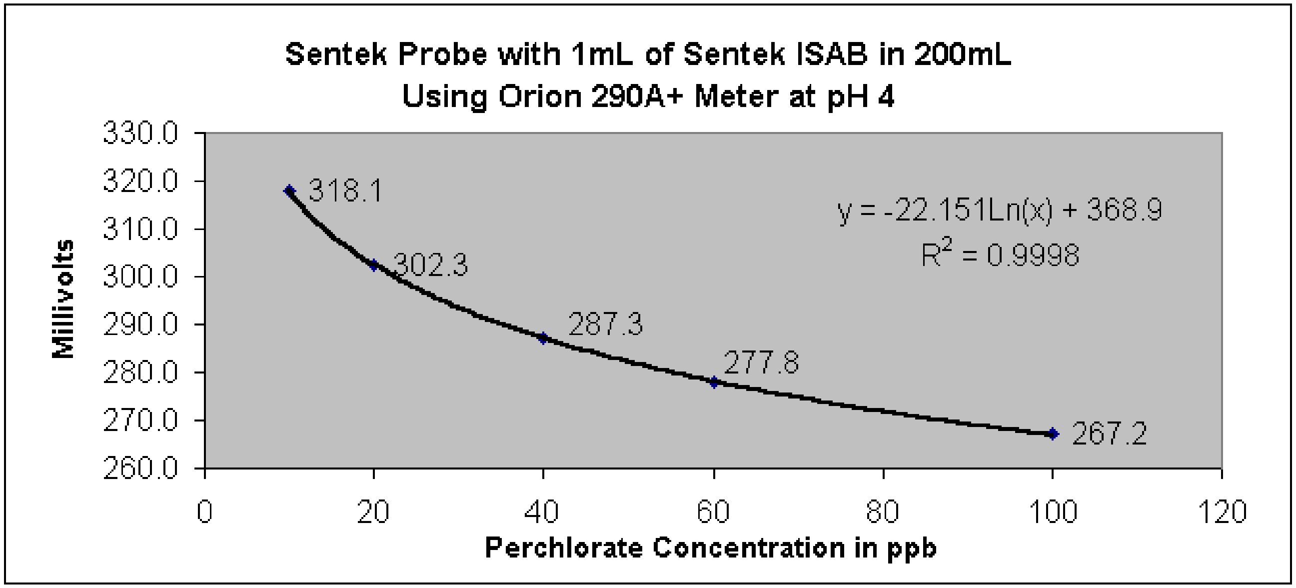
Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water Units: ug/L (ppb) Extraction/Digestion: Acidification to pH 4 with Sulfuric Acid

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

Analyst: Earth Tech, Inc.

Meter: ORION 290A (Portable) Date: February 19, 2001



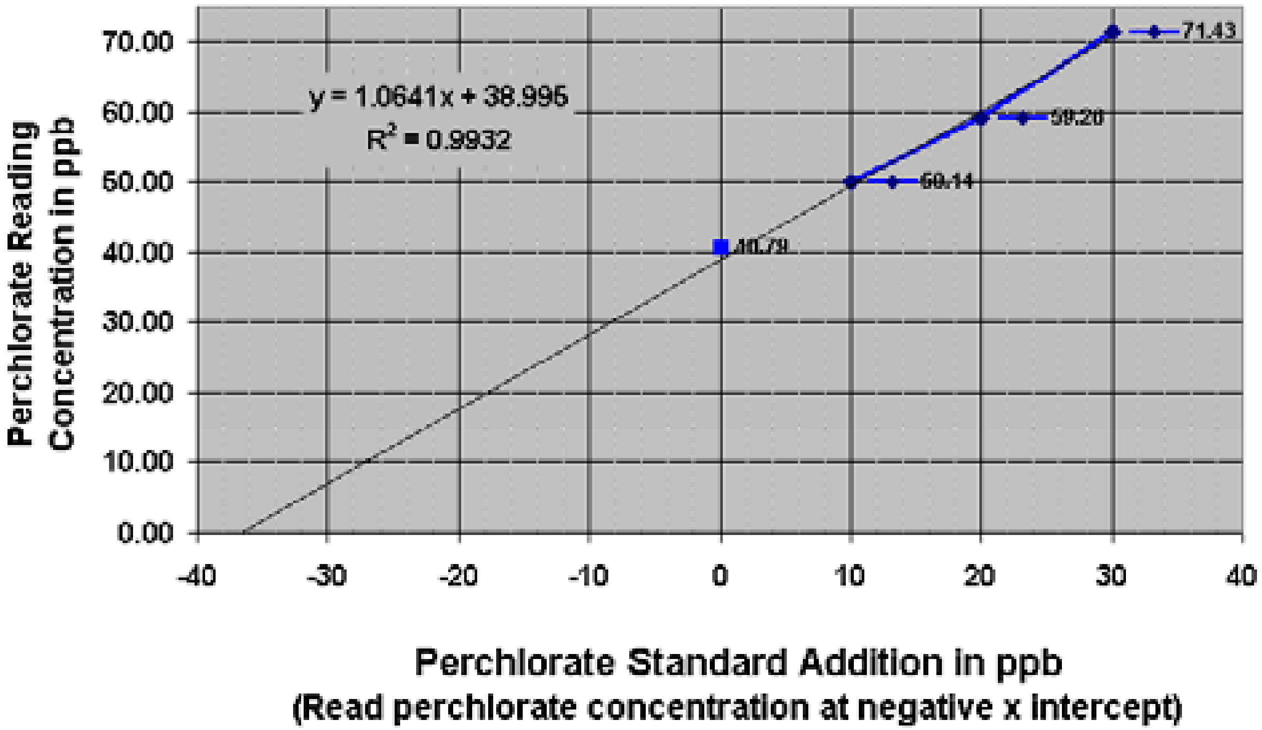
Sentek Probe with 1mL of Sentek ISAB in 200mL
Using Orion 290A+ Meter at pH 4

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	3.96	200 mL	318.1	9.9
20	4.01	200 mL	302.3	20.2
40	4.01	200 mL	287.3	39.8
60	4.02	200 mL	277.8	61.1
100	3.98	200 mL	267.2	98.6
Calibration Date	**2/19/2001**		**Time**	**11:30pm**
Temperature		**22^0C**		
Slope	**22.151**		**Intercept**	**368.9**

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV	4.02	200 mL	282.7	49.0
MB/ICB	3.97	200 mL	335.2	4.6
10 ppb	4.01	200 mL	318.1	**9.9**
10 ppb + 1ppm Phosphate	4.02	200 mL	318.1	**9.9**
10 ppb + 5ppm Phosphate	4.01	200 mL	318.0	**10.0**
10 ppb +10ppm Phosphate	4.01	200 mL	318.0	**10.0**
10 ppb +20ppm Phosphate	4.01	200 mL	317.9	**10.0**
Blank	3.98	200 mL	336.8	**4.3**
Blank +1ppm phosphate	3.99	200 mL	336.9	**4.2**
Blank +5ppm phosphate	3.99	200 mL	337.2	**4.2**
Blank +10ppm phosphate	3.99	200 mL	337.5	**4.1**
Blank +20ppm phosphate	3.99	200 mL	337.6	**4.1**
Blank +50ppm phosphate	4.00	200 mL	337.1	**4.2**
20 ppb	4.02	200 mL	305.0	**17.9**
20ppb +1ppm phosphate	4.02	200 mL	304.9	**18.0**
20ppb +5ppm phosphate	4.02	200 mL	304.5	**18.3**
20ppb +10ppm phosphate	4.01	200 mL	304.3	**18.5**
20ppb +20ppm phosphate	4.02	200 mL	304.1	**18.6**
50 ppb	3.97	200 mL	281.8	**51.0**
50ppb +1ppm phosphate	3.97	200 mL	281.6	**51.5**
50ppb +5ppm phosphate	3.97	200 mL	281.5	**51.7**
50ppb +10ppm phosphate	3.97	200 mL	281.5	**51.7**
50ppb +20ppm phosphate	3.98	200 mL	281.4	**51.9**
20 ppb std	4.01	200 mL	306.9	16.4
ccb	4	200 mL	335.3	4.6

Data in bold used for graph in Table 4-6

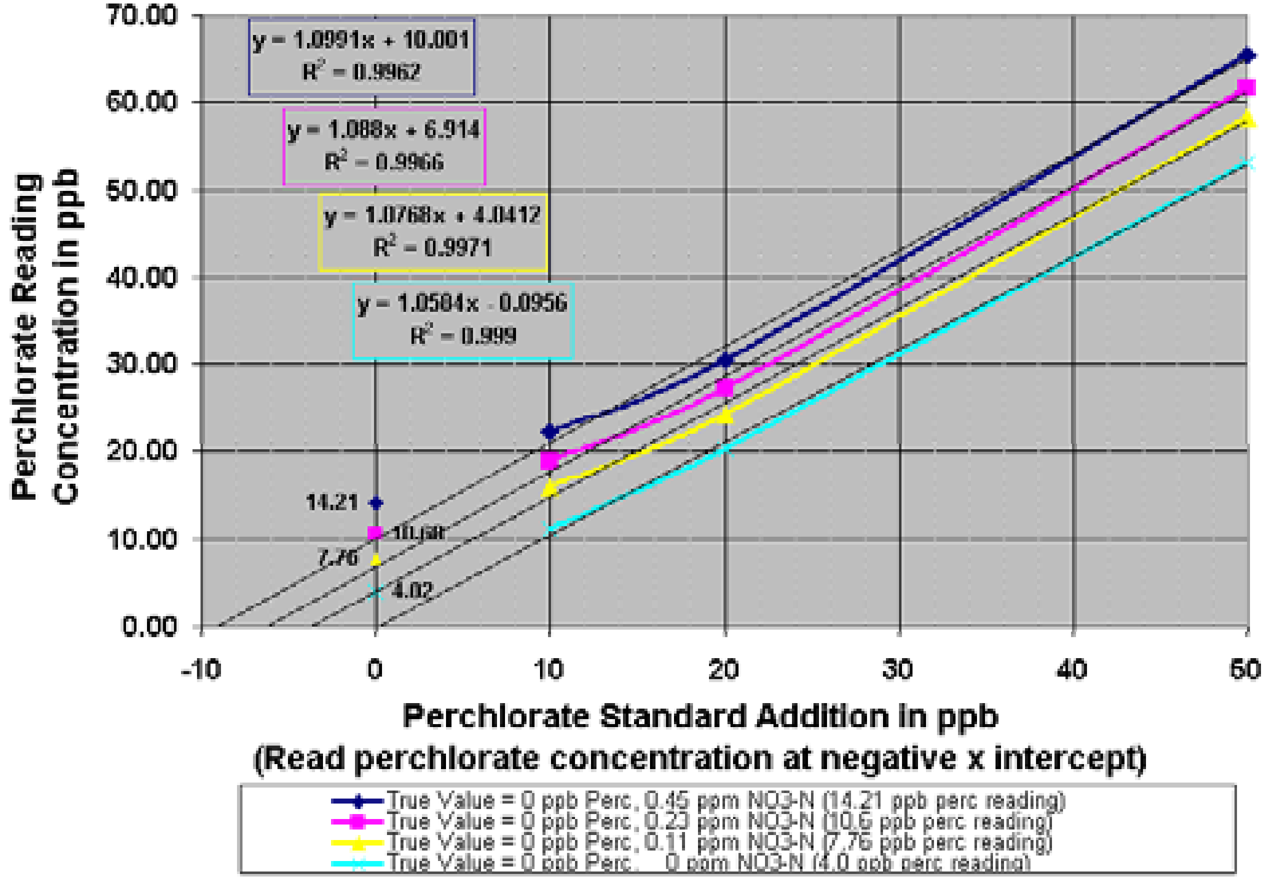
Table 4-22A: Perchlorate Determination by MSA: Linear Fit



True Value = 20 ppb perchlorate with 2.0 ppm NO3-N
Perchlorate Reading = 40.8 ppb
MSA Found Value = 36 ppb perchlorate

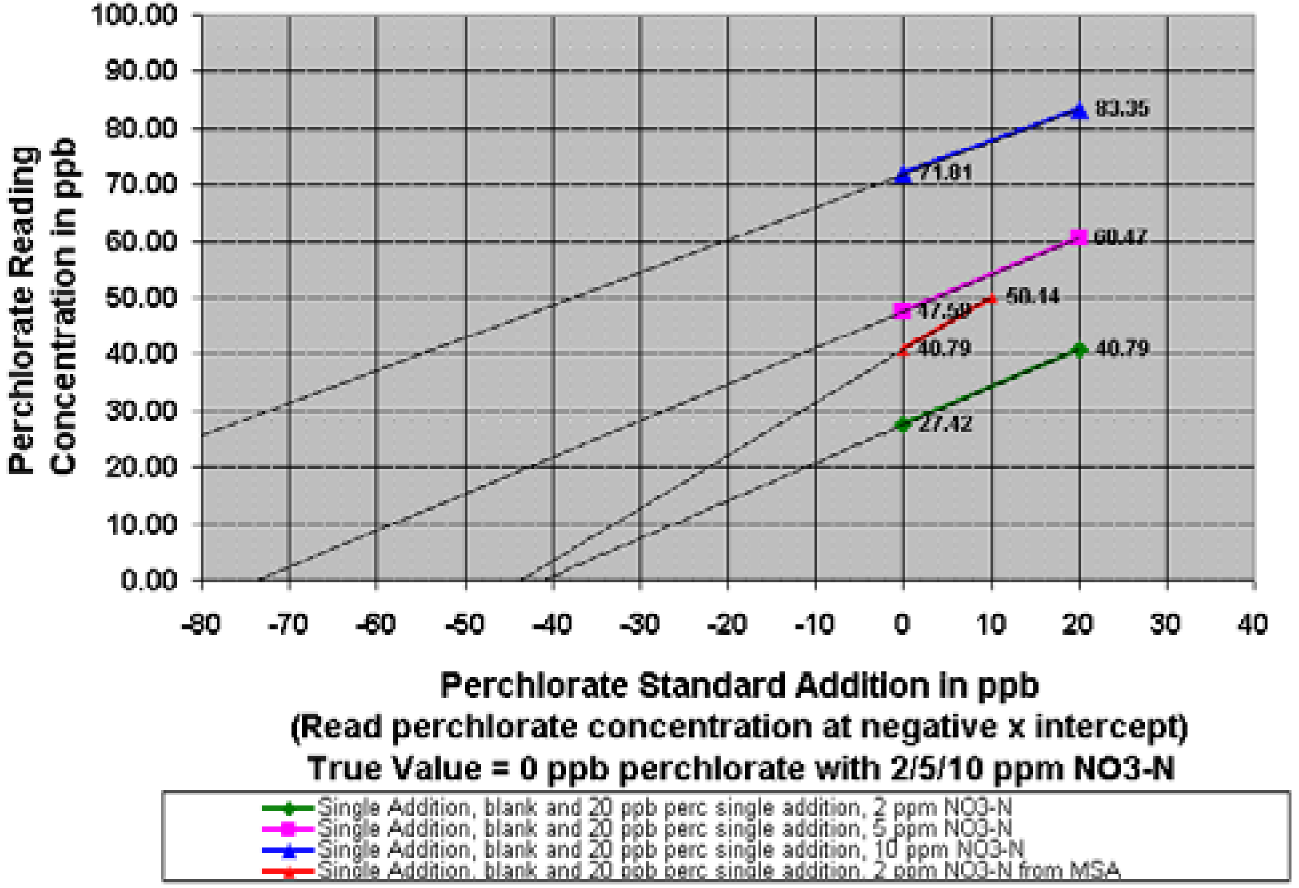
Data From Table 4-18B   ISE = Ion Selective Electrode   ppb = parts per billion (µg/L)   ppm = parts per million (mg/L)

Table 4-22B: Perchlorate Determination by MSA: Low Nitrate Interference, Linear Fit



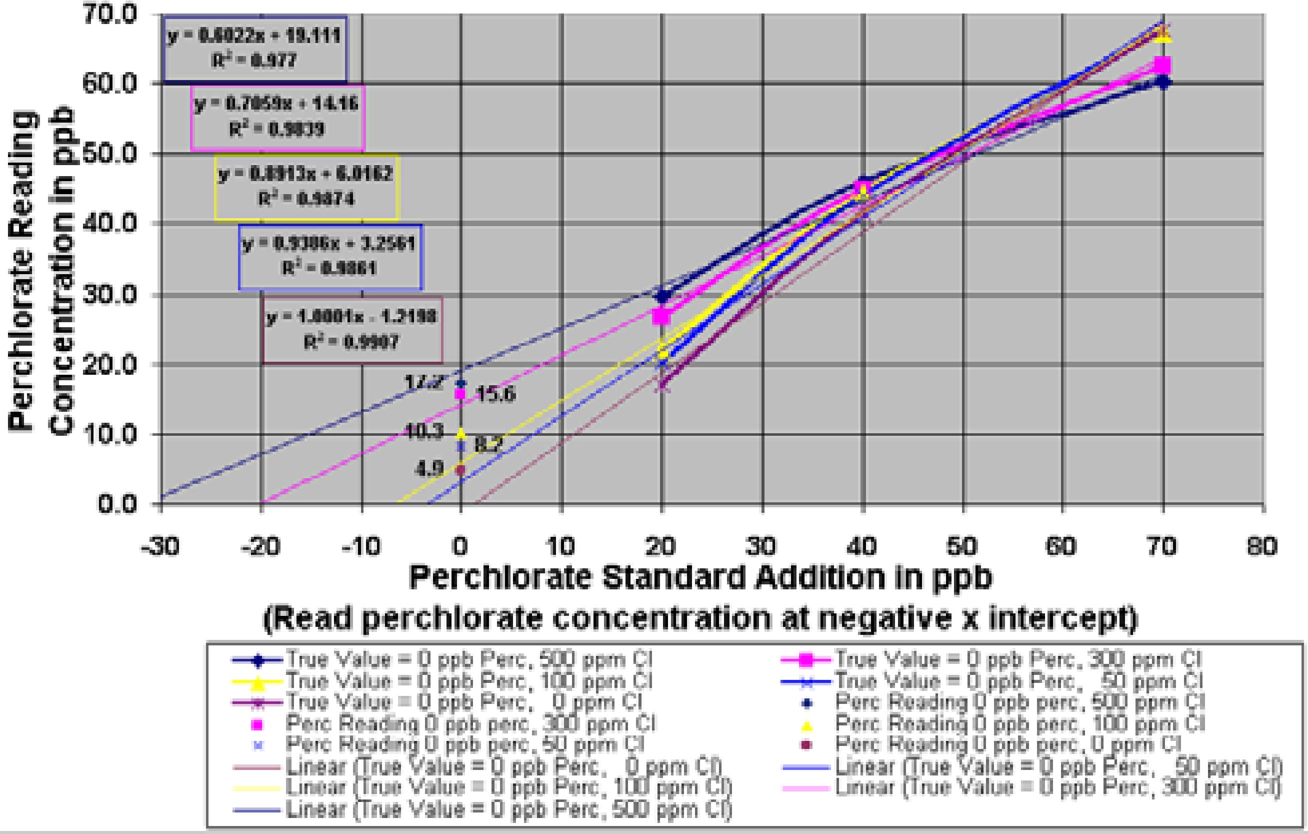
Data From Table 4-17 ISE = Ion Selective Electrode ppb = parts per billion (µg/L) ppm = parts per million (mg/L)

Table 4-22C: Perchlorate Determination by MSA: Single Addition for High Nitrate Interference



