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METHOD 314.0

DETERMINATION OF PERCHLORATE IN DRINKING WATER USING ION CHROMATOGRAPHY

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METHOD 314.0

DETERMINATION OF PERCHLORATE IN DRINKING WATER USING ION CHROMATOGRAPHY

1. SCOPE AND APPLICATION

1.1 This method covers the determination of perchlorate in reagent water, surface water, ground water, and finished drinking water using ion chromatography.

1.2 The single laboratory reagent water Method Detection Limit (MDL, defined in Section 3.16) for the above analyte is listed in Table 1. The MDL for a specific matrix may differ from those listed, depending upon the nature of the sample and the specific instrumentation employed.

1.2.1 In order to achieve comparable detection limits, an ion chromatographic system must utilize suppressed conductivity detection, be properly maintained, and must be capable of yielding a baseline with no more than 5 nanosiemen (nS) noise/drift per minute of monitored response over the background conductivity.

1.3 This method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatograms.

1.4 When this method is used to analyze unfamiliar samples for perchlorate, anion identification should be supported by the use of a laboratory fortified matrix sample. The fortification procedure is described in Section 9.4.1.

1.5 Users of the method data should identify data quality objectives prior to analysis. Users of the method must demonstrate the ability to generate acceptable results, using the procedures described in Section 9.0.

1.6 This method specifies an IC column and analytical conditions which were determined to be the most effective for the widest array of sample matrices. Other IC procedures have been written which incorporate similar columns and conditions, such as hydroxide based mobile phases, low hydrophobicity IC columns, and measurement by suppressed conductivity detection.[1-5] During the development of this method, these other procedures, as well as the columns and conditions outlined in this method, were concurrently investigated with comparable results for test matrices with moderate levels of common inorganic background anions. These findings were consistent with those of the Inter-Agency Perchlorate Steering Committee, Analytical Subcommittee's Report,[6] published in 1998, which reported on the results of an interlaboratory validation of

these other Ion Chromatographic Methods. The columns and conditions identified in this method were recommended since they bore the greatest tolerance for the highest levels of common inorganic anion interference.

2. SUMMARY OF METHOD

2.1 A 1.0 mL volume of sample (see Note), is introduced into an ion chromatograph (IC). Perchlorate is separated and measured, using a system comprised of an ion chromatographic pump, sample injection valve, guard column, analytical column, suppressor device, and conductivity detector.

NOTE: This large sample loop (1.0 mL) can be made using approximately 219 cm (86 inches) of 0.03 inch i.d. PEEK tubing. The exact volume is not critical since all standards and samples will use the same sample loop. However, the volume should be verified to be within 5% of this volume by weighing the sample loop empty, filling the loop with deionized water and re-weighing the loop. The volume can then be approximated by assuming the density of water is 1.0 mg/uL.

3. DEFINITIONS

3.1 ANALYSIS BATCH -- A sequence of samples, which are analyzed within a 30 hour period and include no more than 20 field samples. An Analysis Batch must also include all required QC samples, which do not contribute to the maximum field sample total of 20. The required QC samples include:

- Instrument Performance Check Standard (IPC)
- Laboratory Reagent Blank (LRB)
- Initial Calibration Check Standard (ICCS)
- Laboratory Fortified Blank (LFB)
- Continuing Calibration Check Standard (CCCS), when the batch contains more than 10 field samples
- End Calibration Check Standard (ECCS)
- Laboratory Fortified Matrix (LFM)
- Either a Field Duplicate, a Laboratory Duplicate or a duplicate of the LFM
- (if pretreated samples are included in batch) Pretreated LRB
- (if pretreated samples are included in batch) Pretreated LFB
- (if pretreated samples are included in batch) Pretreated LFM, for each pretreated matrix.

NOTE: Every field sample analysis, including both diluted and pretreated field samples, but excluding any LFM or duplicate field sample analysis which qualify as QC samples, must be applied to the maximum of 20 total field samples permitted in an analysis batch.

3.1.1 A field sample(s), included in the analysis batch, can be reanalyzed following the ECCS provided the 30 hr time limit for the analysis batch has not expired. The laboratory can reanalyze that sample(s) but must initially conduct a second ICCS before the reanalysis and an ECCS after the final reanalysis. The ECCS must be completed within the 30 hr window.

3.2 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution(s) or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 INITIAL CALIBRATION STANDARDS -- A series of CAL solutions used to initially establish instrument calibration and develop calibration curves for individual target anions (Section 10.2).

3.4 INITIAL CALIBRATION CHECK STANDARD (ICCS) -- A CAL solution, which is analyzed initially, prior to any field sample analyses, which verifies the previously established calibration curve. The concentration for the initial calibration check standard MUST be at or below the MRL (Section 3.17) level.

3.5 CONTINUING CALIBRATION CHECK STANDARDS (CCCS) -- A CAL solution which is analyzed after every tenth field sample analyses, not including QC samples, which verifies the previously established calibration curve and confirms accurate analyte quantitation for the previous ten field samples analyzed. The concentration for the continuing calibration check standards should be either at a middle calibration level or at the highest calibration level (Section 10.3.2).

3.6 END CALIBRATION CHECK STANDARD (ECCS) -- A CAL solution which is analyzed after the last field sample analyses which verifies the previously established calibration curve and confirms accurate analyte quantitation for all field samples analyzed since the last continuing calibration check. The end calibration check standard should be either the middle or high level continuing calibration check standard (Section 10.3.2).