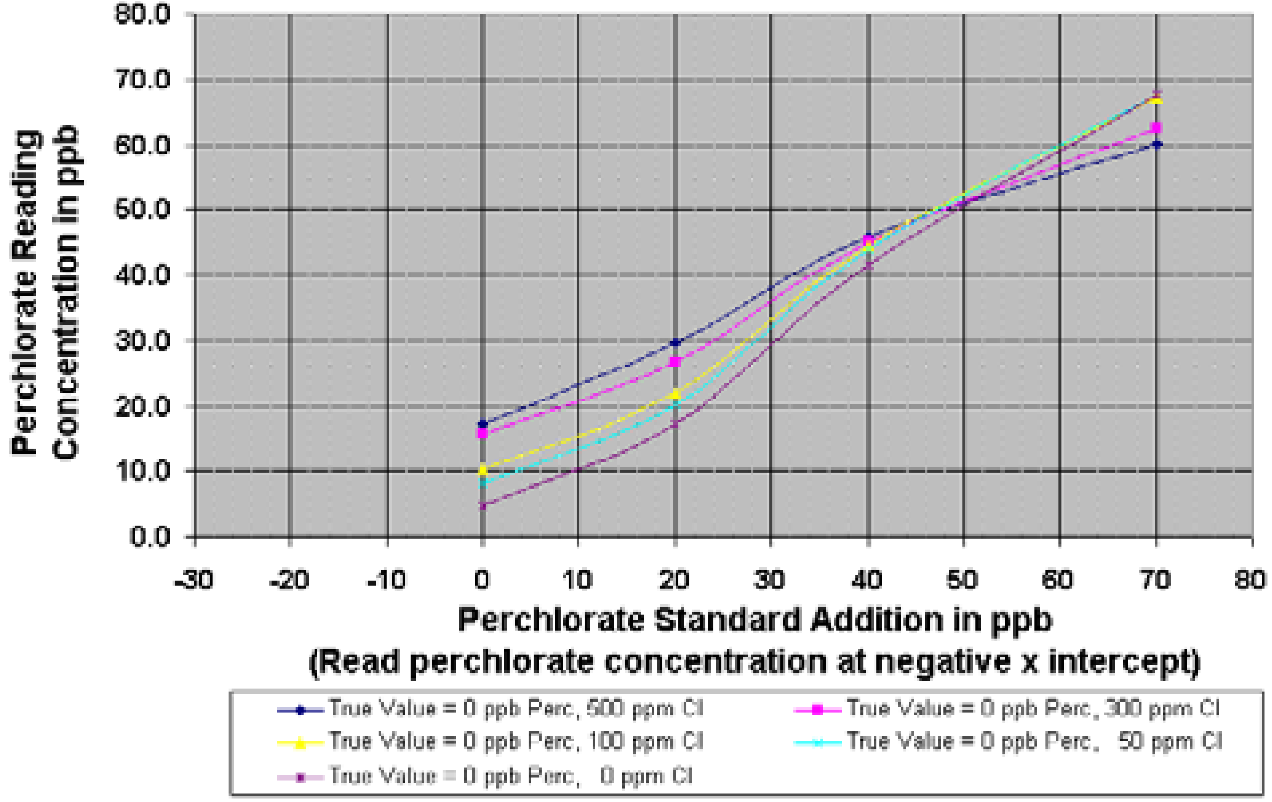
Data From Tables 4-18A and 4-18B ISE = Ion Selective Electrode ppb = parts per billion (µg/L) ppm = parts per million (mg/L)

Table 4-23A: Perchlorate Determination by MSA:
Chloride Interference
20/40/70 ppb Perchlorate Additions - Linear Fit



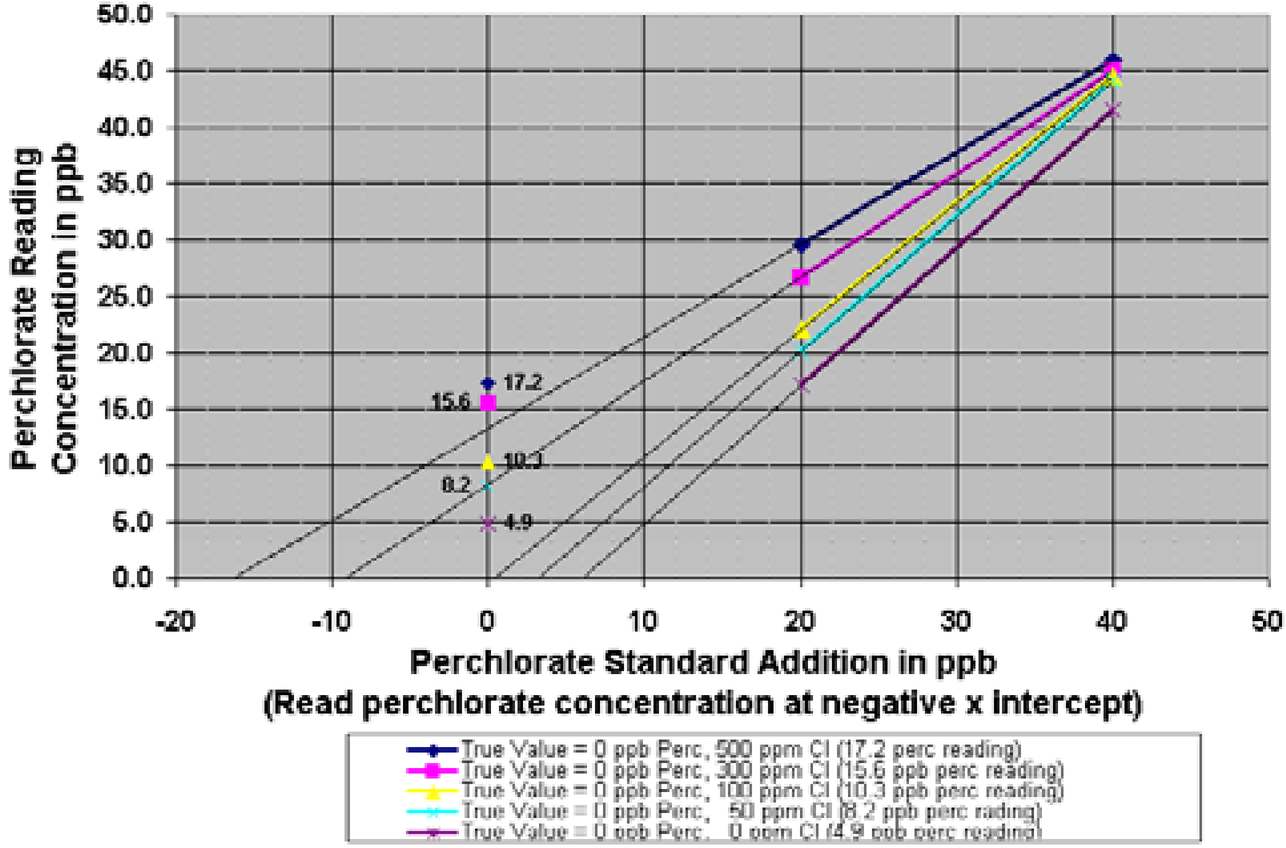
Data From Table 4-14 ISE = Ion Selective Electrode ppb = parts per billion (µg/L) ppm = parts per million (mg/L)

Table 4-23B: Perchlorate Determination by MSA: Background Chloride Interference 0/20/40/70 ppb Perchlorate



Data From Table 4-14 ISE = Ion Selective Electrode ppb = parts per billion (µg/L) ppm = parts per million (mg/L)

Table 4-23C: Perchlorate Determination by MSA: Chloride Interference 20/40 ppb Perchlorate Additions



Data From Table 4-14 ISE = Ion Selective Electrode ppb = parts per billion (µg/L) ppm = parts per million (mg/L)

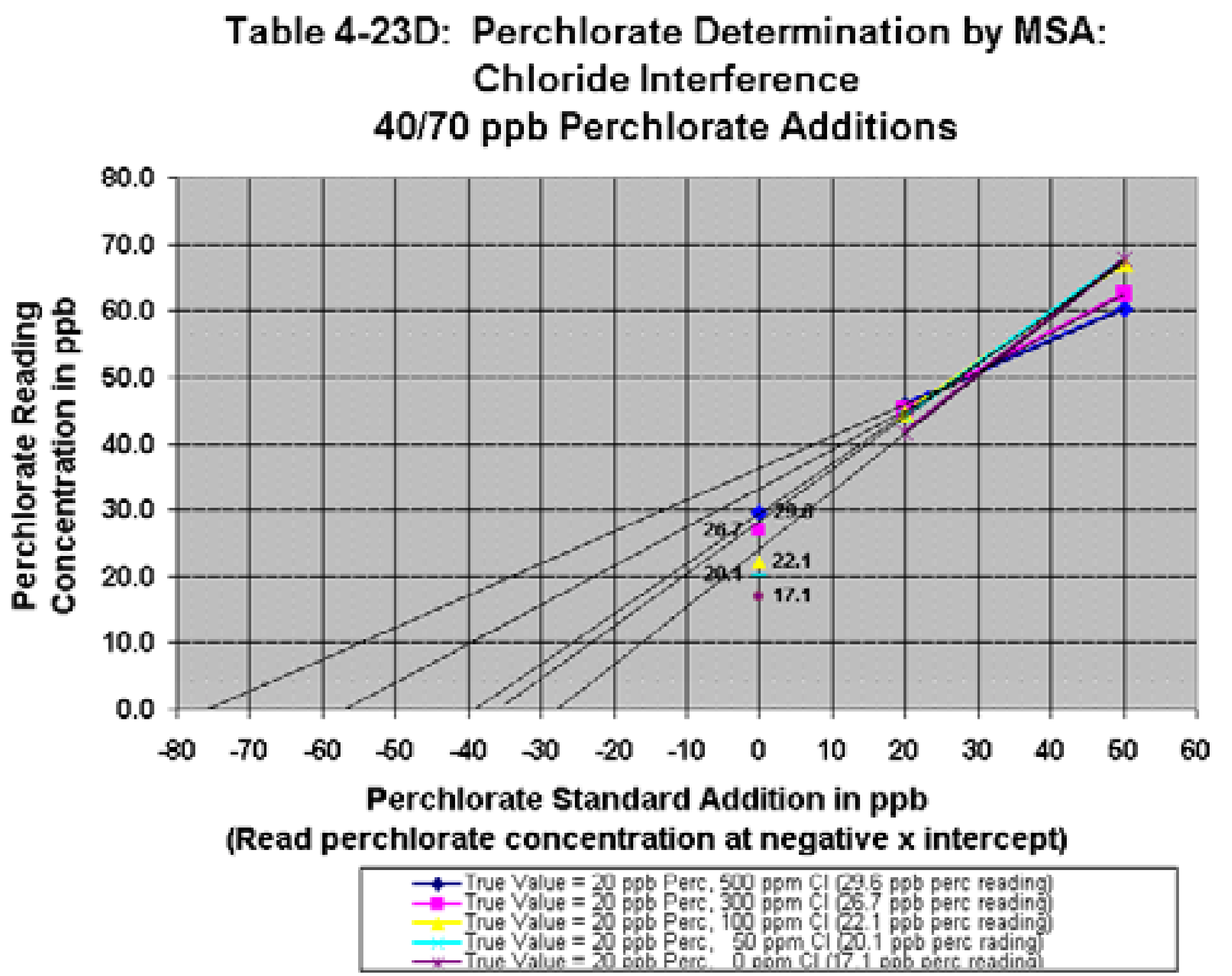


Table 4-23D: Perchlorate Determination by MSA:
Chloride Interference
40/70 ppb Perchlorate Additions

Data From Table 4-14 ISE = Ion Selective Electrode ppb = parts per billion (µg/L) ppm = parts per million (mg/L)

SECTION 5 TABLES

TABLES 5-1 THROUGH 5-6

Table 5-1A - Sample Site/Locations with Historical Interferent Anion Concentrations and Correction Factors

Site-Location ID	Historical Alkalinity as CO3 (ppm)	Historical Chloride Level (ppm)	Chloride Correction Factor, Table 4-7	Historical Nitrate (NO3-N) Level (ppm)	Nitrate (NO3-N) Correction Factor, Table 4-8	Historical Bromide Level (ppm)	Bromide Correction Factor, Table 4-9	Other Known Anions (ppm); TOC (ppm); and Organic Compounds(ppb)
ED-188-MW01	NA	NA	N/A	NA	N/A	NA	N/A	Contains high levels of organic contaminants
ED-189-MW01	205	331	8.1	12.6	68.1	1.0	2.6	F = 0.8; High levels of organic contaminants
ED-189-MW01-DUP	205	331	8.1	12.6	68.1	1.0	2.6	---
ED-189-MW02	NA	490	NA	2.9	NA	1.8	3.8	Contains high levels of organic contaminants
ED-189-MW03	NA	325	10.4	0.29	5.8	1.0	2.6	Contains high levels of organic contaminants
ED-196-MW01	223	380	N/A	0.18	4.1	1.2	2.9	F = 0.8, PO4
ED-196-MW03	NA	330	10.4	0.17	4.0	1.1	2.7	F = 0.7, PO4 = 0.14; toluene=44 ppb
ED-196-MW06	206	425	11.6	1.4	17.7	1.4	3.2	F = 0.64, PO4 <0.1
ED-196-MW06	206	425	11.6	1.4	17.7	1.4	3.2	F = 0.64, PO4 <0.1
ED-199-MW01	NA	245	9.0	0.06	1.5	0.7	2.0	None Detected
ED-199-MW01	NA	245	9.0	0.06	1.5	0.7	2.0	None Detected
ED-274-MW01	NA	32	2.1	0.25	5.3	0.3	0.9	F=0.8
ED-274-MW02	NA	31	2.2	0.10	2.5	0.3	0.9	F=0.9
ED-274-MW03	NA	26	1.7	0.24	5.1	0.3	0.9	F=0.8
ED-285-MW01	EB	NA	0	NA	0	NA	0	EB
ED-285-MW02	218	255	9.1	0.18	4.3	0.8	2.2	F <1
ED-285-MW02-DUP	218	255	9.1	0.18	4.3	0.8	2.2	---
ED-286-MW01	232	300	N/A	0.29	N/A	0.7	2.0	F <1
ED-286-MW01-DUP	232	300	N/A	0.29	N/A	0.7	2.0	---
ED-286-MW03	NA	NA	NA	NA	NA	NA	NA	Contains low levels of organic contaminants
ED-286-MW03 (RE)	NA	NA	NA	NA	NA	NA	NA	---
ED-286-MW03 (RE)	NA	NA	NA	NA	NA	NA	NA	---
ED-286-MW03 (RE)	NA	NA	NA	NA	NA	NA	NA	---
ED-286-MW03-DUP	NA	NA	NA	NA	NA	NA	NA	---
ED-422-MW01	NA	500	7.7	6.3	49.5	1.3	3.1	Contains high levels of organic contaminants
ED-422-MW01	NA	500	7.7	6.3	49.5	1.3	3.1	---
ED-422-MW01-RE1	NA	500	7.7	6.3	49.5	1.3	3.1	---
ED-422-MW01-RE2	NA	500	7.7	6.3	49.5	1.3	3.1	---

ED-422-MW01-RE3	NA	500	7.7	6.3	49.5	1.3	3.1	---
ED-NM-MW01A	295	110	3.1	0.1	2.5	0.4	1.2	F = 0.98, PO4 = 15, TOC = 1.2
ED-NM-MW01A1	EB	0	0.0	0	0.0	0.0	0.0	EB
ED-NM-MW01C	157	721	9.5	1.9	21.7	2.1	4.1	F = 0.99, NO2 = 0.33, PO4 = 4.7, TOC = 0.57, 11 SVOC TICs<20ppb, Tol = 1.3ppb
ED-NM-MW01B	311	117	5.9	0.06	1.5	0.5	1.5	F = 1, PO4 = 1.2, TOC = 0.2, 1 SVOC TICs@29ppb
ED-NM-MW02A	173	10	0.6	0.3	6.0	ND	0.0	F = 1, PO4 = 1.2, TOC = 0.24, 1 SVOC TICs<29ppb
ED-NM-MW02B	161	451	11.9	0.05	1.5	1.3	3.1	PO4 = 0.45, TOC = 0.4, 1 SVOC TIC@16ppb
ED-NM-MW02C	130	130	5.5	0.11	2.7	0.6	1.7	F = 1.3, PO4 = 0.3, TOC = 0.6
ED-NM-MW03A	169	30	2.0	0.4	7.5	ND	0.0	F = 0.82, PO4 = 3.1, TOC = 0.47
ED-NM-MW03B	190	242	11.8	0.16	3.7	0.8	2.2	PO4 = 0.3.4, TOC = 0.9, PERC = 77 (5/2000)
ED-NM-MW03C	115/40.9	485/1160	18.6	0.14	3.3	3.4	5.5	F = 0.7, PO4 = 5.3, TOC = 0.8, 1 SVOC TIC@7ppb
ED-NM-MW04A	254/176	25	1.7	0.41	7.6	ND	0	F = 1, PO4 = 5.3/1, TOC = 0.5, MTBE@2.4ppb
ED-NM-MW04B	210	120	6.2	0.44	8.1	0.4	1.2	F = 0.9, PO4 = 5.4/0.74, TOC = 0.3; 1 SVOC TIC@57ppb
ED-NM-MW04B-DUP	210	120	6.2	0.44	8.1	0.4	1.2	---
ED-NM-MW04C	88	1000	18.5	0.15	3.5	3.5	5.6	F = 3, PO4 = 0.24, TOC = 1.0, 18 SVOC TIC<37ppb
ED-NM-MW05-W14	222	146	6.8	0.06	1.5	0.5	1.5	PO4 = 0.13; Contains high levels of organic contaminants: Ethanol@35000, Tol@1.1, VOC TIC@21, 6 SVOC TIC<770/13 SVOC TIC<240
ED-NM-MW06-W06	167	25	1.7	0.16	3.7	0.2	0.6	PO4 = 0.07, TOC = 0.5, 1 SVOC TIC@45ppb
ED-NM-MW07-W11	101	350	10.7	0.14	3.3	1.4	3.2	PO4 = 0.13, TOC = 12.4, NDMA @3ppt
ED-USGS-W1AE2	NA	NA	NA	NA	NA	NA	NA	Not Available
ED-USGS-W1AE4	NA	NA	NA	NA	NA	NA	NA	No Anions Available, all organics ND
ED-USGS-W1C1	NA	NA	NA	NA	NA	NA	NA	No Anions Available, all organics ND
ED-USGS-W1C2	NA	NA	NA	NA	NA	NA	NA	Not Available
ED-USGS-W1C3	NA	NA	NA	NA	NA	NA	NA	Not Available
ED-USGS-W1C4	NA	NA	NA	NA	NA	NA	NA	Not Available

Table 5-1B - First Semi-Annual Groundwater (SAGW) Event (December 2000) Samples, Perchlorate ISE Readings and Results, and Definitive Level Results by EPA Method 314.0

First SAGW Event (December 2000) Split Sample ID	First SAGW (12/00) ISE ID	Uncorrected Perchlorate ISE Reading (ppb), pH 4.0	Anion Corrected Perchlorate ISE Reading (ppb), pH 4.0	Final Reported Perchlorate ISE Result (ppb), pH 4.0	Perchlorate Definitive Result by EPA 314.0 (ppb)	Definitive Result RL (ppb)
Not Collected This Event	NC	---	---	---	---	---
ED-189-MW01-W24/-W16	P-1	79.7	0.9	ND (<15)	ND (<16)	16
ED-189-MW01-W25/-W17	P-2	Not Analyzed	Not Analyzed	Not Analyzed	ND (<16)	16
ED-189-MW02-W13/-W09	P-3	Not Analyzed	Not Analyzed	Not Analyzed	ND (<16)	16
ED-189-MW03-W08/-W07	P-4	Not Analyzed	Not Analyzed	Not Analyzed	19	16
ED-196-MW01-W09/-W05,-W06	**P-5**	24423	NA (diluted 400X)	**24423**	**20000, 25000**	4000
ED-196-MW03-W11/-W09	P-6	14.0	-3.1	ND (<15)	ND (<4)	4
ED-196-MW06-W15/-W11	P-7	23.4	-9.1	ND (<15)	ND (<16)	16
Not Collected This Event	NC	NC	NC	NC	NC	NC
ED-199-MW01-W14/-W13	P-8	19.3	6.8	ND (<15)	ND (<4)	4
Not Collected This Event	NC	---	---	---	---	---
Not Collected This Event	NC	---	---	---	---	---
Not Collected This Event	NC	---	---	---	---	---
Not Collected This Event	NC	---	---	---	---	---
Not Collected This Event	NC	---	---	---	---	---
ED-285-MW02-W06/-W05	P-9	14.6	-1.0	ND (<15)	ND (<4)	4
ED-285-MW02-W06-DUP/-W05	P-9-DUP (pH 4.4)	7.0	-8.6	ND (<15)	ND (<4)	4
ED-286-MW01-W08/-W03	**P-10**	4336	N/A (diluted 200X)	**4336**	**5900**	P-10
---	NC	---	---	---	---	---
Not Collected This Event	NC	---	---	---	---	---
---	---	---	---	---	---	---
---	---	---	---	---	---	---
---	---	---	---	---	---	---
---	---	---	---	---	---	---
ED-422-MW01-W07/-W06	P-11	63.7	3.4	ND (<15)	6	4
ED-422-MW01-W07-DUP/-W06	P-11-DUP	45.3	-15.0	ND (<15)	6	4
ED-422-MW01-W08/-W06	P-102	60.1	-0.2	ND (<15)	6	4