3.7 FIELD DUPLICATES (FD) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.8 INSTRUMENT PERFORMANCE CHECK SOLUTION (IPC) -- A solution containing a specific concentration of perchlorate and other test substances (namely chloride, sulfate and carbonate) used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.9 LABORATORY DUPLICATE (LD) -- Two sample aliquots (LD1 and LD2), taken in the laboratory from a single sample bottle, and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated specifically with the laboratory procedures by removing variation contributed from sample collection, preservation and storage procedures.

3.10 LABORATORY FORTIFIED BLANK (LFB) – An aliquot of reagent water, or other blank matrix, to which a known quantity of perchlorate is added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.11 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) – An aliquot of an environmental field sample to which a known quantity of perchlorate is added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical result (when compared to the result for the LFB). The background concentrations of perchlorate, in the sample matrix, must be initially determined in a separate aliquot and the measured value in the LFM corrected for this background concentration.

3.12 LABORATORY REAGENT BLANK (LRB) – An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, filtration and reagents that are used with other samples. The LRB is used to determine if perchlorate or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.13 LINEAR CALIBRATION RANGE (LCR) – The concentration range over which the instrument response is linear.

3.14 MATERIAL SAFETY DATA SHEET (MSDS) – Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.15 MATRIX CONDUCTIVITY THRESHOLD (MCT) – The highest permitted conductance of an unknown sample matrix, measured prior to conducting the analysis, which is used to determine when sample matrix dilution or pretreatment is required. The conductance of a sample matrix is proportional to the common anions present in the matrix (which contribute to the level of total dissolved solids [TDS]) which can greatly affect the integrity of this analysis. The value for this threshold is dependant on the conditions, hardware, and state of the hardware employed. Consequently, this threshold is not method defined and must be determined by the individual analytical laboratory during the Initial Demonstration of Capability (IDC) and confirmed in each analysis batch using the Instrument Performance Check (IPC) Solution. Matrix

conductivity is measured in microsiemens/cm (uS/cm) or microMhos/cm (uMhos/cm) which are considered equivalent terms.

3.16 METHOD DETECTION LIMIT (MDL) – The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.[7, 8]

3.17 MINIMUM REPORTING LEVEL (MRL) – The minimum concentration that can be reported as a quantitated value for a target analyte in a sample following analysis. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

3.18 PEAK AREA TO HEIGHT RATIO (A/H) – The ratio of the peak area divided by the peak height which is used as a tool to monitor analytical performance. This ratio is used to establish and monitor the MCT and represents an objective means of assessing analytical performance when analyzing high conductivity matrices. A gradual distortion of the baseline is typically observed in the retention time window for perchlorate as the matrix conductivity increases (consistent with elevated levels of common anions) which will more significantly influence peak height relative to the influence on peak area. As the distortion of the baseline increases, this ratio increases, and the integrity of the measured perchlorate will be compromised.

3.19 PROFICIENCY TESTING (PT) or PERFORMANCE EVALUATION (PE) SAMPLE -- A certified solution of method analytes whose concentration is unknown to the analyst. Often, an aliquot of this solution is added to a known volume of reagent water and analyzed with procedures used for samples. Often, results of these analyses are used as part of a laboratory certification program to objectively determine the capabilities of a laboratory to achieve high quality results.

3.20 QUALITY CONTROL SAMPLE (QCS) – A solution of method analytes of known concentrations that is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.21 STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing perchlorate which is either prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.22 TOTAL DISSOLVED SOLIDS (TDS) -- Both organic and inorganic constituent which are dissolved in a sample matrix and are not removed by particulate filtration.

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in an ion chromatogram. These interferences can lead to false positive results for the target analyte as well as reduced detection limits as a consequence of elevated baseline noise.

4.2 Interferences can be divided into three different categories: direct chromatographic coelution, where an analyte response is observed at very nearly the same retention time as the target anion; concentration dependant coelution, which is observed when the response of higher than typical concentrations of the neighboring peak overlap into the retention window of the target anion; and, ionic character displacement, where retention times may significantly shift due to the influence of high ionic strength matrices (high mineral content or hardness) overloading the exchange sites in the column and significantly shortening target analyte's retention times.

4.2.1 A direct chromatographic coelution may be solved by changing columns, eluent strength, modifying the eluent with organic solvents (if compatible with IC columns), changing the detection systems, or selective removal of the interference with pretreatment. Sample dilution will have little to no effect. The analyst MUST verify that these changes do not induce any negative affects on method performance by repeating and passing all the QC criteria as described in Section 9.

4.2.2 Sample dilution may resolve some of the difficulties if the interference is the result of either concentration dependant coelution or ionic character displacement, but it must be clarified that **sample dilution will alter your Minimum Reporting Limit (MRL)** by a proportion equivalent to that of the dilution. Therefore, careful consideration of project objectives should be given prior to performing such a dilution. An alternative to sample dilution, may be dilution of the eluent as outlined in Section 11.2.6.

4.2.3 Pretreatment cartridges can be effective as a means to eliminate certain matrix interferences. With any proposed pretreatment, the analyst must verify that the target analyte is not affected by monitoring recovery after pretreatment (additional pretreated LFM requirement see Section 11.1.4.6) and that no background contaminants are introduced by the pretreatment (additional pretreated LRB requirement see Sections 9.3.1.1 and 11.1.4.2). With advances in analytical separator column technology which employ higher capacity anion exchange resins, the need for these cartridges has been greatly reduced.

4.2.3.1 Extreme caution should be exercised in using these pretreatment cartridges. Artifacts are known to leach from certain cartridges which can foul the guard and analytical columns causing loss of column capacity indicated by shortened retention times and irreproducible results. Frequently compare your calibration standard chromatograms to those of the column test chromatogram (received when the column was purchased) or use calibration chromatograms generated when the column was initially installed, to insure proper separation and similar response ratios between the target analytes are observed.

4.2.3.2 If LRB background problems are encountered in the retention time window for perchlorate when these pretreatment cartridges have been employed, increase the initial reagent water rinse of the cartridge to approximately five times the volume specified by the manufacturer.

4.3 Sample matrices with high concentrations of common anions such as chloride, sulfate and carbonate can make the analysis problematic by destabilizing the baseline in the retention time window for perchlorate. This is evidenced by observing a protracted tailing following the initial elution of the more weakly retained anions (chloride, carbonate, and sulfate) which extends into the perchlorate retention time window. These common anion levels can be indirectly assessed by monitoring the conductivity of the matrix. Consequently, all sample matrices must be monitored for conductivity (Section 11.1.2) prior to analysis. When the laboratory determined Matrix Conductivity Threshold (MCT, see Section 9.2.8) is exceeded, procedures incorporating sample dilution and/or pretreatment must be performed as specified in Sections 11.1.3 and 11.1.4, respectively.

4.4 All reagent solutions (eluents, external water for ASRS suppressor, etc...) used by the instrument must be filtered through no larger than a 0.45 um nominal pore size membrane or frit to remove particulates and prevent damage to the instrument, columns and flow systems. Sample filtration must also be employed on every sample prior to analysis. This applies not only to field samples but also to the laboratory reagent blank (LRB) and laboratory fortified blank (LFB). The LRB and LFB samples function as controls and must be filtered to confirm no bias is attributable to the filtration.[5] Filter the samples through a membrane or frit with no larger than a 0.45 um nominal pore size. Syringe mounted, cartridge type, filters work well. Filters specifically designed for IC applications should be used.

4.5 Close attention should be given to the potential for carry over peaks from one analysis which will effect the proper detection of perchlorate in a second, subsequent analysis. It is the responsibility of the user to confirm that no late eluting peaks have carried over into a subsequent analysis thereby compromising the integrity of the analytical results.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method have 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 specifically listed below in Section 5.3 for hazardous materials.

5.2 Each laboratory is responsible for maintaining 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 (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable. Additional references on laboratory safety are available.[9-12]

5.3 The following chemicals have the potential to be highly toxic or hazardous, consult MSDS.

5.3.1 Sodium Hydroxide (NaOH), used in the preparation of the eluent is considered caustic.

6. EQUIPMENT AND SUPPLIES

6.1 Ion chromatograph (IC) -- Analytical system complete with eluent reservoirs, an ion chromatographic pump, injection valves, both guard and analytical separator columns, suppressor, conductivity detector, and computer based data acquisition system.

6.1.1 Anion guard column -- Dionex AG16 4 mm (P/N 55377), or equivalent. This column functions as a protector of the separator column. If omitted from the system, the retention times will be shorter.

6.1.2 Anion separator column -- Dionex AS16, 4 mm (P/N 55376), or equivalent (see Sections 6.1.2.1 - 6.1.2.2). The AS16, 4 mm column using the conditions outlined in Table 1 produced the separations shown in Figures 1 through 4.

6.1.2.1 The development of this method included investigations into the performance of alternate 4 mm IC guard and analytical separator columns which have been used for the IC analysis of perchlorate and are specified in procedures external to the U.S.EPA.[1-5] These alternate guard /separator columns included the Dionex AG5 / AS5 and the Dionex AG11 / AS11. The AG5 / AS5 is currently specified in the standard operating procedure (SOP) for the IC analysis of perchlorate by the State of California, Department of Health Services.[1,5] The AG11 / AS11 is used by several commercial labs conducting IC analysis for perchlorate and is recognized by California as an

acceptable alternate to the AG5 / AS5. [2-4] A multilab validation study included both of these analytical columns and indicated comparable results could be attained.[6] In U.S.EPA studies, both the AG5 / AS5 and the AG11 / AS11 performed well for reagent water and simulated drinking water samples with low to moderate common anion levels but as these levels increased, performance began to diminish for both columns. The AG16 / AS16 columns could tolerate much higher levels of these common anions and therefore it is recommended in this method as the column of choice. A summary of the results of examining these three columns for simulated matrices with various common anion levels is presented in Table 4.

6.1.2.2 Any alternate, equivalent column must be characterized as hydrophilic or conversely, must be rated as having low to very low hydrophobicity.[4] This is one characteristic that is consistent for the AS5, AS11 and AS16 analytical separator columns. This requirement for low hydrophobicity is to allow the efficient, reproducible and symmetrical band elution of polarizable anions, such as perchlorate. If the perchlorate analysis is attempted on a hydrophobic column, such as those typically used for the analysis of common anions,[13] poor performance will result due to very asymmetric, tailing peaks. Using a middle to high calibration standard, conduct a typical analysis. Any alternate column must be capable of yielding symmetrical peak elution for this perchlorate response as demonstrated by yielding a Peak Gaussian Factor of between 0.80 and 1.15 using the following equation,

$$PGF = \frac{1.83 \times W(\tfrac{1}{2})}{W(^1/_{10})}$$

where,
$W(\tfrac{1}{2})$ is the peak width at half height, and
$W(^1/_{10})$ is the peak width at tenth height.

NOTE: Values for $W(\tfrac{1}{2})$ and $W(^1/_{10})$ can be attained through most data acquisition software.

6.1.3 Anion suppressor device -- The data presented in this method were generated using a Dionex Anion Self Regenerating Suppressor (4 mm ASRS, ULTRA, P/N 53946). An equivalent suppressor device may be utilized provided comparable conductivity detection limits are achieved and adequate baseline stability is attained as measured by a combined baseline drift/noise of no more than 5 nS per minute over the background conductivity. Proper suppressor

performance is essential to analytical data reproducibility and sensitivity of the conductivity detector.