ED-422-MW01-W09/-W06	P-103	42.2	-18.1	ND (<15)	6	4
ED-422-MW01-W10/-W06	P-104	40.7	-19.6	ND (<15)	6	4
ED-NM-MW01A-W10/-W09	P-12	15.5	8.7	ND (<15)	ND (<4)	4
ED-NM-MW01A-W11(EB)	P-13	4.0	4.0	ND (<15)	ND (<4)	4
Not Collected This Event	NC	---	---	---	---	---
Not Collected This Event	NC	---	---	---	---	---
ED-NM-MW02A-W11/-W09	P-14	10.7	4.1	ND (<15)	ND (<4)	4
Not Collected This Event	NC	---	---	---	---	---
Not Collected This Event	NC	---	---	---	---	---
ED-NM-MW03A-W07/-W06	P-15	9.0	-0.5	ND (<15)	ND (<4)	4
Not Collected This Event	NC	---	---	---	---	---
Not Collected This Event	NC	---	---	---	---	---
Not Collected This Event	NC	---	---	---	---	---
ED-NM-MW04B-W13/-W11	P-16	15.0	-0.5	ND (<15)	ND (<4)	4
ED-NM-MW04B-W13/-W08	P-16-DUP	18.0	2.5	ND (<15)	ND (<4)	4
Not Collected This Event	NC	---	---	---	---	---
ED-NM-MW05-W14/-W11	P-17	Not Analyzed	Not Analyzed	Not Analyzed	ND (<16)	16
ED-NM-MW06-W06/-W05	P-18	8.3	Anions NA	ND (<15)	ND (<4)	4
ED-NM-MW07-W11/-W10	P-19	15.2	-2.0	ND (<15)	ND (<4)	4
ED-USGS-W1AE2-W06/-W03	P-20	8.5	Anions NA	ND (<15)	ND (<4)	4
ED-USGS-W1AE4-W05/-W04	P-21	Sample Expended	Not Analyzed	Not Analyzed	ND (<4)	4
ED-USGS-W1C1-W07/-W05	P-22	6.8	Anions NA	ND (<15)	ND (<4)	4
ED-USGS-W1C2-W08/-W06	P-23	10.1	Anions NA	ND (<15)	ND (<4)	4
ED-USGS-W1C3-W08/-W07	P-24	10.9	Anions NA	ND (<15)	ND (<4)	4
ED-USGS-W1C4-W09/-W05	P-25	5.8	Anions NA	ND (<15)	ND (<4)	4

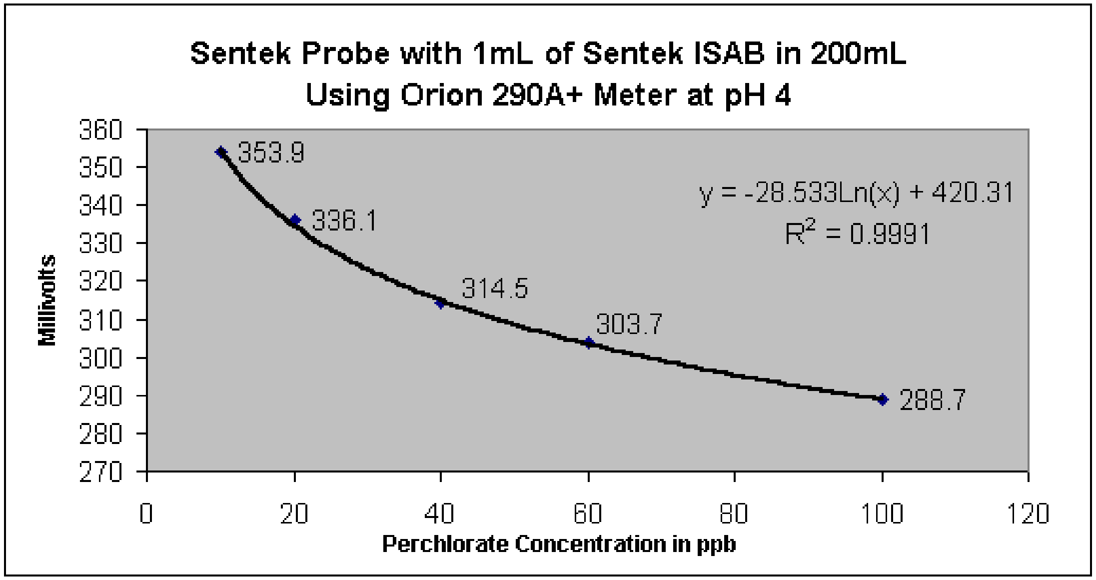
Table 5-1C - Second Semi-Annual Groundwater (SAGW) Event (July-August 2001) Samples, Perchlorate ISE Readings and Results, and Definitive Level Results by EPA Method 314.0

Second SAGW Event (July-August 2001) Split Sample ID	Second SAGW (7-8/00) ISE ID	Uncorrected Perchlorate ISE Reading (ppb), pH 4.0	Anion Corrected Perchlorate ISE Reading (ppb), pH 4.0	Final Reported Perchlorate ISE Result (ppb), pH 4.0	Perchlorate Definitve Result by EPA 314.0 (ppb)	Definitive Result RL (ppb)
ED-188-MW01-W11/-W10	**S-2**	126.5	N/A	**126.5**	**140**	4
ED-189-MW01-W36/-W31,W32	S-1	66.4	-12.4	ND (<15)	ND, ND (<4)	4
---	NC	---	---	---	---	---
ED-189-MW02-WNC/-W24,-W26,-W30	Split NC	---	---	---	11 and ND, ND (<4)	4
ED-189-MW03-W11/-W10	**S-4**	**28.9**	**10.1**	**ND (<15)**	**18**	4
ED-196-MW01-W14/-W12,-W13	S-5	13270.0	13270.0	**13270.0**	**36000, 27000**	8000
ED-196-MW03-W13/-W12	S-6	25.9	8.8	ND (<15)	ND (<16)	16
ED-196-MW06-W24/-W23	S-7	28.8	-3.7	ND (<15)	ND (<16)	16
ED-196-MW06-W24-DUP/-W23	S-7D	30.5	-2.0	ND (<15)	ND (<16)	16
ED-199-MW01-W16/-W15	S-8	16.1	3.6	ND (<15)	ND (<16)	16
ED-199-MW01-W16-DUP/-W15	S-8D	13.9	1.4	ND (<15)	ND (<16)	16
ED-274-MW01-W12/-W13	S-26	2.6	-5.7	ND (<15)	ND (<16)	16
ED-274-MW02-W13/-W14	S-27	13.7	8.1	ND (<15)	ND (<16)	16
ED-274-MW03-W06/-W07	S-28	17.6	9.9	ND (<15)	ND (<16)	16
ED-285-MW01-W(EB)	S-3	1.6	1.6	ND (<15)	N/A	---
ED-285-MW02-W16/-W15	S-9	14.1	-1.5	ND (<15)	ND (<4)	4
Not Collected This Event	NC	---	---	---	---	---
ED-286-MW01-W16/-W14	**S-10**	612	N/A	**612**	**1100**	80
ED-286-MW01-W16-DUP/-W15	**S-10D**	731	N/A	**731**	**920**	80
ED-286-MW03-W16/-W14, -W15	S-29	9.7	Anions NA	ND (<15)	ND (<16)	16
ED-286-MW03-W16-RE1/-W14,-W15	S-29RE1	8.5	Anions NA	ND (<15)	ND (<16)	16
ED-286-MW03-W16-RE2/-W14,-W15	S-29RE2	9.4	Anions NA	ND (<15)	ND (<16)	16
ED-286-MW03-W16-RE3/-W14,-W15	S-29RE3	8.6	Anions NA	ND (<15)	ND (<16)	16
ED-286-MW03-W16-DUP/-W14,-W15	S-29D	10.8	Anions NA	ND (<15)	ND (<16)	16
ED-422-MW01-W09/-W17	S-11	64.2	3.9	ND (<15)	ND (<16)	16
Not Collected This Event	NC	---	---	---	---	---

ED-422-MW01-W10/-W17	S-102	66.5	6.2	ND (<15)	ND (<16)	16
ED-422-MW01-W11/-W17	S-103	65.8	5.5	ND (<15)	ND (<16)	16
ED-422-MW01-W18/-W17	S-104	67.5	7.2	ND (<15)	ND (<16)	16
ED-NM-MW01A-W15/-W16	S-12	13.1	6.3	ND (<15)	ND (<16)	16
Not Collected This Event	NC	---	---	---	---	---
ED-NM-MW01C-W09/-W10	S-13	34.5	-0.8	ND (<15)	ND (<16)	16
ED-NM-MW01B-W06/-W07	S-30	7	-1.9	ND (<15)	ND (<16)	16
ED-NM-MW02A-W14/-W15	S-14	8.7	2.1	ND (<15)	ND (<4)	4
ED-NM-MW02B-W08/-W09	S-31	18.1	1.6	ND (<15)	ND (<16)	16
ED-NM-MW02C-W06/-W07	S-32	10.8	0.9	ND (<15)	ND (<16)	16
ED-NM-MW03A-W10/-W11	S-15	7.2	-2.3	ND (<15)	ND (<4)	4
ED-NM-MW03B-W09/-W10	S-33	13.6	-4.1	ND (<15)	ND (<4)	4
ED-NM-MW03C-W08/-W09	S-34	24.9	-2.5	ND (<15)	ND (<16)	16
ED-NM-MW04A-W08/-W09	S-35	10.1	0.8	ND (<15)	ND (<4)	4
ED-NM-MW04B-W16/-W17	S-16	11.8	-3.7	ND (<15)	ND (<4)	4
Not Collected This Event	NC	---	---	---	---	---
ED-NM-MW04C-W07/-W08	S-20	25.1	-2.5	ND (<15)	ND (<16)	16
ED-NM-MW05-W17/-W20, -W21	S-17	19.3	9.5	ND (<15)	ND, ND (<16)	16
ED-NM-MW06-W07/-W08	S-18	7.8	Anions NA	ND (<15)	ND (<4)	4
ED-NM-MW07-W13/-W14	S-19	16.0	-1.2	ND (<15)	ND (<16)	16
Not Collected This Event	NC	---	---	---	---	---
ED-USGS-W1AE4-W08/-W09	S-21	12.3	Anions NA	ND (<15)	ND (<16)	16
ED-USGS-W1C1-W09/-W10	S-22	12.1	Anions NA	ND (<15)	ND (<16)	16
ED-USGS-W1C2-W10/-W11	S-23	12.5	Anions NA	ND (<15)	ND (<16)	16
ED-USGS-W1C3-W10/-W11,-W17	S-24	10.1	Anions NA	ND (<15)	ND, ND (<16)	16
ED-USGS-W1C4-W11/-W12	S-25	7.4	Anions NA	ND (<15)	ND (<16)	16

Table 52-A

Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode
Matrix: Water Units: ug/L (ppb) Extraction/Digestion: Acidification to pH 4 with Sulfuric Acid
Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE
Analyst: Earth Tech, Inc.
Meter: ORION 290A (Portable) Date: January 24, 2001


Sentek Probe with 1mL of Sentek ISAB in 200mL
Using Orion 290A+ Meter at pH 4

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	4.03	200 mL	353.9	10.3
20	3.97	200 mL	336.1	19.1
40	4.01	200 mL	314.5	40.8
60	3.98	200 mL	303.7	59.6
100	4.01	200 mL	288.7	100.7
Calibration Date	**1/24/2001**		**Time**	**2:15pm**
Temperature		**22^0C**		
Slope	**28.533**		**Intercept**	**420.31**

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV	3.98	200 mL	307.3	52.5
MB/ICB	3.98	200 mL	369.3	6.0
20 ppb std with 5mL ISA	3.99	200 mL	337.4	18.3
100 ppb std	3.99	200 mL	289.6	97.6
25 ppb std	4.01	200 mL	327.7	25.7
P-9	3.97	180 mL	343.9	**14.6**
25 ppb std	3.98	200 mL	327.8	25.6
P-23	4.01	200 mL	354.2	**10.1**
20 ppb std	3.98	200 mL	336.6	18.8
P-16	3.96	200 mL	337.8	**18.0**
20 ppb std	3.98	200 mL	337.1	18.5
blank	4.01	200 mL	372.5	5.3
CCV (60 ppb)	3.99	200 mL	304.2	58.5
CCB	3.99	200 mL	374.1	5.1

Table 5-2B

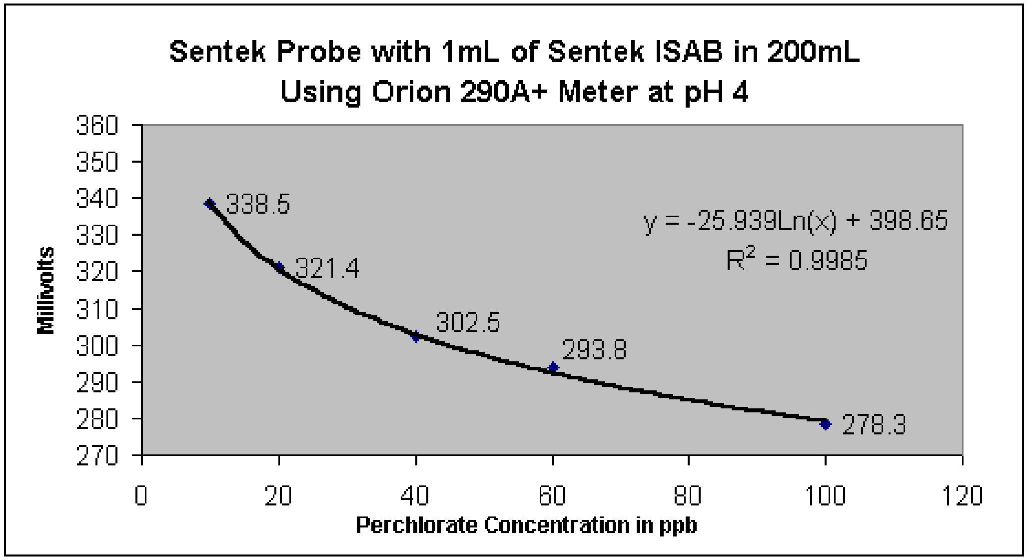
Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water Units: ug/L (ppb) Extraction/Digestion: Acidification to pH 4 with Sulfuric Acid

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

Analyst: Earth Tech, Inc.

Meter: ORION 290A (Portable) Date: January 25, 2001



Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	4.01	200 mL	338.5	10.2
20	3.98	200 mL	321.4	19.7
40	4.02	200 mL	302.5	40.7
60	4.00	200 mL	293.8	57.0
100	4.03	200 mL	278.3	103.5
Calibration Date	**1/25/2001**		**Time**	**11:20am**
Temperature		**21^{0}C**		
Slope	**25.939**		**Intercept**	**398.65**

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV	3.98	200 mL	292.8	59.2
MB/ICB	3.96	200 mL	357.3	4.9
20 ppb std	3.99	200 mL	320.4	20.4
P-19	4.03	140 mL	328.1	**15.2**
20 ppb std	4.00	100 mL	319.1	21.5
80 ppb	3.98	200 mL	284.7	80.9
80 ppb	3.98	100 mL	283.6	84.4
Blank	3.97	200 mL	357.5	4.9
Blank +50ppm Cl	3.95	200 mL	344.1	8.2
Blank +100ppm Cl	3.93	200 mL	338.1	10.3
Blank +300ppm Cl	3.91	200 mL	327.4	15.6
Blank +500ppm Cl	3.91	200 mL	324.8	17.2
CCV (20 ppb std)	3.98	200 mL	320.1	20.7
CCB	3.99	200 mL	362.5	4.0
P-8	3.99	140 mL	321.9	**19.3**
P-14	3.97	140 mL	337.2	**10.7**
20 ppb std	3.95	200 mL	321.3	19.7
P-6	3.95	140 mL	330.2	**14.0**
20 ppb std	3.97	200 mL	321.9	19.3
ccv (60 ppb std)	3.98	200 mL	292.5	59.9
CCB	4.01	200 mL	358.2	4.8

Table 5-2C

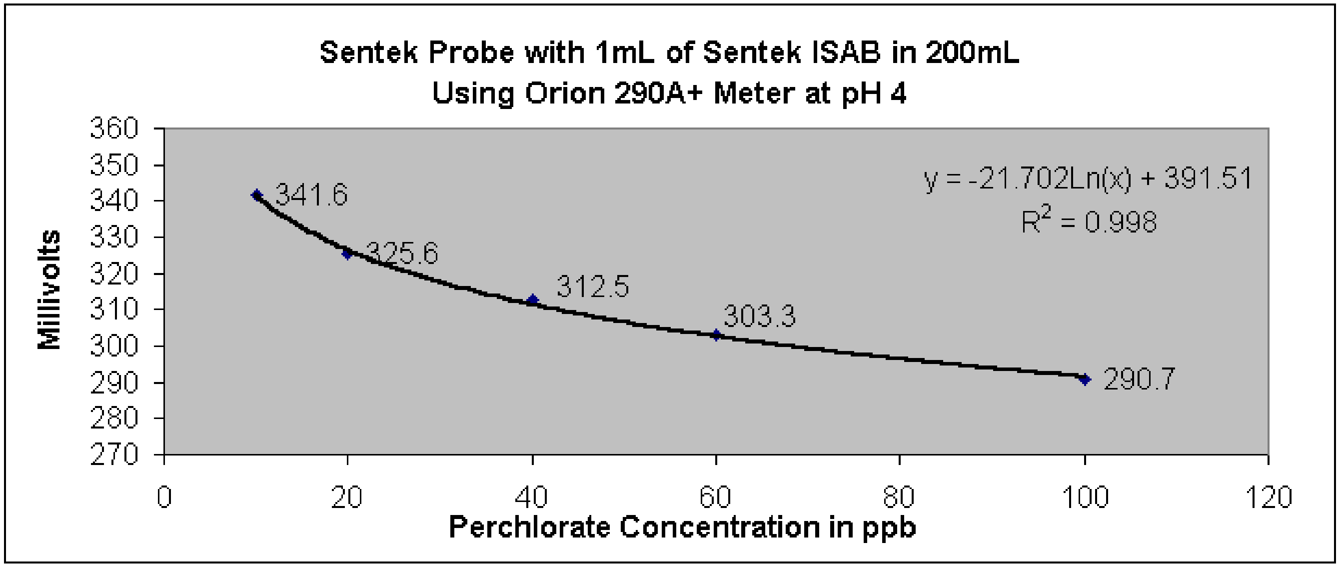
Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water Units: ug/L (ppb) Extraction/Digestion: Acidification to pH 4 with Sulfuric Acid

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

Analyst: Earth Tech, Inc.