6.1.3.1 The ASRS was set to perform electrolytic suppression at a current setting of 300 mA using the external water mode. External water was delivered to the suppressor directly from a pressurized source at a flow rate of 5 mL/min

6.1.3.2 If pretreated samples (Section 11.1.4), or sample matrices which contain appreciable concentrations of transition metal cations (e.g., Fe or Al) are frequently analyzed, cationic components may bind to the suppressor membrane and over time effect suppressor performance. If the instrument begins to have problems with reduced peak response or asymmetrical perchlorate peaks, the suppressor membranes should be cleaned. As a quick and easy cleaning step, the manufacturer's ASRS "Quickstart" procedure for installing a new ASRS should be followed.[14] If this procedure does not correct the problem, follow the manufacturer's recommended cleaning procedure for removing metal contaminants.[15]

6.1.4 Detector -- Conductivity cell (Dionex CD20, or equivalent) capable of providing data as required in Section 9.2.

6.2 Data Acquisition System -- The Dionex Peaknet Data Chromatography Software was used to generate all the data in Tables 1 through 4. Other computer based data systems may achieve approximately the same performance but the user should demonstrate this by the procedures outlined in Section 9.

6.3 Conductivity Meter – Used to monitor sample matrix conductance which is directly related to the common anion levels in a matrix and used to determine if sample pretreatment is required. At a minimum, this meter should be capable of measuring matrix conductance over a range of 1 - 10,000 uS/cm.

6.4 Analytical balance -- Used to accurately weigh target analyte salt for stock standard preparation (±0.1 mg sensitivity).

6.5 Top loading balance -- Used to accurately weigh reagents such as sodium hydroxide solution in the preparation of eluents (±10 mg sensitivity).

6.6 Weigh boats -- Plastic, disposable - for weighing eluent reagents.

6.7 Micro beakers -- Plastic, disposable - used during sample preparation.

6.8 Syringes -- Plastic, disposable, 10 mL - used during sample preparation.

6.9 Pipets -- Pasteur, plastic or glass, disposable, graduated, 5 mL and 10 mL.

6.10 Bottles -- High density polyethylene (HDPE) or glass, amber or clear, 30 mL, 125 mL, 250 mL. For sampling and storage of calibration solutions. Stability studies presented by the Interagency Perchlorate Steering Committee for Analytical Methods [6] and confirmed at the EPA (see Table3A), indicate perchlorate is neither photoreactive nor prone to adsorption to the walls of either HDPE plastic or glass bottles.

6.11 Particulate filters -- 0.45 micron syringe filters, specifically designed for IC applications (Gelman IC Acrodisc, PN 4485, or equivalent). These cartridges are used to remove particulates from the sample matrix while loading the sample manually or if the autosampler employed does not filter the sample during loading.

6.12 Matrix pretreatment cartridges in the barium form -- (Dionex OnGuard-Ba cartridges, PN 046072, or equivalent.) These cartridges are conditioned according to the manufacturer's directions and are used to reduce the matrix levels of sulfate.

6.13 Matrix pretreatment cartridges in the silver form – (Dionex OnGuard-Ag cartridges PN 039637, or equivalent.) These cartridges are conditioned according to the manufacturer's directions and are used to reduce the matrix levels of chloride.

6.14 Matrix pretreatment cartridges in the hydrogen form -- Dionex OnGuard-H cartridges (PN 039596) or equivalent. These cartridges are conditioned according to the manufacturer's directions and are used to reduce cations in the sample matrix. This protects the analytical column by removing silver which has leached from the Ag cartridge and may indirectly minimize the effect of carbonate by removing the cationic counter ion.

7. REAGENTS AND STANDARDS

7.1 Reagent water -- Distilled or deionized water 17.8 Mohm or better, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

7.2 Eluent solution -- 50 mM sodium hydroxide (NaOH, [CASRN 1310-73-2]), dissolve 8.0 grams of 50% (W/W) sodium hydroxide in reagent water to a final volume of 2.0 L. **NOTE:** This eluent solution is specific to the columns listed in Table 1. Any alternate columns will likely have unique and specific conditions identified by the manufacturer.

7.2.1 Solutions of NaOH are very susceptible to carbonate contamination resulting from adsorption of carbon dioxide from the atmosphere. This contamination will result in poor reproducibility of perchlorate retention times, elevated

instrument background conductivity, and increased baseline noise/drift. Consequently, exposure to the atmosphere should be minimized by storing these eluent solutions in sealed reservoirs under low pressure (3 to 5 psi) helium. In addition, these solutions should be regularly prepared and held for no more than 5 days. When refilling the eluent reservoir, completely replace old eluent solution by emptying the old eluent, rinsing the reservoir with reagent water, and refilling with the freshly prepared eluent solution. With this eluent, the suppressed conductivity detector background signal should be between 2 - 5 uS.

7.2.2 This eluent solution must be purged for 10 minutes with helium prior to use. This effectively removes dissolved gases which may form micro bubbles in the IC, compromising system performance and adversely effecting the integrity of the data. Alternatively, an in-line degas apparatus may be employed.

7.2.3 A system or apparatus which automatically generates the hydroxide eluent (Dionex EG40, or equivalent) is an acceptable alternative to physically preparing this hydroxide eluent.

7.3 Perchlorate stock standard solution, 1000 mg/L (1 mg/mL) – A stock standard solution may be purchased as a certified solution or prepared from ACS reagent grade, sodium salt as listed below. (NOTE: Sodium perchlorate represents a molar weight fraction of 81.2 % perchlorate anion)

7.3.1 Perchlorate (ClO_4^-) 1000 mg/L -- Dissolve 0.1231 g sodium perchlorate ($NaClO_4$, CASRN [7601-89-0] in reagent water and dilute to 100 mL in a volumetric flask.

NOTE: Stability of standards -- Perchlorate stock standards, stored at room temperature, appear to be very stable and may be stable for an extended period of time. However, specified expiration dates should be marked on each prepared stock standard as part of any laboratory's quality control program. In this regard, it is recommended that stock standards for perchlorate be held for no more than 12 months and an expiration date should be clearly specified on the label.

7.4 Mixed Common Anion Stock Solution - containing the anions chloride, sulfate and carbonate each at 25 mg/mL anion concentration. This solution is used to prepare simulated common anion samples in the determination of the MCT (Section 9.2.8).

7.4.1 Dissolve the following salts in reagent water to a final volume of 25.0 mL:
1.0 g sodium chloride (NaCl, CASRN [7647-14-5]) = 0.61 g Cl^-
0.93 g sodium sulfate (Na_2SO_4, CASRN [7757-82-6]) = 0.63 g $SO_4^=$
1.1 g sodium carbonate (Na_2CO_3, CASRN [497-19-8]) = 0.62 g $CO_3^=$

7.5 Conductivity Meter Calibration Solution

7.5.1 Potassium Chloride (KCl), 745 mg/L (total salt weight) -- Dissolve 0.745 g potassium chloride (KCl, [CASRN 7447-40-7]) in reagent water and dilute to a final volume of 1.00 L in a volumetric flask. On a properly functioning and calibrated conductivity meter, the reference conductance for this solution is 1410 uS/cm at 25 °C.[16]

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Samples may be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. The volume collected should be sufficient to insure a representative sample, allow for replicate analysis and laboratory fortified matrix analysis, if required, and minimize waste disposal.

8.2 Samples do not need to be shipped iced or stored cold in a refrigerator but every effort should be taken to protect the samples from temperature extremes. A thermally insulated sampling kit, designed to fit sampling bottles securely during shipment, should be used to protect the samples from these temperature extremes.

8.3 Sample preservation and holding times for the anions are as follows:

Analyte	Preservation	Holding Time
Perchlorate	None required	28 days

NOTE: Perchlorate has been shown to be stable for more than 28 days[6] 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 a laboratory to conduct the analysis.

9. QUALITY CONTROL

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The requirements of this program consist of an initial demonstration of laboratory capability, and subsequent analysis in each analysis batch (Section 3.1) of an Instrument Performance Check Standard (IPC), Laboratory Reagent Blank (LRB), Initial Calibration Check Standard (ICCS), Laboratory Fortified Blank (LFB), Continuing and End Calibration Check Standards (CCCS/ECCS), Laboratory Fortified Sample Matrix (LFM) and either a Field, Laboratory or LFM duplicate sample analysis. This section details the specific requirements for each of these QC parameters. The QC criteria discussed in the following sections are summarized in Section 17, Table 5 and

6. The laboratory is required to maintain performance records that define the quality of the data that are generated.

9.2 INITIAL DEMONSTRATION OF CAPABILITY

9.2.1 The Initial Demonstration of Capability (IDC) -- This is used to characterize instrument and laboratory performance prior to performing analyses by this method. The QC requirements for the IDC discussed in the following section are summarized in Section 17, Table 5.

9.2.2 Initial demonstration of low system background -- See Section 9.3.1.

9.2.3 Initial Demonstration of Accuracy (IDA) -- Prepare and analyze 7 replicate LFBs fortified at 25.0 ug/L. Calculate the mean measured concentration ($C_{\bar{x}}$) of the replicate values as follows.

$$C_{\bar{x}} = \frac{(C_1 + C_2 + C_3 + \ldots C_n)}{n}$$

where,

$C_{\bar{x}}$ = Mean recovered concentration of the replicate analysis.
$C_1, C_2, \ldots C_n$ = Recovered concentrations of the replicate 1,2...n.
n = 7

To pass the IDA, the value derived for $C_{\bar{x}}$ must be within ± 10% of the true value or between 22.5 ug/L and 27.5 ug/L.

9.2.4 Initial Demonstration of Precision (IDP) -- Using the data generated for Section 9.2.3, calculate the percent relative standard deviation (%RSD) of the replicate analysis, as indicated below. To pass the IDP, the %RSD must be less than 10%.

$$\%RSD = \frac{(S_{n-1})}{(C_{\bar{x}})} \times 100$$

where,

S_{n-1} = sample standard deviation (n-1) of the replicate analyses.
$C_{\bar{x}}$ = mean recovered concentration of the replicate analysis.

9.2.5 Quality Control Sample (QCS) – After calibration curves have initially been established or have been re-established, or as required to meet data quality needs, verify both the calibration and acceptable instrument performance with the preparation and analyses of an external/second source QCS. If the determined concentrations are not within ± 10% of the stated values,

performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the IDC or continuing with on-going analyses.

9.2.6 Method Detection Limit (MDL) – An MDL must be established using reagent water (blank) fortified at a concentration of three to five times the estimated instrument detection limit.[7,8] To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method over a three day period. These seven MDL replicate analyses may be performed gradually over three days or may represent data that has been collected, at a consistent MDL estimated concentration, over a series of more than three days. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S_{n-1})$$

where,

t = student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates]

S_{n-1} = sample standard deviation (n-1) of the seven replicate analyses.