Meter: ORION 290A (Portable) Date: January 26, 2001

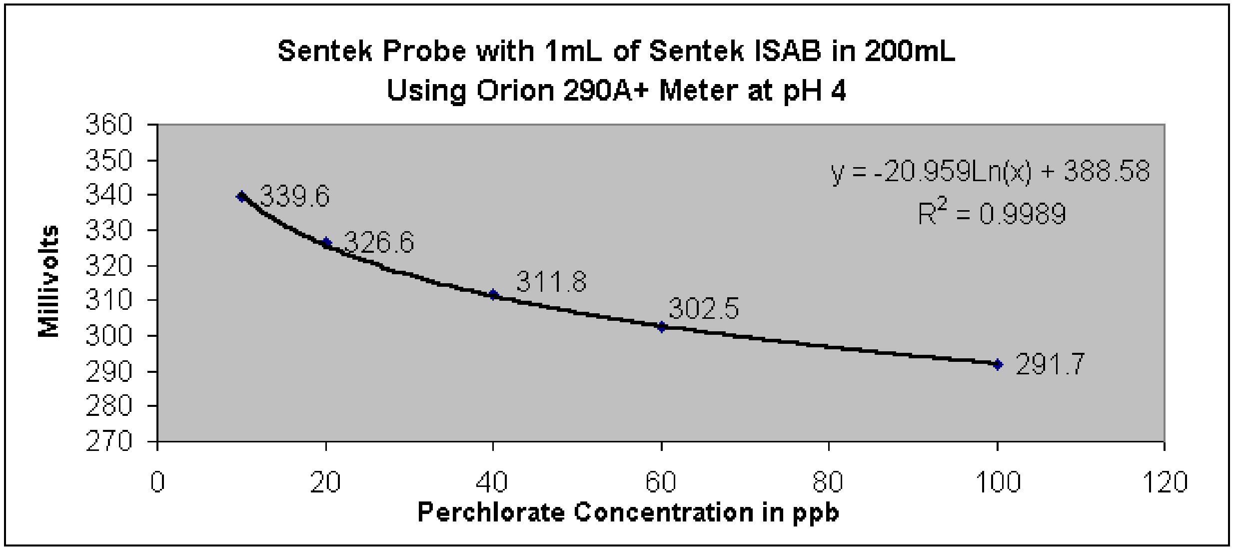


Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	4.01	200 mL	341.6	10.0
20	3.99	200 mL	325.6	20.8
40	3.97	200 mL	312.5	38.1
60	3.98	200 mL	303.3	58.2
100	4.01	200 mL	290.7	104.1
Calibration Date	**1/26/2001**		**Time**	**12:30pm**
Temperature		**21^{0}C**		
Slope	**21.702**		**Intercept**	**391.51**

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV	4.01	200 mL	306.4	50.5
MB/ICB	3.97	200 mL	361.2	4.0
20 ppb std	3.97	200 mL	325.2	21.2
P-7	3.99	140 mL	323.1	**23.4**
P-7 dilution factor = 2	3.99	100 mL	330.8	**16.4**
20 ppb	3.97	180 mL	326.5	20.0
Blank	3.97	200 mL	362.9	3.7
20 ppb std	3.97	200 mL	325.5	20.9
P-7 (dil fac=2) + 20 ppb	3.98	200 mL	316.6	**31.6**
P-12	3.97	140 mL	332.1	**15.4**
20 ppb std	3.98	200 mL	325.4	21.0
Blank	3.98	140 mL	344.1	**8.9**
P-13	3.95	140 mL	361.4	**4.0**
P-18	3.96	140 mL	345.6	**8.3**
P-20	3.95	140 mL	345.2	**8.4**
ccv (20 ppb std)	3.97	200 mL	325.9	20.6
ccb		200 mL	361.9	3.9

Table 5-2D

Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode
Matrix: Water Units: ug/L (ppb) Extraction/Digestion: Acidification to pH 4 with Sulfuric Acid
Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE
Analyst: Earth Tech, Inc.
Meter: ORION 290A (Portable) Date: January 29, 2001



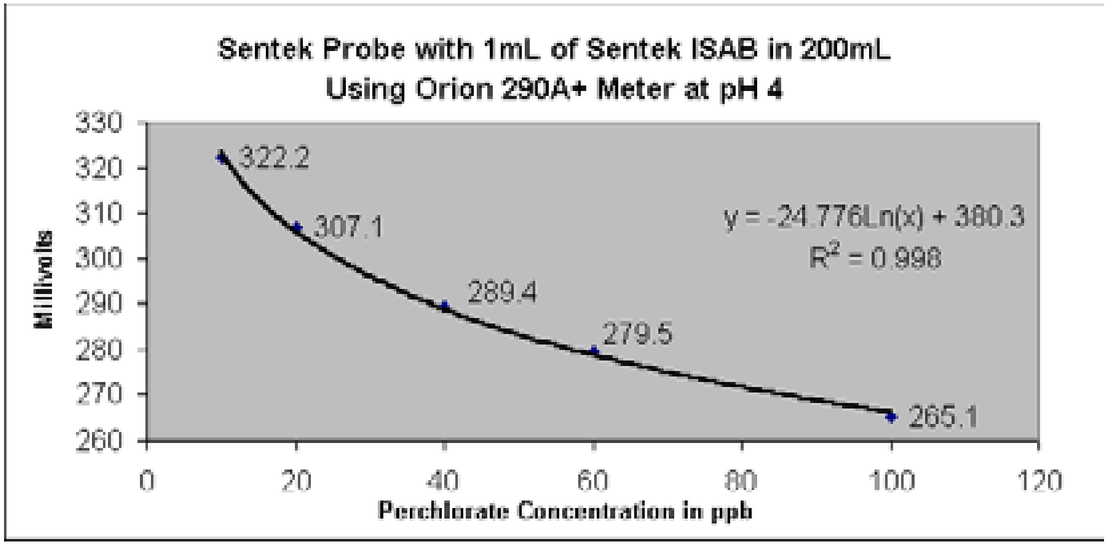
Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	3.99	200 mL	339.6	10.3
20	4.01	200 mL	326.6	19.2
40	3.98	200 mL	311.8	39.0
60	4.00	200 mL	302.5	60.8
100	3.99	200 mL	291.7	101.7
Calibration Date	**1/29/2001**		**Time**	**11:40am**
Temperature		**21°C**		
Slope	**20.959**		**Intercept**	**388.58**

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV	3.98	200 mL	313.7	35.6
MB/ICB	3.99	200 mL	354.2	5.2
20 ppb std	4.01	200 mL	325.2	20.6
100 ppb std	4.02	200 mL	291.6	102.2
P-11	4.02	140 mL	301.5	**63.7**
20 ppb std	3.96	200 mL	326.9	19.0
P-24	3.99	140 mL	338.5	**10.9**
20 ppb std	3.97	200 mL	324.4	21.4
P-25	3.99	140 mL	351.8	**5.8**
P-22	3.99	140 mL	348.5	**6.8**
P-10 (200x dilution)	3.96	200 mL	324.1	**21.7**
P-5 (400x dilution)	3.99	200 mL	302.4	**61.1**
P-5 (400x dilution) + 20ppb	3.98	200 mL	297.1	**78.6**
ccv (20 ppb std)	3.98	200 mL	325.9	19.9
ccb	3.97	200 mL	370.4	2.4

Table 5-2E

Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode
Matrix: Water Units: ug/L (ppb) Extraction/Digestion: Acidification to pH 4 with Sulfuric Acid
Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE
Analyst: Earth Tech, Inc.

Meter: ORION 290A (Portable) Date: February 23, 2001



Sentek Probe with 1mL of Sentek ISAB in 200mL
Using Orion 290A+ Meter at pH 4

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	4.02	200 mL	322.2	10.4
20	4.01	200 mL	307.1	19.2
40	4.01	200 mL	289.4	39.2
60	3.99	200 mL	279.5	58.5
100	3.98	200 mL	265.1	104.5
Calibration Date	**2/23/2001**		**Time**	**11:15am**
Temperature		**21^0C**		
Slope	**24.776**		**Intercept**	**380.3**

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV	3.99	200 mL	284.8	47.2
MB/ICB	3.98	200 mL	348.5	3.6
P-102	3.98	200 mL	278.8	**60.1**
20 ppb std	4.01	200 mL	307.6	18.8
P-102	4.01	200 mL	279.1	**59.4**
P-102+ 20ppb	4.02	200 mL	275.9	**67.6**
20 ppb std	4.01	200 mL	307.5	18.9
P-103	4.01	200 mL	287.6	**42.2**
100 ppb	4.00	200 mL	269.7	86.8
P-104	4.04	200 mL	288.5	**40.7**
P-102 + 20 ppb	4.03	200 mL	281.1	**54.8**
P-11 (old, w. scum)	3.91	200 mL	285.8	45.3
ccv (20 ppb std)	4.01	200 mL	310.8	16.5
ccb	3.99	200 mL	349.4	3.5

Table 5-2F

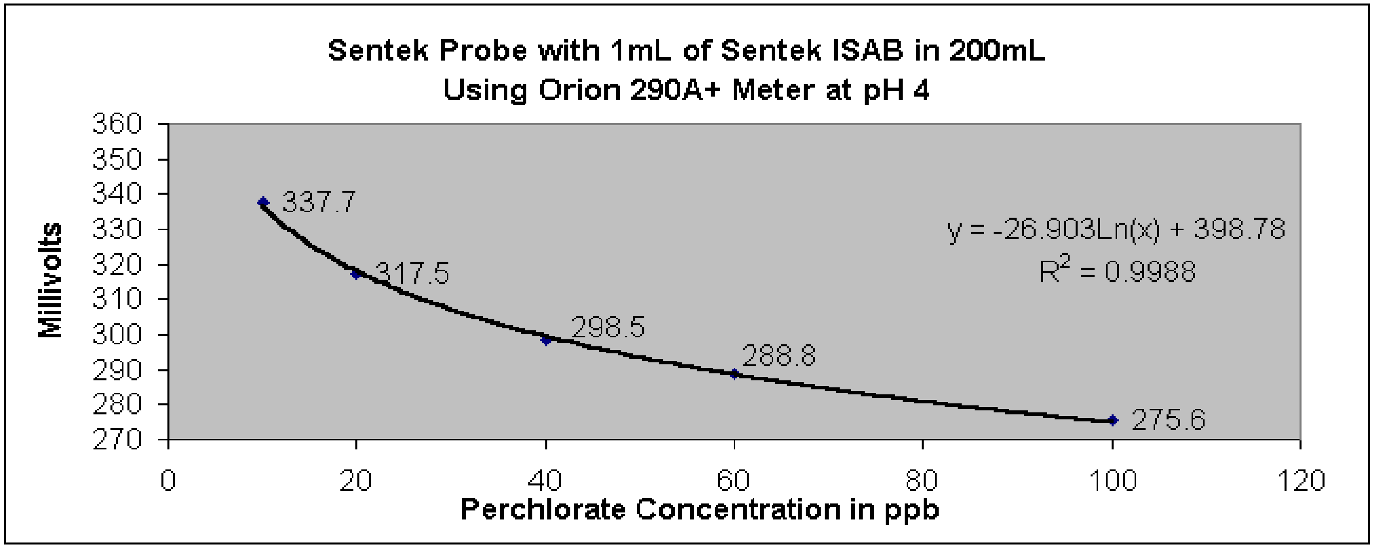
Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water Units: ug/L (ppb) Extraction/Digestion: Acidification to pH 4 with Sulfuric Acid

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

Analyst: Earth Tech, Inc.

Meter: ORION 290A (Portable) Date: March 2, 2001



Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	3.96	200 mL	337.7	9.7
20	4.01	200 mL	317.5	20.5
40	4.01	200 mL	298.5	41.6
60	4.02	200 mL	288.8	59.6
100	3.98	200 mL	275.6	97.4
Calibration Date	**3/2/2001**		**Time**	**12:00pm**
Temperature		**23.5^{0}C**		
Slope	**26.903**		**Intercept**	**398.78**

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV	3.96	200 mL	293.2	50.6
Blank	3.97	200 mL	357.7	4.6
Blank + 0.5 ppm Bromide	3.97	200 mL	351.1	5.9
Blank + 1 ppm Bromide	3.97	200 mL	348.2	6.6
Blank + 2 ppm Bromide	3.97	200 mL	344.5	7.5
Blank + 5 ppm Bromide	3.97	200 mL	335.2	10.6
20 ppb	4.01	200 mL	319.5	19.0
10 ppb std	3.96	200 mL	337.8	9.6
10 ppb std+ 0.5 ppm bromide	3.96	200 mL	334.1	11.1
10 ppb std+ 1 ppm bromide	3.96	200 mL	331.1	12.4
10 ppb std+ 2 ppm bromide	3.96	200 mL	327.6	14.1
10 ppb std+ 5 ppm bromide	3.96	200 mL	321.3	17.8
20 ppb	4.01	200 mL	318.6	19.7
20 ppb std+ 0.5 ppm bromide	4.01	200 mL	315.8	21.9
20 ppb std+ 1 ppm bromide	4.01	200 mL	313.7	23.6
20 ppb std+ 2 ppm bromide	4.01	200 mL	311.6	25.5
20 ppb std+ 5 ppm bromide	4.01	200 mL	308.1	29.1
50 ppb	3.95	200 mL	292	52.9
20 ppb std+ 0.5 ppm bromide	3.95	200 mL	291.5	53.9
20 ppb std+ 1 ppm bromide	3.95	200 mL	291.1	54.7
20 ppb std+ 2 ppm bromide	3.95	200 mL	290.6	55.8
20 ppb std+ 5 ppm bromide	3.95	200 mL	289.7	57.7
20 ppb	3.98	200 mL	318.5	19.8
Blank	4.01	200 mL	354.2	5.2
P-1	4.02	200 mL	281	**79.7**
100 ppb std	4.01	200 mL	270.6	117.3
ccb	4.01	200 mL	355.1	5.1

Table 5-3A

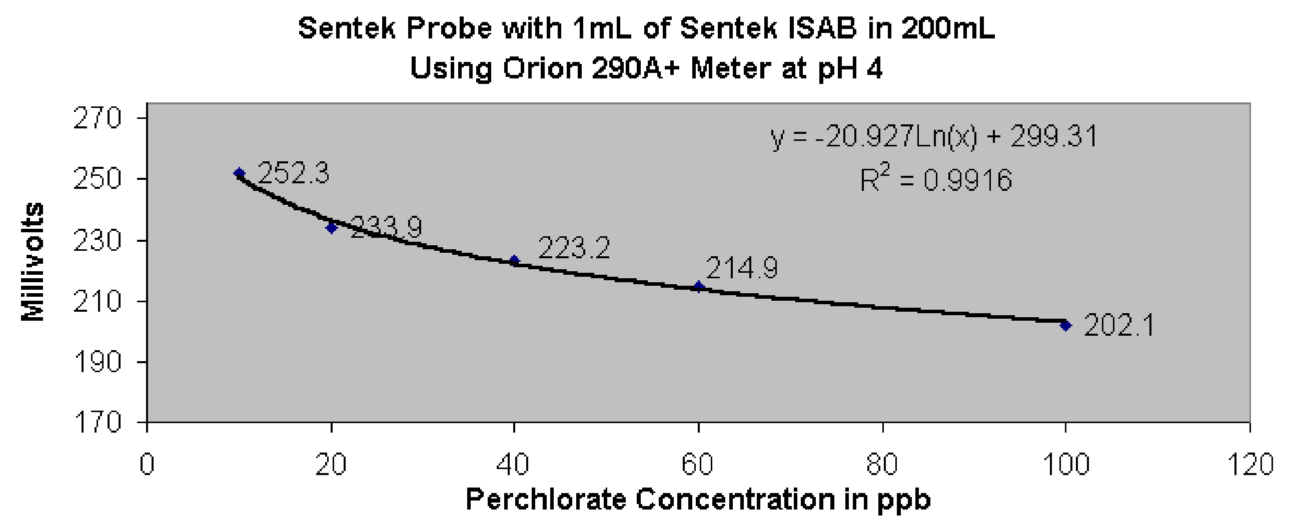
Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water Units: ug/L (ppb) Extraction/Digestion: Acidification to pH 4 with Sulfuric Acid

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

Analyst: Earth Tech, Inc.

Meter: ORION 290A (Portable) Date: September 6, 2001

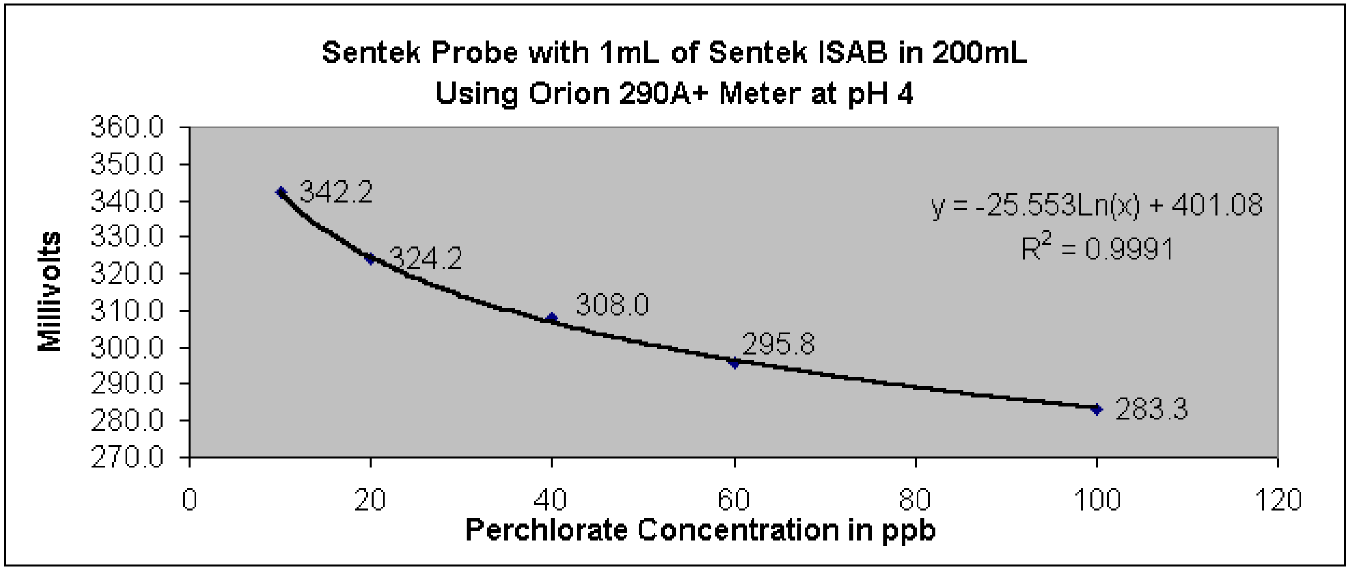


Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	3.95	200 mL	252.3	9.45
20	4.04	200 mL	233.9	22.77
40	3.94	200 mL	223.2	37.98
60	3.93	200 mL	214.9	56.46
100	4.02	200 mL	202.1	104.08
Calibration Date	**9/6/2001**		**Time**	**13:05**
Temperature		**21.8 - 24.6^{0}C**		
Slope	**20.927**		**Intercept**	**299.3**

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV (25/50 ppb std)	3.96	200 mL	216.2	53.1
Blank	4.01	200 mL	291.6	1.4
10 ppb std	3.96	200 mL	251.7	9.7
S-3	3.96	200 mL	290.0	**1.6**
S-3 MS	3.97	200 mL	243.2	**14.6**
S-4 High Org. Severe interference	3.95	200 mL	79.9	35758.4
LCS (50 ppb std)	3.96	200 mL	221.7	40.8
temp up to 24.6				
LCS (50 ppb std)	3.96	200 mL	221.2	41.8
S-6	3.95	200 mL	231.2	**25.9**
CCV (50 ppb sensitivity check)	3.92	200 mL	216.1	53.3
S-9	3.87	200 mL	243.9	**14.1**
S-10	4.07	200 mL	159.5	797.0
S-10 D	4.03	200 mL	156.2	933.1
S-10 (1x10)	3.93	200 mL	213.2	**61.2**
S-10 D (1x10)	4.02	200 mL	209.5	**73.1**
CCV (50 ppb)	3.94	200 mL	213.9	59.2
Blank	4.05	200 mL	270.3	4.0
S- 12	3.94	200 mL	245.4	**13.1**
S - 14	3.98	200 mL	254.1	**8.7**
S 15	3.95	200 mL	257.9	**7.2**
S 16	3.93	200 mL	247.7	**11.8**
S 18	4.06	200 mL	256.4	**7.8**
S 19	4.06	200 mL	241.3	**16.0**
CCV (50 ppb)	3.93	200 mL	216.1	53.3
Blank	4.06	200 mL	268.9	4.3

Table 5-3B

Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode
Matrix: Water Units: ug/L (ppb) Extraction/Digestion: Acidification to pH 4 with Sulfuric Acid
Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE
Analyst: Earth Tech, Inc.
Meter: Computer Interface - LAVAL ELIT 8804 Date: September 10, 2001