9.2.6.1 MDLs should be periodically verified, but MUST be initially determined when a new operator begins work or whenever there is a significant change in the background, or instrument response.

NOTE: Do not subtract blank values when performing MDL calculations.

9.2.7 Minimum Reporting Level (MRL) – The MRL is the threshold concentration of an analyte that a laboratory can expect to accurately quantitate in an unknown sample. The MRL should be established at an analyte concentration either greater than three times the MDL or at a concentration which would yield a response greater than a signal to noise ratio of five. Setting the MRL too low may cause repeated QC failure upon analysis of the ICCS. **Although the lowest calibration standard may be below the MRL, the MRL must never be established at a concentration lower than the lowest calibration standard.**

9.2.8 Matrix Conductivity Threshold (MCT) – The MCT is an individual laboratory defined value which must be determined by preparing a series of sequentially increasing, common anion fortified, reagent water samples each contain a constant perchlorate concentration. Initially, a reagent water prepared LFB, containing no common anions, must be analyzed which contains perchlorate at a suggested concentration of 25 ug/L perchlorate. Next, the series of sequentially

increasing anionic solutions are prepared, each containing perchlorate at a suggested concentration of 25 ug/L, which also containing the individual common anions of chloride, sulfate and carbonate, all included at uniform increasing concentrations of 200, 300, 400, 500, 600, 800, and 1000 mg/L for each anion. A concentration of 25 ug/L perchlorate has been suggested assuming the MRL has been set in the range of 3.0 ug/L to 5.0 ug/L. If a laboratory's MRL is higher, choose a perchlorate concentration for this exercise at approximately 5 times that MRL.

9.2.8.1 Prepare the mixed common anion stock solution (see Section 7.4) containing chloride, sulfate and carbonate, each at 25 mg/mL.

9.2.8.2 Prepare a perchlorate secondary stock dilution standard at 1.00 mg/L from the 1000 mg/L perchlorate stock standard (Section 7.3) by diluting 0.50 mL of the stock solution to a final volume of 500 mL.

9.2.8.3 Prepare the LFB at suggested perchlorate concentration of 25 ug/L by diluting 0.625 mL of the perchlorate secondary stock dilution standard (Section 9.2.8.2) to a final volume of 25.0 mL.

9.2.8.4 Next, prepare the series of common anion fortified reagent water samples by adding 0.20 mL, 0.30 mL, 0.40 mL, 0.50 mL, 0.60 mL, 0.80 mL, and 1.00 mL of the mixed common anion stock solution (Section 7.4) into separate 25 mL volumetric flasks. Next, add 0.625 mL of the perchlorate secondary stock dilution standard (Section 9.2.8.2) to each 25 mL volumetric flask and dilute to volume with reagent water to yield a final perchlorate concentration of 25.0 ug/L.

9.2.8.5 Measure and record the conductance of each of these prepared solutions on a calibrated conductivity meter (This meter must be calibrated as described in Section 10.4 prior to measuring conductance). To use as a relative reference conductance, the 400 mg/L mixed anion sample, which contains chloride at 400 mg/L, sulfate at 400 mg/L and carbonate at 400 mg/L, should display a conductance of between 3200 uS/cm and 3700 uS/cm.

9.2.8.6 Analyze each solution, recording the peak area to height (A/H) ratio and the quantified concentration of perchlorate. In many data acquisition and instrument control software, the peak area to height ratio is a definable parameter which can be specified for printout on the analysis report.

9.2.8.7 Both the A/H ratio and quantified perchlorate concentration for the LFB and the 200 mg/L mixed common anion solution should be reproducibly consistent but as the common anion levels increase, the A/H ratio will also begin to increase as the peak height is distorted and reduced. As the peak is distorted, the area will also eventually begin to be distorted and the quantitated concentration will be reduced, but this is typically secondary, with the ratio of peak area to height initially predicting this pending quantitation problem.

9.2.8.8 Calculate the A/H ratio percent difference ($PD_{A/H}$) between the average A/H ratio for the LFB (A/H_{LFB}) and the average A/H ratios for each mixed common anion solutions (A/H_{MA}) using the following equation.

$$PD_{A/H} = \frac{|(A/H_{LFB} - A/H_{MA})|}{A/H_{LFB}} \times 100$$

9.2.8.9 As the conductivity of the matrices increase, the $PD_{A/H}$ will increase. The MCT is the matrix conductance where the $PD_{A/H}$ exceeds 20%. To derive the MCT, perform a linear regression on these data by plotting $PD_{A/H}$ (as the independent variable, x) versus the matrix conductance (as the dependent variable, y). The resulting regression data should yield an r^2 value of > 0.95. (See Figure 5) Record the "constant" (intercept value) and the "X-coefficient" (slope) and calculate the MCT as follows,

MCT = (20%) x (X-coefficient) + (constant)

NOTE: Be careful to consistently apply percentages as either whole numbers or as fractional values (20% = 0.20) for both the regression analysis and the MCT calculation.

9.2.8.10 As an alternate to the regression analysis, the laboratory can choose to establish their MCT at the conductance level of the highest mixed anion solution which yielded a $PD_{A/H}$ value below the 20 % threshold.

9.2.8.11 As a final procedure, the laboratory should confirm their perchlorate MRL in a mixed common anion solution which reflects a conductance near (within +/- 10%) that specified as the MCT. This solution must contain perchlorate, at the laboratory determined MRL, as well as the common anions chloride, sulfate and carbonate, prepared consistent with the instruction for the mixed anion solutions in this section and at a concentration estimated to generate a conductance near the MCT.

The conductance of this solution must be measured at within ±10% of the MCT and following the analysis, the recovered perchlorate must be between 70 - 130% of the MRL concentration. If the MRL recovery fails this criteria, the MCT should be lowered by 10% and this MRL verification must be repeated.

9.2.8.12 Prior to conducting any field sample analysis, the conductivity of that matrix must be determined. When the conductance of a field sample is above the MCT, sample dilution or pretreatment, as described in respective Sections 11.1.3 and 11.1.4 must be performed.

9.3 ASSESSING LABORATORY PERFORMANCE - The following items must be included in every analysis batch (Section 3.1).

9.3.1 Laboratory Reagent Blank (LRB) – An LRB must be prepared and treated exactly as a typical field sample including exposure to all glassware, equipment, solvents, filtration and reagents that are used with field samples. Data produced are used to assess instrument performance of a blank sample and evaluate contamination from the laboratory environment. Values that exceed ½ the MRL indicate a laboratory or reagent contamination is present. The source of the contamination must be determined prior to conducting any sample analysis. Any sample included in an automated analysis batch which has an invalid LRB, indicated by a quantitated perchlorate that exceeds ½ the MRL, must be reanalyzed in a subsequent analysis batch after the contamination problem is resolved.

9.3.1.1 When sample matrices have been pretreated to reduce the risk of high common anion interference (Section 11.1.4), a second LRB must be prepared, pretreated in exactly the same manner, and analyzed to confirm no background effects from the pretreatment process are present. If an analysis batch only contains pretreated samples, then only a pretreated LRB is required.

9.3.2 Instrument Performance Check (IPC) -- The MCT, which was determined as part of the IDC in Section 9.2.8, must be verified through the analysis of an IPC. The IPC is three tiered and is used to verify the state of the IC system, over time, to quantitate perchlorate in highly ionic matrices. This must be conducted with each analysis batch since over time, column performance can change.

9.3.2.1 Prepare a mixed common anion solution which reflects a conductance near (within +/- 10%) that specified as the MCT. This solution must be prepared consistent with the instruction in Section 9.2.8, and containing the common anions chloride, sulfate and carbonate as well

as perchlorate at a suggested concentration of 25 ug/L. This perchlorate concentration has been specified assuming the MRL has been set in the range of 3.0 ug/L to 5.0 ug/L. If a laboratory's MRL is higher, chose a perchlorate concentration for this exercise at approximately 5 times that MRL.

9.3.2.2 Confirm the conductance of the IPC and analyze it as the initial sample in the analysis batch. If, after several weeks of storage, the measured conductance of this solution has shifted by more than 10% from the original measured value, prepare a fresh IPC solution. Following the analysis, calculate the $PD_{A/H}$ (Section 9.2.8.8), by comparing the peak area to height ratio of this IPC mixed anion standard (A/H_{MA}) for this analysis batch to the value that was derived for the LFB (A/H_{LFB}) either in the original IDC or in the previous analysis batch. As the first tier criteria, the value for $PD_{A/H}$ must be less than 25% before proceeding with the analysis batch.

9.3.2.3 At the second tier criteria, the measured recovery for perchlorate in this IPC must fall between 80% and 120 % (20.0 ug/L to 30.0 ug/L for a 25 ug/L fortification).

9.3.2.4 As a third tier and final criteria for the IPC, the laboratory must closely monitor the perchlorate retention time for this analysis. Small variations in retention time can be anticipated when a new solution of eluent is prepared but if sudden shifts of more than 5% are observed in the perchlorate retention time, some type of instrument problem may be present. Potential problems include improperly prepared eluent, erroneous method parameters programmed such as flow rate or some other system problem. The observed retention time for perchlorate should closely replicate the times established when the column was originally installed. As a column ages, it is normal to see a gradual shift and shortening of retention times, but if after several years of use, extensive use over less than a year, or use with harsh samples, this retention time has noticeably shifted to any less than 80% of the original recorded value, the column requires cleaning (according to manufacturer's instructions) or replacement. A laboratory should retain a historic record of retention times for perchlorate to provide evidence of an analytical column's continued performance.

9.3.2.5 If any of the conditions defined in Section 9.3.2.2 through 9.3.2.4 are not met, the MCT must be repeated and revised to a more appropriate lower matrix conductivity threshold or the source of the problem must be determined and the IPC reanalyzed.

9.3.3 Laboratory Fortified Blank (LFB) – Prepare a secondary dilution stock using the same stock solution used to prepare the calibration standards. This separate, secondary dilution stock is used as a concentrate to fortify the LFB and the LFMs (Section 9.4.1). An external source stock or QCS, which is used to verify the accuracy of the calibration curve when it was initially prepared (Section 10.2.5), should not be used to prepare this secondary dilution stock. Laboratories are required to analyze a LFB (filtered as if it were a field sample) with each analysis batch immediately following the ICCS. The LFB must be prepared with the same solution used to prepare the LFM and should be prepared at concentrations no greater than ten times the highest concentration observed in any field sample and should be varied to reflect the range of concentrations observed in field samples. By analyzing the LFB initially, a control check is performed on the concentrated solution used to prepare the LFM. If any deviations in the perchlorate concentration are present, it will be reflected in the LFB and not exclusively attributed to a matrix upon analysis of the LFM. Calculate accuracy as percent recovery (Section 9.4.1.3). The recovery for perchlorate must fall in the range of 85 - 115% prior to analyzing samples. If the LFB recovery for an analysis batch does not meet these recovery criteria the data are considered invalid, and the source of the problem should be identified and resolved before continuing analyses.

9.3.3.1 When sample matrices have been pretreated to reduce the risk of high common anion interference (Section 11.1.4), a second LFB must be prepared, pretreated in exactly the same manner, and analyzed to confirm no background effects or recovery bias induced by the pretreatment are present. If an analysis batch only contains pretreated samples, then only a pretreated LFB is required.