Sentek Probe with 1mL of Sentek ISAB in 200mL
Using Orion 290A+ Meter at pH 4

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	4.0	200 mL	342.2	10.0
20	4.0	200 mL	324.2	20.3
40	4.0	200 mL	308.0	38.2
60	3.9	200 mL	295.8	61.6
100	4.1	200 mL	283.3	100.4
Calibration Date	**9/10/2001**		**Time**	**13:10**
Temperature		**23.7-24.5^{0}C**		
Slope	**25.553**		**Intercept**	**401.1**

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV (50 ppb)	4.0	200 mL	303.4	45.7
Blank	4.0	200 mL	375.6	2.7
10 ppb std	4.1	200 mL	340.4	10.8
S-27	4.0	200 mL	334.2	**13.7**
S-8	4.0	200 mL	330.1	**16.1**
S-29	4.0	200 mL	343.1	**9.7**
S-29 D	4.0	200 mL	340.2	**10.8**
S-8 D	4.0	200 mL	333.8	**13.9**
CCV (40 ppb)	4.0	200 mL	307.3	39.3
Blank	4.0	200 mL	369.7	3.4
S-20	4.0	200 mL	318.8	**25.1**
S-30	4.0	200 mL	351.4	**7.0**
S-32	4.0	200 mL	340.4	**10.8**
S-7	4.0	200 mL	315.3	**28.8**
S-7 D	4.0	200 mL	313.7	**30.5**
LCS (50 ppb)	4.0	200 mL	301.0	50.1
Blank	4.1	200 mL	368.9	3.5
S-22	4.0	200 mL	337.4	**12.1**
S-23	4.0	200 mL	336.6	**12.5**
S-21	4.0	200 mL	337.0	**12.3**
S-24	4.0	200 mL	342.1	**10.1**
CCV (20 ppb)	4.0	200 mL	320.1	23.8
Blank	4.0	200 mL	359.9	5.0
S-2	4.0	200 mL	276.3	**132.1**
S-25	4.0	200 mL	350.0	**7.4**
S-35	4.0	200 mL	342.1	**10.1**
S-26	4.0	200 mL	178.6	***6045.1***

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
S-13	4.0	200 mL	310.6	**34.5**
LCS (50 ppb)	4.0	200 mL	297.3	58.0
Blank	4.0	200 mL	355.1	6.0
S-34	4.0	200 mL	318.9	**24.9**
S-33	4.0	200 mL	334.4	**13.6**
S-31	4.0	200 mL	327.1	**18.1**
S-28	4.0	200 mL	327.8	**17.6**
S-102	4.0	200 mL	293.8	**66.5**
S-103	4.0	200 mL	294.1	**65.8**
S-104	4.0	200 mL	293.4	**67.5**
S-11	4.0	200 mL	294.7	**64.2**
CCV (20 ppb)	4.0	200 mL	321.1	22.9
Blank	4.0	200 mL	362.1	4.6
S-1	4.0	200 mL	297.2	**58.4**
S-4	4.0	200 mL	315.2	**28.9**
S-17	4.0	200 mL	325.4	**19.3**
S-1 D	4.1	200 mL	293.9	**66.4**
LCS (50 ppb)	4.0	200 mL	297.0	58.8
Blank	4.1	200 mL	360.1	5.0

Table 5-3C

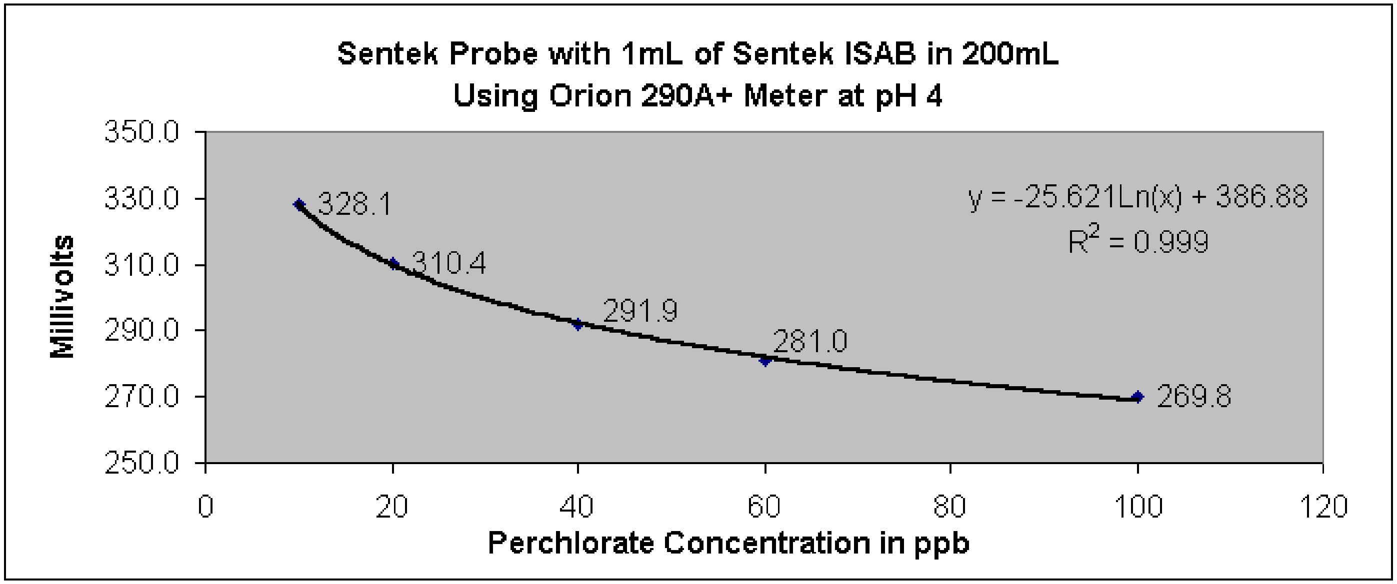
Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water Units: ug/L (ppb) Extraction/Digestion: Acidification to pH 4 with Sulfuric Acid

Instrument: Sentek 367-75 Solid State Perchlorate Combination ISE

Analyst: Earth Tech, Inc.

Meter: Computer Interface - LAVAL ELIT 8804 Date: September 12, 2001



Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10	4.0	200 mL	328.1	9.9
20	4.0	200 mL	310.4	19.8
40	4.1	200 mL	291.9	40.7
60	4.0	200 mL	281.0	62.3
100	4.0	200 mL	269.8	96.4
Calibration Date	**9/12/2001**		**Time**	**12:09**
Temperature		**22.2-24.5^{0}C**		
Slope	**25.621**		**Intercept**	**386.9**

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
LCS/ICV (50 ppb std)	4.0	200 mL	288.0	47.4
Blank	4.0	200 mL	382.4	1.2
S-26 (1:100)	4.0	200mL	373.1	1.7
S-26 (1:10)	4.0	200mL	366.6	2.2
S-26	3.9	200 mL	375.8	**1.5**
S-29	4.0	200 mL	332.1	**8.5**
S-29 MS	4.1	200 mL	237.7	**337.7**
S-2	4.0	200 mL	267.4	106.1
S-2 (1:5)	4.1	200 mL	304.1	**25.3**
S-2 (1:5) MS	4.1	200 mL	335.8	7.3
LCS (50 ppb)	4.0	200 mL	291.4	41.5
Blank	4.1	200 mL	360.0	2.9
Reconditioned Probe				
LCS (50 ppb)	4.0	200 mL	292.5	39.8
S-2 (1:5) MS	4.1	200 mL	236.5	**354.0**
S-2 (1:5) MS Remade	4.1	200 mL	237.0	**347.2**
S-2 needed more acid	*8.2*	*200 mL*	*256.0*	*165.4*
S-2 added more acid	4.1	200 mL	273.2	84.5
S-2 (1:5) MS needed more acid	***8.2***	*200 mL*	*229.2*	*470.7*
S-2 (1:5) MS added more acid	4.0	200 mL	236.5	**354.0**
S-2 added more acid+10 min	4.1	200 mL	274.3	81.0
S-2 added more acid+MS-re	4.1	200 mL	270.2	**95.0**
S-2 added more acid+MS-re+30 min	4.0	200 mL	235.8	**363.8**
S-29	4.0	200 mL	329.5	**9.4**
S-29 MS+30 min	4.0	200 mL	339.8	6.3
S-29 MS+MS-re (Remade)	4.0	200 mL	239.0	**321.1**
S-29 MS+MS-re+15 min	4.1	200 mL	239.3	**317.4**

Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
S-29	4.0	200 mL	331.7	**8.6**
S-29+MS-re	4.0	200 mL	311.5	**19.0**
S-26	4.0	200 mL	362.0	**2.6**
LCS (50 ppb)	4.0	200 mL	293.5	38.3
blank	4.1	200 mL	355.0	3.5
S-29+MS-re	4.0	200 mL	240.6	**301.7**
20 ppb ccv	4.1	200 mL	315.4	16.3
Blank+MS@4 min	4.1	200 mL	312.6	18.2
Blank+MS@10 min	4.1	200 mL	315.2	16.4
Blank+MS@40 min w recond	4.1	200 mL	315.4	16.3
S-5	4.1	200 mL	168.2	5090.8
S-5 (1:100)	4.1	200 mL	261.6	132.9
S-5 (1:200)	4.1	200 mL	279.4	**66.4**
Blank+MS (25 PPB)	4.0	200 mL	322.1	12.5
CCV 20 PPB	4.1	200 mL	324.0	11.6
blank	4.1	200 mL	353.8	3.6

+MS = 0.1 mL 50 ppm std instead of 10 mL 50 ppb std

S-2 pH = 8.5+

Table 5-4

Field Sample IDs	ISE Sample ID	ISE Result	Definitive Result	Precision (RPD)
ED-196-MW01-W09/-W05	P-5	24423	20000	19.9
ED-196-MW01-W09/-W06	P-5		25000	
ED-286-MW01-W08/-W03	P-10	4336	5900	30.6
ED-422-MW01-W07/-W06	P-11	ND (<15)	6	Both <15 ppb ISE RL
ED-422-MW01-W07-DUP/-W06	P-11-DUP	ND (<15)	6	Both <15 ppb ISE RL
ED-422-MW01-W08/-W06	P-102	ND (<15)	6	Both <15 ppb ISE RL
ED-422-MW01-W09/-W06	P-103	ND (<15)	6	Both <15 ppb ISE RL
ED-422-MW01-W10/-W06	P-104	ND (<15)	6	Both <15 ppb ISE RL
ED-188-MW01-W11/-W10	S-2	126.5	140	10.1
ED-189-MW03-W11/-W10	S-4	(10.1) ND (<15)	18	56.2
ED-196-MW01-W14/-W12	S-5	13270	36000	92.3
ED-196-MW01-W14/-W13	S-5	13270	27000	68.2
ED-286-MW01-W16/-W15	S-10	612	1100	57.0
ED-286-MW01-W16/-W14		612	920	40.2
ED-286-MW01-W16-DUP/-W14	S-10D	731	920	22.9
ED-286-MW01-W16-DUP/-W15		731	1100	40.3

Table 5-5

Field Sample ID	ISE Sample ID	Uncorrected ISE Reading	Corrected ISE Result	Uncorrected %R		Uncorrected %R
ED-196-MW01-W09	P-5 (1:200)	61.10	43.10			
ED-196-MW01-W09-MS	P-5 (1:200)-MS	78.60	60.60	87.5	%R	87.5%R
only anions, low NO3						
ED-196-MW06-W15	P-7 (1:2)	16.40	-16.10			
ED-196-MW06-W15-MS	P-7 (1:2)-MS	31.60	-0.90	76.0	%R	0 %R
only anions, med-low NO3						
ED-422-MW01-W07	P-11	63.74	3.44			
ED-422-MW01-W07-MS	P-11-MS	67.60	7.30	19.3	%R	0 %R
ED-422-MW01-W07-MSD	P-11-MSD	54.80	-5.50	-64.0	%R	0 %R
ED-422-MW01-W07 RE	P-11RE	40.70	-19.60			
ED-422-MW01-W07-RE-MS	P-11RE-MS	67.60	7.30	134.5	%R	0 %R
ED-422-MW01-W07-RE-MSD	P-11RE-MSD	54.80	-5.50	-64.0	%R	0 %R
high nitrate and organics						
ED-286-MW03-W16	S-29	9.70	NA			NA
ED-286-MW03-W16-RE1	S-29RE1	8.50	NA			NA
ED-286-MW03-W16-RE2	S-29RE2	9.40	NA			NA
ED-286-MW03-W16-RE3	S-29RE3	8.60	NA			NA
ED-286-MW03-W16-DUP	S-29D	10.80	NA			NA
ED-286-MW03-W16-MS	S-29-MS	337.00	NA	1309.2	%R	NA
ED-286-MW03-W16-MS RE1	S-29-MS RE1	317.00	NA	1229.2	%R	NA
ED-286-MW03-W16-MS RE2	S-29-MS RE2	19.00	NA	37.2	%R	NA
ED-286-MW03-W16-MS RE3	S-29-MS RE3	310.00	NA	1201.2	%R	NA
med nitrate and low organics (VOCs at 0.5-2.5 ppb)						
ED-188-MW01-W11	S-2	126.50	NA			
ED-188-MW01-W11 (1:5)	S-2 (1:5)	25.30	NA			
ED-188-MW01-W11 (1:5)-MS	S-2 (1:5)-MS	7.30	NA	-72.0	%R	NA
ED-188-MW01-W11 (1:5)-MS RE1	S-2 (1:5)-MS RE1	354.00	NA	1314.8	%R	NA
ED-188-MW01-W11 (1:5)-MS RE2	S-2 (1:5)-MS RE2	347.00	NA	1286.8	%R	NA
unknown nitrate and high organics (Freon 113 at 22 ppb, TCE at 11 ppb, others 0.5-4 ppb)						
ED-285-MW01-W(EB)	S-3	1.60	1.60	ND (<15)	N/A	---
ED-285-MW01-W(EB)-MS		14.60	14.60	65.0	%R	65 %R

Table 5-6

Field Sample ID	ISE Sample ID	Uncorrected ISE Reading	Corrected ISE Result	Type of Sample: Dup or Rep	RPD Uncorrected	RPD Corrected
ED-285-MW02-W06	P-9	14.6	-1.0	Parent Sample	Field Dup. RPD	Lab. Dup. RPD
ED-285-MW02-W06-DUP	P-9-DUP (pH 4.4)	7.0	-8.6	Field Dup	0.0 Both ND (<15)	0.0 Both ND (<15)
ED-422-MW01-W07-MS	P-11-MS	67.6	7.3	MS/MSD	MS/MSD RPD	MS/MSD RPD
ED-422-MW01-W07-MSD	P-11-MSD	54.8	-5.5	MS/MSD	20.9	0.0 Both ND (<15)
ED-286-MW03-W16	S-29	9.7	NA	Parent Sample	Lab Rep. RPDs	NA
ED-286-MW03-W16-RE1	S-29RE1	8.5	NA	Lab Replicate	0.0 All ND (<15)	NA
ED-286-MW03-W16-RE2	S-29RE2	9.4	NA	Lab Replicate	0.0 All ND (<15)	NA
ED-286-MW03-W16-RE3	S-29RE3	8.6	NA	Lab Replicate	0.0 All ND (<15)	NA
ED-286-MW03-W16-DUP	S-29D	10.8	NA	Field Duplicate	0.0 All ND (<15)	NA
ED-NM-MW04B-W13	P-16	15.0	-0.5	Parent Sample	Field Dup. RPD	Lab. Dup. RPD
ED-NM-MW04B-W13	P-16-DUP	18.0	2.5	Field Duplicate	18.2	0.0 All ND (<15)
ED-188-MW01-W11	S-2	106.1	N/A	Parent Sample	Ser. Dil. RPD	N/A
ED-188-MW01-W11 (1:5)	S-2 (1:5)	25.3	25.3	Ser Dilution	17.5	N/A
ED-286-MW01-W16	S-10	612.0	N/A	Parent Sample	Field Dup. RPD	N/A
ED-286-MW01-W16-DUP	S-10D	731.0	N/A	Field Duplicate	17.7	N/A
ED-286-MW03-W16	S-29	9.7	Anions NA	Parent Sample	Field/Lab RPDs	NA
ED-286-MW03-W16-RE1	S-29RE1	8.5	Anions NA	Lab Replicate	0.0 All ND (<15)	NA
ED-286-MW03-W16-RE2	S-29RE2	9.4	Anions NA	Lab Replicate	0.0 All ND (<15)	NA
ED-286-MW03-W16-RE3	S-29RE3	8.6	Anions NA	Lab Replicate	0.0 All ND (<15)	NA
ED-286-MW03-W16-DUP	S-29D	10.8	Anions NA	Field Duplicate	0.0 All ND (<15)	NA
ED-422-MW01-W09	S-11	64.2	3.9	Parent Sample	Field Dup. RPDs	Field Dup. RPDs
ED-422-MW01-W10	S-102	66.5	6.2	Field Duplicate	3.5	0.0 All ND (<15)
ED-422-MW01-W11	S-103	65.8	5.5	Field Duplicate	2.5	0.0 All ND (<15)
ED-422-MW01-W18	S-104	67.5	7.2	Field Duplicate	5.0	0.0 All ND (<15)

NA = Not Available

N/A = Not Applicable, result reported from dilution

ATTACHMENTS

ATTACHMENT 1:
STANDARD OPERATING PROCEDURE (VERSION 1.0): LOW CONCENTRATION METHOD FOR THE DETERMINATION OF PERCHLORATE IN AQUEOUS SAMPLES USING ION SELECTIVE ELECTRODES

STANDARD OPERATING PROCEDURE

Low Concentration Method for the Determination of Perchlorate in Aqueous Samples Using Ion Selective Electrodes

1.0 Scope and Application

The primary use for this method is to determine 15-100 µg/L concentrations of perchlorate in water samples at or near field sampling sites. Matrices with high concentrations of specific anions, especially nitrate, may not be appropriate for the use of this method due to significant positive bias and potential loss of sensitivity after analysis of samples high in nitrate. Matrices with very high concentrations of interfering anions must be evaluated to determine if this method meets project objectives.

The method is especially useful for matrices with less than 1000 mg/L chloride and 1.5 mg/L nitrate as nitrogen (NO_3-N). Correction factors must be applied for concentrations in excess of 50 mg/L chloride, 0.12 mg/L NO_3-N, or 1.2 mg/L bromide. Interference due to carbonate and bicarbonate is eliminated by the acidification of all standards and samples to pH 4.0 (± 0.1) with sulfuric acid.

The California action limit for perchlorate in water is 0.018 mg/L (equivalent to18 µg/L); therefore, this method is intended to meet a target detection limit (TDL) of 18 µg/L, which is 12 to 40 times below the 200 to 700 µg/L manufacturer-specified detection limits for perchlorate ion selective electrodes (ISEs). The method is expected to support a reporting limit (RL) of 15 µg/L, supported by a low calibration point of 10 µg/L, and a method detection limit (MDL) less than 7.5 µg/L, using solid state ISEs.

Due to the potential for positive bias due to matrix interference, ten percent of samples analyzed by this method should generally be confirmed by definitive-level analysis, especially to confirm when application of anion-specific correction factors lower perchlorate readings to below project action limits. Samples with uncorrected perchlorate readings less than action limits can be considered to effectively indicate lack of perchlorate if subsequent QC sample recoveries are within specified accuracy criteria.

Due to the potential for significant interferences from specific anions, the matrix must be characterized as to concentrations of nitrate, chloride, and bromide. Alternatively, analysis by the method of standard additions (MSA) may be used to compensate for unknown anion interference, especially for perchlorate readings less than 30 µg/L. Further studies of the effectiveness of MSA to compensate for anion interferences are required.

2.0 Method Summary

Perchlorate is determined by ISE using a specialized solid state ion-specific perchlorate electrode with built in reference element and a portable ISE meter. A computer interface may be used in place of the ISE meter. All standards and samples must be at approximately the same background ionic strength, therefore ionic strength adjustor (ISA) is added to all standards and samples. All standards and samples are acidified to pH 4.0 (± 0.1) with sulfuric acid to remove carbonate/bicarbonate interference. It is recommended that a pH meter be set up along side the ISE.

Analyses are performed on 200 mL aliquots of sample continuously stirred using a magnetic stirring bar rotating at a slow to moderate rate without causing a vortex. Analyses must be performed at approximately the same temperature as the calibration. As the sensitivity required to meet the TDL and RL are significantly below the intended range of the ISE, millivolt readings may take several minutes to stabilize. Millivolt readings are logged instead of direct perchlorate concentration read-out using ISE meter or computer interface calibration features. Millivolt readings for calibration standards and samples can be entered onto a spreadsheet capable of producing a logarithmic calibration curve, or plotted on logarithmic or semilogarithmic graph paper. Perchlorate readings can then be obtained from the spreadsheet by formula, or manually read from the graph paper.

Correction factors must be applied to perchlorate readings for interference caused by significant concentrations of chloride, nitrate, bromide, or fluoride, as appropriate for the matrix. If nitrate is present above 0.2 mg/L NO_3-N, reconditioning of the perchlorate ISE using 100-2000 µg/L perchlorate solutions and acidified blanks between every sample is required. Otherwise, ISE conditioning is required prior to calibration and is recommended at regular intervals.

3.0 Sample Handling and Preservation

Samples may be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. The recommended sample volume is 500 mL to insure a representative sample, allow for replicate analysis, and minimize waste disposal. Additional volume should be collected for samples designated for matrix spike analysis, if required.

No sample preservation is required. Analytical holding time is 28 days. Samples are not required to be shipped iced or stored cold in a refrigerator; however, samples collected for perchlorate analysis are recommended to be stored at 4 ± 2^{o}C from the time of collection until prior to analysis, and every effort should be taken to protect the samples from temperature extremes and exposure to sources of ultraviolet light. The use of ice packs or a thermally insulated sampling kit, designed to fit sampling bottles securely during shipment, may be used to protect the samples from high temperatures. Samples must be allowed to reach the same ambient temperature at which calibration is performed prior to analysis.

Note that EPA studies have shown perchlorate to be stable for more than 28 days(1) but extended holding time studies (beyond 35 days) were not conducted by EPA. Typically, when analytes are believed to be stable, a 28 day holding time is established as a sufficient time period to permit analysis of samples.

4.0 Interferences

This method requires operation of perchlorate ISEs at sensitivity significantly below intended manufacturer-specified detection limits, and is therefore subject to potential matrix interferences. Sample matrices should be evaluated to determine appropriateness of this method with respect to specific project objectives. Several common anions have been demonstrated to cause significant positive interference (greater than 20% of perchlorate concentration, or 20% of the 15 µg/L RL for perchlorate results less than the RL) for this method. In addition, loss of sensitivity has been demonstrated to occur after analysis of samples high in carbonate, bicarbonate, or nitrate.

Interference due to carbonate and bicarbonate is eliminated by the acidification of all standards and samples to pH 4.0 (± 0.1) by the addition of 0.2 to 0.5 normal (N) sulfuric acid. Matrices with greater than 0.2 mg/L NO_3-N require reconditioning of the perchlorate ISE using acidified blanks and acidified 100-2000 µg/L perchlorate solutions between every sample to prevent loss of sensitivity (refer to Section 10.2). Matrices high in nitrate may not be appropriate for this method. Samples with nitrate concentrations of 1.1 to 5.5 mg/L NO_3-N cause positive bias of 15-45 µg/L perchlorate (one-to-three times the RL). The user may need to determine the maximum level of nitrate correction acceptable for project objectives if samples include high-nitrate matrices.

Matrices with concentrations of nitrate less than 0.12 mg/L NO_3-N, bromide less than 1.2 mg/L, and chloride less than 50 mg/L will not be significantly affected by known interferences. Higher concentrations of these anions require application of correction factors according to Tables 1 through 3. Anion concentrations from historical or contemporary data may be applied. If such data does not exist, ISEs for these anions may be used utilizing the same ISE meter or computer interface. Alternatively, analysis by MSA may be used to compensate for unknown anion interference, especially for perchlorate readings less than 30 µg/L. However, further studies of the effectiveness of MSA to compensate for anion interferences are required.

Note that for low-nitrate matrices, the only anion likely to require application of correction factors is chloride, for which correction factors are relatively small (12 µg/L perchlorate for 500 mg/L chloride). During method development studies, concentrations of up to 0.5 mg/L NO_3-N, 300 mg/L chloride, or more than 5.0 mg/L bromide did not produce false positives in spiked blanks. When perchlorate readings associated with acceptable QC indicate that perchlorate is not present above project action limits, perchlorate can be confidently considered not to be present at that level, and correction factors need not be addressed, since all of the interferences are for positive bias.

In general, a minimum of ten percent of samples analyzed by this method should be confirmed by definitive-level split sample analysis. Whenever project objectives are potentially affected by the application of correction factors such that perchlorate readings are adjusted to within ±20% of a project action limit (or ±40% using historical anion data), confirmation of the analysis is recommended by definitive-level analysis according to EPA Method 314.0 or other approved methodology.

This method is not appropriate for samples high in cyanide or thiocyanate. These anions are presented in perchlorate ISE literature as potential interferents, but interference studies on these anions were not been performed during method development. Acidification to pH 4.0 of samples with cyanide, and to a lesser extent thiocyanate, causes generation of cyanide gas, which is poisonous.

5.0 SAFETY

This method does not address all safety issues associated with its use. The laboratory or field team leader is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

This method is designed for potential use in the field by trained technicians or experienced laboratory analysts. Before commencing use of this method, the user must undergo initial training to become familiar with the equipment and chemicals used in the method. This training will include practice handling the chemicals and solutions, performing serial dilutions using pipettes and volumetric glassware, reading all MSDSs for chemicals used, and reading all instrument manuals and the method standard operating procedure (SOP).

Safety glasses and protective gloves and clothing must be worn while handling perchlorate salts and solutions, sulfuric acid, and environmental samples which may contain unknown contaminants.

The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

The following chemicals have the potential to be highly toxic or hazardous. The MSDS for each chemical should be consulted.

Sulfuric acid (Sec. 7.3).
Sodium perchlorate, potassium perchlorate, and magnesium perchlorate (Sec. 7.4).

Although stable under most conditions, perchlorate salts are considered to be explosive and are strong oxidizers. Handle and store with care. Do not allow perchlorate salts or solutions to contact other materials, especially reducing agents, organic compounds, reactive metals, or skin or eyes. Wear eye and skin protection when handling perchlorate salts and solutions. In case of contact with skin, flush with water for 5 minutes or more. In case of contact with eyes, flush with water for 15 minutes or more. Seek medical attention if burning or irritation persists.

All perchlorate solutions included in this SOP are considered oxidizers and hazardous materials, and must be properly labeled with concentration identification and right-to-know OXIDIZER 5.1 labels. Carefully follow all requirements and protocols for mixing, diluting, and storing the chemicals in this method. Follow all procedures for cleaning containers specified in Section 14.0 (Clean-up Protocols), and for collecting, storing, and disposing of wastes specified in Section 15.0 (Waste Management).

6.0 Apparatus and Equipment

Ion Specific Electrode (ISE): The method requires use of a perchlorate-specific ISE. During method development, the Sentek 367-75 Solid State Perchlorate Combination ISE was used and found to perform satisfactorily; however, equivalent equipment can be used, and no requirement or recommendation of brand or manufacturer is implied. Note that a double junction reference electrode ISE was found not to meet sensitivity requirements during method development for this method. Therefore, a solid state combination ISE is recommended, as it also can be stored dry and no inner or outer chamber reference electrode solutions are required. Having a back-up perchlorate ISE module is recommended in case of severe deterioration of sensitivity or failure.

Data Acquisition System: An ISE meter such as the Orion Model 290A Advanced Portable ISE/pH/mV/ORP/ Temperature Meter is required. A computer interface such as the Laval ELIT 8804 Computer Interface (Four Channel Serial Port RS232 Communication Port Connection and Laval ELIT Extended Software for ISE Interface 8804 for 10,000 Measuring Points) may be used instead of an ISE meter. The above referenced equipment was used during method development and found to perform satisfactorily, however, equivalent equipment can be used, and no requirement or recommendation of brand or manufacturer is implied. Due to sensitivity requirements and time required to stabilize, millivolt readings are logged instead of direct perchlorate concentration read-out using ISE meter or computer interface calibration features. Entry of the logged data into a spreadsheet program capable of producing a logarithmic calibration curve is recommended for calibration and perchlorate concentration readout. Alternatively, data may be plotted on semilogarithmic graph paper.

pH Meter: A pH electrode and meter is required to determine when standards and samples have been acidified to pH 4.0 (± 0.1).

Additional ISEs: ISEs for chloride, nitrate, and/or bromide may be used to determine concentrations of interfering anions if appropriate historical or contemporary data is not available. The ISE meter or computer interface for the perchlorate ISE can be used for data acquisition.

Conductivity Meter: A conductivity meter may provide useful insights into relative levels of anions. This meter should be capable of measuring conductance over a range of 1 - 10,000 microsiemens/cm (uS/cm) or microMhos/cm (uMhos/cm), which are considered equivalent terms.

Flexible-Arm Electrode Stand and Holder: A flexible device to hold the perchlorate ISE, pH meter, thermometer, and any other electrodes to be used simultaneously is recommended. The device should be able to move the electrodes in and out of the containers holding the standard or sample.

Magnetic Stirrer: A magnetic stirrer is required for this method.

Analytical Balance: If stock standards for calibration standards, second source check standards, or ISA solutions are to be made from reagent salts, an analytical balance capable of accurately weighing target analyte salts to ±0.01 g is required. Analytical balances with higher accuracy can be used to reduce the concentration of primary stock perchlorate solutions. Perchlorate stock solutions and ISA solutions are commercially available, and may be purchased if available.

Desiccator Cabinet: Dry perchlorate chemicals are recommended to be stored in a desiccator cabinet if standards are to be made from reagent salts.

Autopipettor: A variable volume 100-1000 µL autopipettor with disposable tips is highly recommended for dilution of primary and working standards to make calibration and check standards, and to add ISA to standards and samples.

Containers and Glassware: All containers for perchlorate solutions must be chemical resistant. Standard laboratory glassware or chemically resistant plastic-ware such as polymethylpentene or high density polypropylene (HDPE) should be used for concentrated perchlorate solutions. All containers should be thoroughly washed and rinsed with distilled or deionized water before use. The following glassware/plastic-ware are recommended:

Assorted pipettes: 0.1 mL, 0.2 mL, 0.5 mL, 1.0 mL, 2.0 mL, 10 mL (or autopipettor)

Pipetting Aid: Device to aid in pipetting without skin contact, such as the Eppendorf Pipette Helper

100 mL, 200 mL, and/or 1,000 mL volumetric flask(s) with stopper or screw cap (glass or polymethylpentene) 400 mL beakers (for analysis of 200 mL aliquots). Appropriate wide mouth screw cap

plastic containers may be used, allowing extended storage of standards and samples after analysis, as long as the mouth is wide enough for the ISE, pH electrode, thermometer, and magnetic stirrer.

Thermometer(s)

Assorted polymethylpentene and polypropylene storage containers for primary and working standards (250-400 mL recommended) and waste solutions (1-4 L recommended)

Assorted supplies: Plastic spatulas, stirring rods, plastic dropper for sulfuric acid, plastic squeeze bottles for rinsing electrodes and glassware, larger plastic bottles for storing wastes, 100 mL graduated cylinder(s), disposable graduated plastic syringe pipettes (1-12 mL), 6"X6" tare (weighing) paper, chemwipes, etc.

Personal Protective Equipment (PPE): Safety glasses, protective gloves, and clothing must be worn while handling perchlorate solutions, sulfuric acid, and environmental samples, which may contain unknown contaminants.

7.0 Reagents, Standards, and Solutions

All standards should be made from reagent grade chemicals or certified solutions. ASTM Type I distilled or deionized water, free of the anion of interest, should be used in the preparation of all standards and solutions.

Use of a variable volume 100-1000 µL autopipettor with disposable tips is highly recommended for dilution of primary and working standards to make calibration and check standards, and to add ISA to standards and samples. If a variable volume autopipettor is not available, use traditional 1.0-10.0 mL high accuracy pipettes and 100-200 mL volumetric flasks to make the required standards by appropriate serial dilutions.

Perchlorate salts are hygroscopic, they will adsorb water, thus causing gravimetric errors in the concentrations of the calibration standards. Keep the perchlorate salts in a cool (not refrigerated) desiccator cabinet at all times, except to briefly weigh out aliquots for preparation of standards. Keep bottles tightly closed and keep screw threads clean (carefully wipe with dry chemwipe or paper towel if necessary).

7.1 Primary Ionic Strength Adjustor (ISA) Solution

Purchase a commercially available ISA appropriate to the ISE used for the project, or make an ISA working solution from reagent salts or solutions. In method development, ISA solutions made from 0.1 M sodium acetate (recommended as the Sentek perchlorate ISA) and from 2.0 M ammonium sulfate (recommended as the ISA for Orion double junction perchlorate ISEs) were found to perform satisfactorily at 25% of the manufacturer-recommended concentrations, as follows.

For the Sentek ISA, the use of 1 mL of “Sentek Perchlorate ISAB” (1.0 M sodium acetate) per 200 mL sample is recommended for the low concentration method (ISAB refers to the buffering capacity of this ISA). For the Orion ISA, the use of 1.0 mL of Orion 930711 ISA (2.0 M ammonium sulfate) per 200 mL sample is recommended for the low concentration method. Although both ISAs are acceptable, use of the Sentek ISAB is recommended when using the Sentek ISE on the basis that sodium acetate is the internal solution for the built-in reference electrode.

If the Orion ISA or Sentek ISAB are not available, ISA solution can be made from reagent salts by adding 8.21 g sodium acetate or 26.43 g ammonium sulfate to a 100 mL volumetric flask, and diluting to the mark with distilled water. Transfer to 120 mL wide mouth polymethylpentene Nalgene bottle with screwcap. Clearly label bottle ISAB - 1M $NaCH_3CO_2$ or ISA - 2 M $(NH_4)_2SO_4$ and expiration date (date solution made +5 days). Store in cooler or refrigerator. May be stored and used for 5 days.

All standards and samples must be spiked with proportionally equivalent concentrations of the same ISA. Different concentrations of ISA or ISAB should not be used interchangeably within a calibration, although minor changes in ISA are not expected to significantly affect data quality. Note that concurrent calibrations can be maintained to account for any differences in adjustments to samples (such as pH, ISA/ISAB concentration, or temperature) by making the same adjustments to the calibration and check standards.

EVERY STANDARD OR SAMPLE TO BE ANALYZED REQUIRES ADDITION OF ISA. If the ISA is not added, the analysis may be severely biased low and must be rejected. ISA can be transferred using graduated syringe pipettes or a variable volume autopipettor.

7.2 Perchlorate Standards for Calibration

7.2.1 Primary Perchlorate Standards for Calibration

A stock standard perchlorate solution at 1,000 or 10,000 mg/L (mg/L) prepared from American Chemical Society (ACS) reagent grade material is required for preparation of calibration standards. Purchase a commercially available 1000 mg/L perchlorate stock standard solution, usually made from sodium perchlorate; or prepare a primary stock solution from one of the following ACS reagent grade salts:

Potassium Perchlorate, Analytical Grade (MW 138.55)
1 M = 138.55 g $KClO_4$/L = 99.45 g ClO_4^-/L = 99,450 mg/L (mg/L) ClO_4^-
139.32 g $KClO_4$/L = 100.00 g ClO_4^-/L = 100,000 mg/L ClO_4^- (1.0055 M)

Sodium Perchlorate, Analytical Grade (MW 122.45)
1 M = 122.45 g $KClO_4$/L = 99.45 g ClO_4^-/L = 99,450 mg/L (mg/L) ClO_4^-
123.13 g $KClO_4$/L = 100.00 g ClO_4^-/L =100,000 mg/L ClO_4^- (1.0055 M)

Depending on project accuracy requirements, a 1,000 mg/L primary perchlorate stock solution can be made using an analytical balance with ±0.01 g accuracy, if a 1,000 mL volume of primary stock solution is acceptable for waste disposal and storage considerations. A 10,000 mg/L primary stock solution must be made if using an analytical balance with ±0.01 g accuracy and a 100 mL volume of primary stock standard is preferred for waste disposal and storage considerations. An analytical balance with ±0.001 g or greater accuracy can be used to make 100 mL of 1,000 mg/L primary perchlorate stock solution.

Add 1.39 (1.3932) g $KClO_4$ or 1.23 (1.2313) g $NaClO_4$ to a 100 mL glass volumetric flask (for 10,000 mg/L solution) or a 1,000 mL glass volumetric flask (for 1,000 mg/L solution), dilute to mark with distilled water. Stopper or cap the flask, or transfer to appropriate Teflon FEP Nalgene bottle or equivalent with screwcap and right-to-know OXIDIZER 5.1 label. Clearly label bottle 1^o PERCHLORATE STD / 0.1 M / 1,000 or 10,000 mg/L ClO4- and expiration date (date solution made +180 days). Do not add ISA solution to this primary standard.

7.2.2 Intermediate Perchlorate Working Standard for Calibration

The primary stock solution is used to prepare intermediate working standards for use in preparation of daily calibration standards by serial dilution. Any combination of working standard concentrations and serial dilutions is acceptable as long as all calculations are carefully checked, but the following sequence is suggested.

To prepare a 50 mg/L working standard, pipette 5.0 mL of 1,000 mg/L (or 0.5 mL of 10,000 mg/L) 1° PERCHLORATE STD into a 100 mL glass volumetric flask, dilute to mark with distilled water. Transfer to an appropriate Teflon FEP Nalgene, polymethylpentene Nalgene, or equivalent bottle with screwcap and right-to-know OXIDIZER 5.1 label. Clearly label bottle PERCHLORATE WORKING STD / 50 mg/L ClO4- and expiration date (date solution made +28 days). **Do not add ISA solution to this or any intermediate working standard**.

Store in refrigerator or in a cool dark place. Perchlorate stock standards, stored at room temperature, may be stable for an extended period of time. Avoid exposure to sunlight or elevated temperatures. Specified expiration dates should be clearly marked on the label of each prepared stock standard. Properly stored unused or rarely used primary stock 10,000 µg/L or 1,000 µg/L perchlorate standards should not be held for more than 6 months, or according to vendor recommendation. Depending on project facilities and how often the standards are opened and used, it is recommended that frequently used primary stock standards be freshly prepared more often. Intermediate stock 1,000 µg/L perchlorate standards should not be held for more than 28 days, and lower concentration intermediate stock and dilute working standards should be prepared weekly. Calibration standards are prepared daily. Verify solutions on an ongoing basis by analysis of second source standards and periodic review of instrument millivolt readings.

7.2.3 Prepare Calibration Standards Daily

Prepare calibration standards at 10 µg/L, 20 µg/L, 40 µg/L, 60 µg/L, and 100 µg/L on a daily basis by the dilution of the intermediate perchlorate working standard. If less method sensitivity is required for project requirements, choose higher concentrations to focus of the calibration range to the concentrations of interest. If the working range is elevated significantly above the 10-100 µg/L range specified for this low concentration method, such that calibration within the manufacturer specified range of 200-700 µg/L to 99,500 µg/L is appropriate, then this method may be used for guidance (for example, for soils), but full strength ISA (four times the amount specified for the low concentration method) should be used per ISE manufacturer recommendation, and matrix interference will not be significant.

Any combination of working standard concentrations and serial dilutions is acceptable as long as all calculations are carefully checked, but the following sequence is suggested. Pipette 1.0 mL, 2.0 mL, 4.0 mL, 6.0 mL, and 10.0 mL of 50 mg/L perchlorate working standard into a 200 mL volumetric flask, and dilute to a total volume of 200 mL with distilled water (if a 100 mL volumetric flask is used, dilute to mark and combine with another 100 mL volume of water). Transfer to an appropriate container for analysis with a magnetic stirrer, such as a 400 mL beaker or appropriate wide mouth screw-cap plastic container. Clearly label each container 10, 20, 40, 60, or 100 mg/L Perchlorate Calibration Standard and preparation/expiration date (standards must be made daily).

Add ISA: Add 1.0 mL of 1.0 M sodium acetate or 1.0 mL of 2.0 M ammonium sulfate per 200 mL) to each calibration standard, as specified in Section 7.1. If the ISA is not added to the calibration standards, the calibration will be severely affected and all results will be unusable.

7.3 Perchlorate Second Source Standard: Initial Calibration Verification (ICV)/ Laboratory Control Sample (LCS)

As all calibration standards and samples must be prepared using the same chemicals, the ICV and LCS are functionally equivalent. The ICV/LCS is a second source standard used to verify the accuracy of the instrument calibration and monitor ongoing batch QC. Prepare a 1000 µg/L or 10,000 µg/L primary perchlorate stock solution using a material source different from that of the calibration stock for use in preparing the ICV/LCS.

7.3.1 Primary Perchlorate Standard for ICV/LCS

Purchase a commercially available certified 1,000 mg/L perchlorate stock standard using a vendor different from the vendor of the calibration standards, being sure the standard is from a different source or lot number; or prepare an ICV/LCS primary stock standard from one of the above referenced salts not used for calibration standards, or from the following reagent salt:

Magnesium Perchlorate (anhydrone), Reagent Grade (MW 223.21)
    1 M = 223.21 g $Mg(ClO_4)_2$/L
    0.5 M = 111.61 g $Mg(ClO_4)_2$/L = 99.45 g ClO_4^-/L = 99,450 mg/L (mg/L) ClO_4^-
    112.22 g $Mg(ClO_4)_2$/L = 100.00 g ClO_4^-/L = 100,000 mg/L ClO_4^-

Prepare a primary perchlorate ICV/LCS stock solution as specified for calibration standards in Section 7.2.1, above, or using 1.12 (1.122) g $Mg(ClO_4)_2$. **Do not add ISA solution to this primary standard.** Clearly label bottle 1□ PERCHLORATE ICV/LCS STD /1,000 or 10,000 mg/L ClO_4^- and expiration date. This solution is used as a master solution to prepare an intermediate working standard to be used in preparation of the daily ICV/LCS standards by serial dilution, as specified for calibration standards in Section 7.2.2, above. **Do not add ISA solution to this or any intermediate working standard**. Any combination of working standard concentrations and serial dilutions is acceptable as long as all calculations are carefully checked.

7.3.2 Prepare ICV/LCS Daily

Prepare one or more LCSs at 25 or 50 µg/L (depending on project QC objectives, see Section 8.2.4, below) on a daily basis by dilution of the intermediate LCS working standard. 25 or 50 µg/L LCSs can be prepared as specified for calibration standards in Section 7.2.3, above, using 2.5 or 5.0 mL of 50 mg/L intermediate perchlorate working standard diluted to 200 mL. Clearly label each standard, including expiration date (date standard made for the LCS). **Add ISA to each ICV/LCS, as specified in Section 7.1. Failure to add the ISA will generally result in severe low bias.**

7.4 Perchlorate Reagent and Solution Storage, Cleanup, and Waste

Although stable under most conditions, perchlorate salts are considered to be explosive and are strong oxidizers. Handle and store with care. Keep the perchlorate salts in a desiccator cabinet or in a dry, dark place (avoid heat or refrigeration) at all times, except to briefly weigh out aliquots for preparation of standards. Keep bottles tightly closed and keep screw threads clean (carefully wipe with dry paper towel if necessary). Do not mix with other substances. If solid perchlorate salts must be discarded, they must be properly labeled with concentration identification and OXIDIZER 5.1 labels and disposed of as hazardous waste according to state and federal guidelines.

Store all perchlorate solutions in a refrigerator or in a cool dark place. Perchlorate solutions are strong oxidizers. Store according to all applicable requirements. Do not store with reducing agents. All solutions must be allowed to reach ambient temperature before analysis.

If calibration standards or LCSs are to be prepared in the field, transfer adequate volumes of the working standards into polymethylpentene, polypropylene, or equivalent bottles with screwcap for transport to the site. Standards transported to the site must be discarded at the end of the day.

Transfer discarded solutions to a 1 Liter polypropylene wide mouth screw top container (or other appropriate polypropylene waste collection container) labeled HIGH CONC PERCHLORATE WASTE with right-to-know OXIDIZER 5.1 label.

Triple rinse glassware with water into 1000 mL polypropylene beaker and transfer rinsate to 1 Liter polypropylene wide mouth screw top container (or other appropriate polypropylene waste collection container) labeled LOW CONC PERCHLORATE WASTE with right-to-know OXIDIZER 5.1 label. Wash triple rinsed plastic or glassware with soap and water in sink, triple rinse with distilled water, drip dry. Follow all procedures for cleaning containers specified in Section 14.0 (Clean-up Protocols).

Maintain and dispose of all wastes according to applicable state and federal regulations. Follow all procedures for collecting, storing, and disposing of wastes specified in Section 15.0 (Waste Management).

8.0 Quality Control (QC)

The QC requirements for this method include frequency and acceptability criteria for initial calibrations, second source check standards (ICV/LCS), continuing calibration verification standards (CCV), method blanks (MB), continuing calibration blanks (CCB), matrix spike samples (MS), and laboratory duplicate samples. Field QC, such as field duplicate sample analyses and field blanks may be required if specified to meet project-specific QC objectives.
This section details the specific requirements for each of these QC parameters.

The primary use for this method is to determine 15-100 μg/L (parts per billion [μg/L]) concentrations of perchlorate in water samples at or near field sampling sites by trained technicians or experienced laboratory analysts. As a field screening method, ten percent of samples analyzed by this method should generally be confirmed by definitive-level analysis at a fixed base laboratory. Therefore, some elements of QC generally specified for ongoing laboratory analyses, such as a formal initial demonstration of capability with MDL studies, linear range studies, etc., are not included for the low concentration method.

The user should maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

8.1 Initial Demonstration of Proficiency

An initial demonstration of proficiency may be required to characterize instrument performance and laboratory performance prior to performing analyses by this method. However, for field screening use, acceptability of the initial calibration curve for each analytical run will meet this requirement, as follows.

8.1.1 Linear Calibration Range (LCR) – The LCR must be determined to meet project objectives. The method is intended to have a 10-100 µg/L LCR; however, the method is expected to perform acceptably and with less matrix interference at higher concentrations. The calibration curve must use a sufficient number of standards at appropriate intervals to insure that the resulting curve is linear. To demonstrate linearity for the low concentration method, the coefficient of determination (r^2) must be greater than or equal to 0.990 (equivalent to $r \geq 0.995$) and/or the concentration calculated for each calibration standard from its millivolt response using the calibration curve should be within ± 20% of its true value; and ICV/LCSs and CCVs must meet accuracy criteria of ± 20%.

8.1.2 Method Detection Limit (MDL) Studies - Depending on project objectives and the intended use of the data, MDL studies may be required. However, for field screening use, demonstration of the ability to distinguish between a blank and a standard below the project reporting limit (RL) or practical quantitation limit (PQL) is acceptable. Blanks must be less than one-half the RL or PQL, and the low calibration standard must meet ±20% accuracy criteria.

During method development, an MDL of 3 µg/L was determined. Method blanks were generally in the 2-5 µg/L range, and the RL was set at 15 µg/L to meet the California action limit and target detection limit (TDL) of 18 µg/L. To support the 15 µg/L RL, blank results must be less than 7.5 µg/L and readings for a 10 µg/L standard must be 8.0-12.0 µg/L.

8.2 Method Performance QC

8.2.1 Method and Calibration Blanks - At least one MB must be prepared with each batch of 20 or fewer samples. As all calibration standards and samples must be prepared using the same chemicals, the MB and initial and continuing calibration blanks (ICB and CCBs) are functionally equivalent. An ICB/MB must be analyzed after the ICV/LCS and before any samples, and a CCB must be analyzed at a minimum of every 10 samples and at the end of the analytical sequence. Reanalysis of the ICB/MB is acceptable as the CCB. Values that exceed one half the RL/PQL indicate that laboratory or reagent contamination should be suspected and corrective action must be taken before continuing the analysis, including reanalysis of any samples with detected results less than five times the result for the blank.

8.2.2 Laboratory Control Sample (LCS) - For each batch of 20 or fewer samples processed, at least one LCS must be carried through the entire sample preparation and analytical process. As all calibration standards and samples must be prepared using the same chemicals, the ICV and LCS are functionally equivalent as second source standards. An ICV/LCS must be analyzed after every calibration and before any samples, and for each additional batch of 20 or fewer samples.

8.2.3 Calibration Verification - For all determinations, the second source check standard (ICV/LCS) and an initial calibration blank (ICB/MB) must be analyzed immediately following daily calibration to verify that the instrument is functioning within method criteria before samples are analyzed. A continuing calibration verification standard (CCV) and CCB must be analyzed after every ten samples and at the end of the analytical run. CCV analyses must verify that the calibration is still within specified criteria. The LCS and CCV may alternate for extended analytical runs of more than 20 samples.

8.2.4 ICV/LCS and CCV Concentrations - The ICV/LCS and CCV should be prepared at concentrations appropriate to project objectives. The ICV/LCS must be prepared from a different source than the calibration standards. The CCV can be from the same source as the calibration standards, and may utilize initial calibration solutions. For projects with an action limit of 18 µg/L, ICV/LCS concentrations of 25 µg/L or 50 µg/L are recommended, depending on project objectives, and CCV concentrations of 20 µg/L are recommended, with alternating standards at 25 or 50 µg/L and 20 µg/L to verify mid-range accuracy and sensitivity near the action limit.

8.2.5 Analytical Sequence - The following analytical sequence is recommended: ICAL, ICV/LCS, ICB/MB, 10 samples (including matrix specific QC samples), CCV, CCB, 10 samples, CCV, CCB. If a second batch of samples is to be analyzed, the last CCV, CCB can be omitted and the sequence continued with: LCS, CCB/MB, 10 samples (including matrix specific QC samples), CCV, CCB, etc.

Note that millivolt readings for each ICAL standard should be quantitated utilizing the calibration curve, and all results should be within ± 20% of true values. Analytical data for all QC analyses including calibration verification and blanks must be kept on file with the sample analysis data.

8.2.6 Acceptance Criteria for Method Performance QC

Acceptance criteria for the ICV/LCS and CCV should be set to meet project-defined requirements. In general, the accuracy criterion for the low concentration method should be set at ± 20% of the spiked or true value.

8.2.7 Corrective Action for Method Performance QC - If ICAL standard, ICV/LCS, or CCV recovery is not acceptable, sample analysis must be discontinued, the problem must be identified and corrective action must be taken.

Verify that the temperature has not changed by more than 1-2^{o}C since analysis of calibration standards and that pH has been correctly adjusted. Re-prepare and reanalyze an unacceptable ICV/LCS. For CCVs or LCSs run after field samples, verify that loss-of-sensitivity interference due to nitrate or carry-over due to high concentrations of perchlorate or other interferents is not the cause by reconditioning the ISE module with an acid blank and 100-2000 µg/L perchlorate solution (refer to Section 10.2). If the problem is identified and corrected, reanalyze all samples since the last acceptable ICV/LCS or CCV. If necessary, implement ISE reconditioning between every analysis.

If the problem cannot be identified, check that all calibration standards, CCVs, and second source standards were correctly prepared. If necessary, reprepare all standards and recalibrate. If the problem persists, refinish the tip of the ISE with fine emery paper according to manufacturer directions, or replace the ISE module. Reanalyze all samples since the last acceptable ICV/LCS or CCV in an acceptable analytical run.

8.3 Matrix-Specific QC

8.3.1 Matrix spike (MS) - Perform matrix spike analysis on at least one sample per batch of 20 or fewer samples. A higher frequency may be required to demonstrate the ability of the method to accurately work in matrices requiring application of significant correction factors for interfering anions. Performing MS analyses on samples with differing concentrations of nitrate may be particularly informative.

The sample aliquot used for MS analysis must be a duplicate of the aliquot used for sample analysis. The perchlorate concentration in the MS should be chosen to verify accurate determination of perchlorate in the environmental matrix at concentrations critical to project objectives. For projects with an action limit of 18 µg/L, spike concentrations of 20 µg/L or 25 µg/L are recommended. Prepare the MS using the same stock working solution as the calibration standards, as this will remove the bias contributed by an externally prepared stock and focus on any potential bias introduced by the field sample matrix.

If the concentration of spike is less than 25% of the background concentration of the matrix, the matrix recovery should not be calculated. With an LCR of 10-100 µg/L and an MS of 25 µg/L, this will only occur for samples with results exceeding the calibration range. In such cases, choose another sample for MS analysis with results near the action limit to verify accuracy of results at concentrations critical to project objectives, or spike a diluted aliquot of the sample for MS analysis at the same dilution used for final quantitation to verify accuracy of higher results.

Calculate the percent recovery for perchlorate, corrected for the concentration measured in the unspiked sample <u>before</u> application of all correction factors, according to the following equation:

$$\%R = (C_s - C) \times 100 / S$$

where:
$\%R$ = percent recovery
C_s = concentration of sample plus spike
C = sample background concentration
S = concentration of spike added to sample

8.3.2 MS Acceptance Criteria and Corrective Action - Acceptance criteria for the MS should support project-defined requirements. In general, the acceptability criteria for matrix spike recoveries for this method should be set at 65-135 %R. If the recoveries for perchlorate matrix spikes fall outside 65-135 %R, verify that the temperatures for the duplicate analyses did not differ by more than 1-2^{o}C and that pH was correctly adjusted. In addition verify that loss-of-sensitivity interference due to nitrate or carry-over due to high concentrations of perchlorate or other interferents is not the cause by reconditioning the ISE module with an acid blank and 100-2000 µg/L perchlorate solution (refer to Section 10.2) and reanalyzing the parent sample and MS.

If the problem is identified and corrected, it may be necessary to reanalyze some or all of the samples in the batch. If necessary, implement ISE reconditioning between every analysis. If corrective actions do not alleviate the problem and the performance for all other QC performance criteria is acceptable, the accuracy problem is judged to be matrix related. The results for perchlorate in all samples with similar concentrations of interfering anions must be labeled suspect due to matrix interference.

Due to the sensitivity of the low concentration method to anion interferences, ongoing evaluation of matrix spike recoveries is required to help determine the accuracy of this method when correction factors must be applied. Repeated failure to meet specified MS criteria may indicate the low concentration method is inappropriate for the matrix.

Split sample analyses by EPA Method 314.0 (or equivalent) of all questionable samples may be required to determine the appropriateness of the low concentration method for the matrix (refer to Section 8.3.6). In such cases, raising the RL or LCR and re-evaluation of the ability of the low concentration method to meet project objectives, especially for specific samples with high nitrate concentrations, may be required.

8.3.3 Laboratory Duplicate Sample Analysis – Perform duplicate sample analysis on at least one sample per batch of 20 or fewer samples. The duplicate analysis should be performed on two separate aliquots taken from one sample container, prepared and analyzed in the same manner as each other and all other samples in the batch. Duplicate sample results should be within 20 relative percent difference (RPD). Calculate RPD according to the following equation:

$$RPD = (C_1 - C_2) \times 100 / \tfrac{1}{2} (C_1 + C_2)$$

Where:
RPD = relative percent difference for the sample pair
C_1 and C_2 = perchlorate concentrations for the two samples

8.3.4 Laboratory Duplicate Sample Acceptance Criteria and Corrective Action - Acceptance criteria for duplicate sample analyses should support project-defined requirements. In general, the precision criterion for the low concentration method should be set at ≤20 RPD. If RPDs fall outside the specified criteria, verify that the temperatures for the duplicate analyses did not differ by more than 1-2°C and that pH was correctly adjusted for both samples. In addition verify that loss-of-sensitivity interference due to nitrate or carry-over due to high concentrations of perchlorate or other interferents is not the cause by reconditioning the ISE module with an acid blank and 100-2000 µg/L perchlorate solution (refer to Section 10.2) and reanalyzing the duplicate samples.

If the problem is identified and corrected, it may be necessary to reanalyze some or all of the samples in the batch. If necessary, implement ISE reconditioning between every analysis. If corrective actions do not alleviate the problem and the performance for all other QC performance criteria is acceptable, the precision problem is judged to be matrix related. The results for perchlorate in all samples with similar concentrations of interfering anions must be labeled suspect due to matrix interference.

8.3.5 Field Duplicate Sample Analyses - Field duplicate samples may also be analyzed to monitor the precision of the sampling technique. The recommended criterion for field duplicate samples is ≤30 RPD. If RPDs fall outside the specified criteria, follow suggested corrective actions specified for laboratory duplicate samples, above. If corrective actions do not alleviate the problem and the performance for laboratory duplicate analyses are acceptable, the precision problem is judged to be field sampling technique or matrix related.

8.3.6 Split Samples - In general, a minimum of ten percent of samples analyzed by this method should be confirmed by definitive-level split sample analysis. Split samples should be true duplicate samples collected from the same sampling container or device at the same location and time, with one sample analyzed for perchlorate by this method and the other sent to a laboratory for analysis according to EPA Method 314.0 or other approved methodology. The recommended criterion for split samples is ≤30 RPD.

Whenever project objectives are potentially affected by the application of correction factors such that perchlorate readings are adjusted to within ±20% of a project action limit (or ±40% using historical anion data), confirmation of the analysis is recommended. If split samples were not collected in the field for the sample in question, the aliquot used for ISE analysis may be sent for analysis.

9.0 Calibration

Perform calibrations according to the instruction manual for the ISE meter used, and according to the requirements in this section. Calibration must be performed daily or whenever excessive drift is demonstrated. Note that changes in temperature may affect readings; therefore, recalibration may be required if the ambient temperature of samples being analyzed changes. If analyses are to be performed in the field, the instrument may be calibrated in the morning before deployment into the field, or in the field before sample analysis. The meter may require recalibration periodically, so all calibration solutions must be transported in a cooler to the field.

9.1 Define LCR - A five-point calibration is required for the purposes of the low-concentration method when the LCR is 10-100 µg/L. The low calibration standard should be at or slightly below the project RL. Do <u>not</u> include a blank in ISE calibrations. Prepare calibration standards at 10 µg/L, 20 µg/L, 40 µg/L, 60 µg/L, and 100 µg/L on a daily basis. If less method sensitivity is required for project requirements, choose higher concentrations to focus of the calibration range to the concentrations of interest. Preparation of calibration standards is described in Section 7.2.

9.2 Initial Calibration - Prepare 200 mL of each calibration standard in an appropriate beaker or screw-cap jar, add 1 mL of "Sentek Perchlorate ISAB" (1.0 M sodium acetate) or 1 mL of Orion 930711 ISA (2.0 M ammonium sulfate) per 200 mL standard, as specified in Section 7.1. Add 0.2 N sulfuric acid drop-wise to each standard until pH stabilizes at 4.0 (± 0.1). Record perchlorate ISE millivolt readings for each calibration standard, analyzing low concentration standards first according to analytical procedures specified in Section 10.1. Millivolt readings are logged into a notebook instead of using ISE meter or computer interface calibration features due to difficulties in determining when millivolt readings have stabilized at the low perchlorate concentrations for this method. Also record temperature and pH for each analysis. Instrument set-up and analysis procedures are specified in **Section 10.1**.

9.3 Calibration Curve – Prepare a calibration curve for perchlorate concentration versus millivolt readings on a spreadsheet capable of producing a logarithmic calibration curve. This allows graphic representation of the calibration curve with equation and output of the coefficient of determination (r^2), and direct output of perchlorate readings from millivolt readings by application of the calibration curve equation in a spreadsheet formula.

Functionally equivalent curves can be prepared by plotting the perchlorate concentration versus the natural logarithm of the millivolt reading, producing a semi-logarithmic calibration curve; or by plotting the natural logarithm of perchlorate concentration versus the natural logarithm of the millivolt readings, producing a linear calibration curve. Alternatively, the calibration data can be entered into a programmable calculator or plotted on semilogarithmic or linear graph paper, and perchlorate readings manually read from the calculator or graph paper.

9.4 Calibration Curve Acceptability Criteria - Demonstration and documentation of acceptable initial calibration is required prior to sample analysis. To demonstrate calibration curve acceptability for the low concentration screening level method, the coefficient of determination (r^2) must be greater than or equal to 0.990 (equivalent to $r \geq 0.995$), and the concentration calculated for each calibration standard from its millivolt response using the calibration curve must be within ± 20% of its true value, as specified in Section 8.1. If using graph paper, the acceptability of the calibration curve is verified if each calibration standards meets the ± 20% of true value requirement.

9.5 Calibration Verification - The calibration curve must be verified by analyzing a second source check standard (ICV/LCS) and ICB/MB prior to sample analysis, and CCVs and CCBs every 10 samples, as specified in Section 8.2. These calibration check standards must be within 20% of true values, and blanks should be less than one half the RL, or corrective action must be performed, as specified in Section 8.2.7.

10.0 Procedure

10.1 Instrument Set-up and Sample Analysis

Precondition the perchlorate ISE in a 500 µg/L perchlorate solution for a minimum of 15 minutes (1 hour for a new module) prior to use, as specified in Section 10.2. Connect the ISE and other detectors to the appropriate meters, turn on meters, and prepare for analysis according to appropriate instruction manuals. Set up the perchlorate ISE along with a thermometer and pH electrode, plus any additional anion ISEs desired, such that all detectors can be placed in the sample solution without touching each other or the sides of the container.

Prepare 200 mL of each standard or sample in an appropriate beaker or screw-cap jar by adding 1 mL of "Sentek Perchlorate ISAB" (1.0 M sodium acetate) or 1.0 mL of Orion 930711 ISA (2.0 M ammonium sulfate) per 200 mL of standard or sample, as specified in Section 7.1. Use equivalent additions of the same ISA solution for all calibration standards, QC samples, and samples. **If the ISA is not added to all samples and calibration standards, the analyses will be severely affected and all results will be unusable.** If the LCR is elevated significantly above the 15-100 µg/L range specified for this low concentration method, such that calibration within the manufacturer specified range of 200-700 µg/L to 99,500 µg/L is appropriate, then full strength ISA (four times the above referenced ISA solutions per 200 mL sample) should be used per ISE manufacturer recommendation for all standards and samples.

Calibrate and check the system calibration as described in the appropriate instruction manuals for the ISE meter according to the requirements in Section 9.0. If required, perform corrective action as described in Section 8.2.7.

Place sample with magnetic stir bar on a magnetic stirrer set to slow or medium speed such that no or minimal vortex is present. Place the perchlorate ISE along with a thermometer and pH electrode, plus any additional anion ISEs desired, into the sample. Detectors should not touch each other or the sides of the container. **Be sure ISA has been added to every sample and standard.**

Add 0.2 N sulfuric acid drop-wise to the standard until pH stabilizes at 4.0 (± 0.1). Use of 0.4 N sulfuric acid may be appropriate for samples with high levels of carbonate/bicarbonate.

Monitor millivolt readings until the readings stabilize such that upward or downward drift has stopped. This may take several minutes, especially for low concentrations of perchlorate, or if temperatures are low. Note that stabilization at an exact millivolt reading may not be possible. If stabilization takes excessive time, reconditioning of the ISE as specified in Section 10.2 may be required.

Record millivolt readings for the perchlorate ISE, pH, and temperature for each analysis, as well as date and other relevant information, into a bench data log book for permanent record.

If a sample concentration exceeds the calibration range, the sample must be diluted with reagent water to fall within the working range, and reanalyzed. **Be sure to add ISA proportional to dilution before proceeding with analysis**. Pre-spiking of water used for dilutions with ISA at the same concentration as samples is a convenient way to maintain ISA proportionality.

Remove sample from magnetic stirrer, thoroughly rinse perchlorate electrode, pH electrode, and thermometer with deionized water from a squeeze bottle, and shake off excess water (do not blot dry). Remove magnetic stir bar using a second magnet, rinse, and place in next sample. Place next sample on magnetic stirrer and proceed with analysis as above.

Storing the ISE briefly in a reconditioning solution followed by a thorough rinse between each sample, has been found to help maintain sensitivity in general. If nitrate is present in samples above 0.2 mg/L NO_3-N, or if loss of sensitivity is otherwise noted, reconditioning of the perchlorate ISE using acidified blanks and 100-2000 µg/L perchlorate solutions between every sample is required, as specified in Section 10.2.

Analyze samples according to the following analytical sequence, as specified in Section 8.2.5: ICAL, ICV/LCS, ICB/MB, 10 samples (including matrix specific QC samples), CCV, CCB, 10 samples, CCV, CCB. If a second batch of samples is to be analyzed, the last CCV, CCB can be omitted and the sequence continued with: LCS, CCB/MB, 10 samples (including matrix specific QC samples), CCV, CCB, etc.

10.2 ISE Conditioning

Due to the nature of the perchlorate ISE, regenerating perchlorate sites in the perchlorate ISE membrane is a routine requirement to maintain sensitivity. The perchlorate ISE requires special preconditioning prior to first use, then daily before calibration. For the low concentration method, the initial preconditioning should be performed for a minimum of one hour (overnight is acceptable), and the daily preconditioning should be performed for 15-20 minutes, in a 500 µg/L perchlorate solution. The ISE should then be placed in a blank and allowed to stabilize before commencing calibration.

All perchlorate conditioning solutions and blanks must be adjusted with ISA and sulfuric acid to pH 4.0 the same as all standards and samples.

When long periods of time become necessary for millivolt readings to stabilize, or if low recoveries for check standard recoveries are encountered after analysis of field samples, reconditioning of the ISE is required to maintain sensitivity. Some anions, notably nitrate, and possibly some organic chemicals, have been found to cause loss of sensitivity between analyses. Sample matrices with nitrate concentrations greater than 0.2 mg/L NO3-N were found to require implementation of reconditioning.

When required, recondition between every analysis by placing the perchlorate ISE in an acidified blank for one minute to clean, then in a 100-2000 µg/L perchlorate solution acidified to pH 4 for one to six minutes to recondition. The concentration and length of time required should be proportional to the severity of the problem, depending on nitrate concentration or how long is required for millivolt readings to stabilize. Follow by immersion in an acidified blank for one to two minutes before sample analysis, again depending on time required for millivolt readings to stabilize.

Use of 500 or 2000 µg/L concentration solutions should be progressively implemented when the 100 µg/L solution is found not to regenerate sensitivity within four to six minutes, or after analysis of any sample with known high concentrations of nitrate. A quick check of sensitivity can be performed by immersing the ISE in a 20 µg/L standard to verify that millivolt readings are in the correct range. Use of stronger solutions does not adversely affect accuracy, but requires additional time for the ISE to restabilize in a blank before sample analysis.

Even when not required, routinely storing the ISE briefly in a 20 µg/L perchlorate solution followed by a thorough rinse between each sample, has been found to help maintain sensitivity in general. This can lead to faster analysis times because millivolt readings stabilize more quickly, with fewer reanalyses required due to declining check standard recoveries.

If sensitivity for a specific ISE module is found to decline with extended use, Sentek recommends using an abrasive such as fine emery paper to renew the exposed PVC surface of the electrode. See manufacturer directions for this procedure. Note that exposure to samples containing organic solvents may permanently degrade the electrode membrane.

11.0 Calculations

11.1 Convert Millivolt Readings to Perchlorate Readings - Prepare a calibration curve, as specified in **Section 9.3**. If a spreadsheet is used, enter all sample IDs (including calibration standards and QC samples with true value concentrations, perchlorate ISE millivolt readings, pH, and temperature into adjacent columns. Also enter date and other relevant information from the data log-book. Graph perchlorate concentration (in µg/L) versus millivolt readings for the calibration standards, and show the resulting equation for the calibration curve.

Enter a formula based on the calibration curve equation into a perchlorate concentration column for each of the analyses, including the initial calibration standards, referencing the millivolt reading cell to input the value of the millivolt reading. The spreadsheet can then calculate and display the perchlorate concentration in the results column. This result is a raw perchlorate result, referred to as the "perchlorate reading" throughout this method. Refer to Attachment 2 for an example spreadsheet.

Alternatively, the calibration data can be entered into a programmable calculator or plotted on logarithmic or semilogarithmic graph paper and perchlorate readings manually read from the graph paper, as discussed **in Section 9.3.**

For the low concentration method, any perchlorate reading less than the 15 µg/L RL should be reported as non-detected at the RL, even when sensitivity has been demonstrated for the 10 µg/L low concentration standard, due to the effects of potential matrix interference.

The perchlorate readings can be used for reporting of all method QC results, including ICAL, ICV/LCS, CCV, ICB/MB, and CCB check standards. The perchlorate readings for all environmental samples and matrix-specific QC samples must be corrected for matrix interference, as specified in Section 11.2, below.

11.2 Apply Correction Factors for Anion Interferent for Final Perchlorate Results – For samples with concentrations of specific anions known to cause positive interference greater than 20% (or 3 µg/L for non-detects) correction factors must be subtracted from positive perchlorate readings to calculate final perchlorate results (refer to Tables 1, 2, and 3). When perchlorate readings with acceptable associated QC indicate that perchlorate is not present above project action limits, perchlorate can confidently be considered not to be present at that level, and correction factors need not be addressed, since all of the interferences are for positive bias.

Subtract applicable correction factors from the initial perchlorate reading for concentrations in excess of 0.12 mg/L NO_3-N, 50 mg/L chloride, or 1.2 mg/L bromide. Matrices with lower concentrations of these anions will not be significantly affected by known interferences. Anion concentrations from historical or contemporary data may be applied. If such data does not exist, ISEs for these anions may be used with the same ISE meter or computer interface used for the perchlorate determinations. Alternatively, analysis by MSA may be used to compensate for unknown anion interference, as specified in Section 11.3, especially for perchlorate readings less than 30 µg/L. However, further studies of the effectiveness of MSA to compensate for anion interferences are required.

If chloride exceeds 50 mg/L (parts per million – mg/L), apply correction factors from Table 1.

If nitrate exceeds 0.12 mg/L NO3-N, apply correction factors from Table 2, and reconditioning of the ISE module between every sample is required.

If bromide exceeds 1.2 mg/L, which is higher than is typically found in environmental samples, apply correction factors from Table 3.

Note that for many matrices, the only anion likely to require application of correction factors is chloride, for which correction factors are relatively small (12 µg/L perchlorate for 500 mg/L chloride), and historic levels may not significantly change.

11.3 Method of Standard Additions

When a perchlorate reading greater than the RL or PQL is suspected of being due in part or entirely due to matrix interference, but anion correction factors cannot be applied due to lack of anion data, the use of MSA may be used to compensate for unknown anion interference, especially for perchlorate readings less than 30 µg/L. Further studies of the effectiveness of MSA to compensate for anion interferences are required.

MSA incorporates the sequential addition of three increments of a standard solution (spikes) to a sample. Measurements are made on the original sample and after each addition. The slope, x-intercept and y-intercept are determined by least-squares analysis. The analyte concentration is determined by the absolute value of the x-intercept. Regression may be performed mathematically on a programmable calculator or on a computer; or the results for the three spiked additions of perchlorate may be graphed and the resulting line or curve extended through the y-axis until it intersects the x-axis. Ideally, the spike volume is low relative to the sample volume (should not exceed 10% of the volume). MSA may counteract matrix effects, especially if such effects are constant or linear.

To perform MSA on a sample, analyze the sample and three spikes consecutively. After analysis of the parent sample, spike the sample with 10 µg/L perchlorate, reanalyze, and record the perchlorate reading. Repeat with an additional 10 µg/L spike two more times such that perchlorate readings are recorded for 10 µg/L, 20 µg/L, and 30 µg/L perchlorate spikes.

MSA additions are generally performed with volumes of 10% or less of the original sample volume. If additions total more than 5%, the proportional addition of ISA to the spiking solution may be appropriate. Further study of MSA for this method is recommended.

All MSA perchlorate readings must be within the linear calibration range. Due to complex interference curves for high levels of interference, dilution of the sample prior to MSA is recommended for samples with initial perchlorate readings greater than 30 µg/L. **Be sure to add ISA proportional to dilution before proceeding with analysis.**

MSA is generally performed with spikes of 50%, 100%, and 150% of initial analyte reading. For the low concentration method, the use of 10 µg/L perchlorate spikes is recommended to avoid complex curves and to meet linearity requirements.

The data for each MSA analysis shall be recorded and clearly identified in the raw data documentation. Plot or input added perchlorate concentration as the x-variable and perchlorate reading as the y-variable. Do not enter the values for the initial (unspiked) perchlorate reading. The slope, x-intercept, y-intercept and correlation coefficient (r) for the least squares fit of the data should be reported from the spreadsheet, calculator, or computer program.

The perchlorate result for the sample by MSA is the absolute value of the x-intercept as calculated by linear regression. Non-linear regression techniques may be appropriate due to the complex interference curves for the low concentration method. Further study is recommended

If the coefficient of determination (r^2) is less than 0.990 or the correlation coefficient (r) less than 0.995 for the regression, the result should be considered quantitatively uncertain. Due to the complex interference curves involved, linearity for MSA regression may be significantly affected. If the coefficient of determination (r^2) is less than 0.980 or the correlation coefficient (r) less than 0.99 for the regression, the result should be considered significantly impacted and may not be usable.
Each full MSA counts as two analytical samples towards determining 10% QC frequency (i.e., five full MSAs can be performed between calibration verifications). For ISE meters capable of operation in MSA mode, MSA can be used to determine QC samples during that run.

12.0 Record Keeping

Maintain a standards preparation log, sample extraction log, and a sample analysis log. Include record of ISA addition to each sample and standard. The analysis run log should include time of initial calibration (ICV, CCV, or LCS). All logs should include the date and initials of the analyst.

Maintain a sample results log or worksheet, which may be integrated with the extraction/analysis logs. Include calibration standard IDs, QC sample IDs (including true values), field sample IDs, pH, temperature, millivolt reading, and initial (uncorrected) perchlorate readings for each analysis. The results log or worksheet, or a sample results reporting worksheet or form should also include all anion concentrations and correction factors, and final corrected perchlorate results reported. The source of anion concentrations used for correction factors should be included in the data.

13.0 Method Performance

Method performance studies for this method have not been completed. For a complete discussion of method development to date, refer to the Letters of Findings for Tasks 1 and 4, Sections 1.0 and 4.0 of the report for which this SOP is Attachment 1.

14.0 Clean-Up Protocols

Perchlorate salts and perchlorate solutions are considered hazardous materials. Care must be exercised not to allow perchlorate or perchlorate-containing rinsates to escape to the environment. In addition, acidified solutions and field samples containing regulated contaminants should be treated as hazardous materials.

All solutions or solids containing perchlorate, including analytical standards, field and QC samples, or perchlorate salts, must be properly discarded (see Section 15.0, Waste Management, below). Triple rinse glassware, plasticware, sample sleeves, or other equipment with water, catching all rinsate into an appropriate polypropylene beaker, and transfer rinsate to 1-4 Liter polypropylene wide mouth screw top container (or other appropriate polypropylene waste collection container) labeled LOW CONC PERCHLORATE WASTE. Wash triple rinsed plastic or glassware with soap and water in sink, triple rinse with distilled water, drip dry.

Keep work area clean and free of obstructions to prevent spillage of hazardous solutions. In case of spills, soak up perchlorate solutions with paper towels or other absorbent material, squeeze out excess into rinsate collecting container, and dispose of paper towel or absorbent as solid waste. Protective gloves or other personal protective equipment contaminated with perchlorate should be triple rinsed into a rinsate collecting container, then disposed of as non-hazardous trash (perchlorate is very soluble, triple rinsing is expected to remove all traces of perchlorate).

15.0 Waste Management

Perchlorate wastes must be stored in satellite waste storage areas, in appropriate containers (polypropylene) labeled with perchlorate identification and right-to-know OXIDIZER 5.1 labels, and disposed of as hazardous waste according to state and federal guidelines.

All perchlorate solutions included in this SOP are strong oxidizers, are considered hazardous materials, and must be properly labeled with concentration identification and OXIDIZER 5.1 labels. Store expended standards and samples with high concentration detected results in polypropylene wide mouth screw top containers container (or other appropriate polypropylene waste collection container) labeled HIGH CONC PERCHLORATE WASTE with OXIDIZER 5.1 labels. Collect and store rinsates from the washing of perchlorate contaminated surfaces and samples with low concentration detected results in polypropylene wide mouth screw top containers container (or other appropriate polypropylene waste collection container) labeled LOW CONC PERCHLORATE WASTE with OXIDIZER 5.1 labels.

All discarded solutions and rinsates are considered hazardous waste and must also be properly labeled and maintained according to state and federal storage and disposal regulations.

The Environmental Protection Agency requires that waste management practices be conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes should be stored, characterized and disposed of in an acceptable manner. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, by complying with the letter and spirit of any waste discharge permit and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel," available from the American Chemical Society, 1155 16th Street NW, Washington, DC 20036, (202) 872-4477.

16.0 References

1. Inter-Agency Perchlorate Steering Committee, Analytical Subcommittee Report (1998). Report on the interlaboratory validation of IC methods for perchlorate.

2. Methods for Chemical Analysis of Water and Wastes, U.S. EPA Manual 600/4-79-020 (U.S. EPA, 1983 with additions)

3. Physical/Chemical Methods, SW-846 3rd edition (U.S. EPA, 1986a), and Updates I, II, IIA, and III

ATTACHMENT 2:
EXAMPLE SPREADSHEET

Attachment 2 Spreadsheet

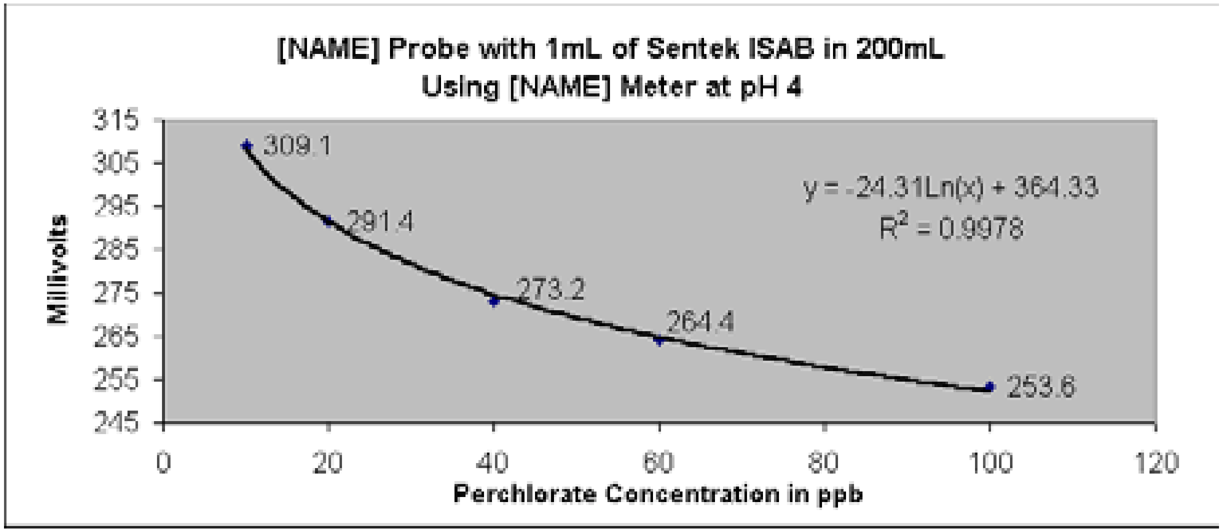
Analytical Method: Low Concentration Method for the Determination of Perchlorate by Ion Selective Electrode

Matrix: Water Units: ug/L (ppb) Extraction/Digestion: Acidification to pH 4 with Sulfuric Acid

Instrument: [NAME] Solid State Perchlorate Combination ISE

Analyst:

Meter: Date:



Sample/Calibration ID	pH	Sample Volume	Millivolts Reading	Concentration in ppb
10		200 mL	309.1	=(EXP(-((D27-364.3)/24.31)))
20		200 mL	291.4	=(EXP(-((D28-364.3)/24.31)))
40		200 mL	273.2	=(EXP(-((D29-364.3)/24.31)))
60		200 mL	264.4	=(EXP(-((D30-364.3)/24.31)))
100		200 mL	253.6	=(EXP(-((D31-364.3)/24.31)))
Calibration Date	**##/##/##**		**Time**	**12:45pm**
Temperature		**##.#^{0}C**		
Slope	**24.31**		**Intercept**	**364.3**