9.4 ASSESSING ANALYTE RECOVERY AND DATA QUALITY - The following must be included in every analysis batch (Section 3.1).

9.4.1 Laboratory Fortified Sample Matrix (LFM) – The laboratory must add a known amount of each target analyte to a minimum of 5% of the collected field samples or at least one with every analysis batch, whichever is greater. Samples which exceed the MCT must either be diluted (Section 11.1.3) or pretreated to reduce the common anion levels (Section 11.1.3). Samples which are pretreated have additional LFM requirements described in Section 11.1.4.6, and must be fortified before pretreatment. For a LFM to be valid, the target analyte concentrations must be greater than the native level and should adhere to the requirement outlined in Section 9.4.1.2. It is recommended that the solutions used to fortify the LFM be prepared from the same stocks used to prepare the calibration standards and not from external source stocks. This will remove the

bias contributed by an externally prepared stock and focus on any potential bias introduced by the field sample matrix.

9.4.1.1 The fortified concentration must be equal to or greater than the native sample concentration. Fortified samples that exceed the calibration range must be diluted to be within the linear range. In the event that the fortified level is less than the observed native level of the unfortified matrix, the recovery should not be calculated. This is due to the difficulty in calculating accurate recoveries of the fortified concentration when the native sample concentration to fortified concentration ratio is greater than one.

9.4.1.2 For normal drinking waters, the LFM typically should be prepared in the range of 20 - 50 ug/L. The LFM should not be prepared at concentration greater than ten times the highest concentration observed in any field sample and should be varied to reflect the range of concentrations expected in field samples.

9.4.1.3 Calculate the percent recovery for each target analyte, corrected for concentrations measured in the unfortified sample. Percent recovery should be calculated using the following equation:

$$\%REC = \frac{(C_s - C)}{s} \times 100$$

where,
%REC = percent recovery,
C_s = measured perchlorate in the fortified sample,
C = measured native perchlorate sample concentration, and
s = concentration equivalent of analyte added to sample.

9.4.1.4 Recoveries may exhibit a matrix dependence. If the recovery for perchlorate falls outside 80 - 120%, and the laboratory's performance for all other QC performance criteria is acceptable, the accuracy problem encountered with the fortified sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample and the LFM must be labeled suspect/matrix to inform the data user that the result is suspect due to matrix effects. Repeated failure to meet suggested recovery criteria indicates potential problems with the procedure and should be investigated.

9.4.2 FIELD, LABORATORY DUPLICATES OR DUPLICATE LFM – The laboratory must analyze either a field duplicate, a laboratory duplicate, or a

duplicate LFM for a minimum of 5% of the collected field samples or at least one with every analysis batch, whichever is greater. The sample matrix selected for this duplicate analysis must contain measurable concentrations of the target anions in order to establish the precision of the analysis set and ensure the quality of the data. Without prior knowledge or strong suspicion that an unknown sample has measurable perchlorate concentrations, the best alternative is to analyze a duplicate LFM.

9.4.2.1 Calculate the relative percent difference (RPD) of the initial quantitated concentration (I_C) and duplicate quantitated concentration (D_c) using the following formula.

$$RPD = \frac{|(I_C - D_c)|}{([I_C + D_c]/2)} \times 100$$

9.4.2.2 Duplicate analysis may exhibit a matrix dependance. If the RPD for the duplicate measurements of perchlorate falls outside ± 15% and if all other QC performance criteria are met, laboratory precision is out of control for the sample and perhaps the analytical batch. The result for the sample and duplicate should be labeled as suspect/matrix to inform the data user that the result is suspect due to a potential matrix effect, which led to poor precision. This should not be a chronic problem and if it frequently recurs (>20% of duplicate analyses), it indicates a problem with the instrument or individual technique that must be corrected.

9.4.3 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options, such as the use of different columns (which meet the criteria in Section 6.1.2.2), injection volumes, and/or eluents, to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 9.2 and adhere to the condition of conductivity baseline stability found in Section 1.2.1.

9.4.4 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should perform analysis of quality control check samples and participate in relevant proficiency testing (PT) or performance evaluation (PE) sample studies.

10. CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable initial calibration is required prior to the IDC and before any samples are analyzed, and is required intermittently throughout sample analysis to meet required QC performance criteria outlined in this method and summarized in Table 6. Initial calibration verification is performed using a QCS as well as with each analysis batch using an initial, continuing (when more than 10 field samples are analyzed), and end calibration check standards. The procedures for establishing the initial calibration curve are described in Section 10.2. The procedures to verify the calibration with each analysis batch is described in Section 10.3.

10.2 INITIAL CALIBRATION CURVE

10.2.1 Establish ion chromatographic operating parameters equivalent to those indicated in Table 1.

10.2.2 Estimate the Linear Calibration Range (LCR) -- The LCR should cover the expected concentration range of the field samples and should not extend over more than two orders of magnitude in concentration. The restriction of two orders of magnitude is prescribed since beyond this it is difficult to maintain linearity throughout the entire calibration range.

10.2.2.1 If quantification is desired over a larger range, then two separate calibration curves should be prepared.

10.2.2.2 A minimum of three calibration standards are required for a curve that extends over a single order of magnitude and a minimum of five calibration standards are required if the curve covers two orders of magnitude.

10.2.2.3 Since the anticipated concentration range for perchlorate in actual field samples is expected to cover two orders of magnitude, the use of at least five calibration standards in the range 4 - 400 μg/L is recommended.

10.2.3 Prepare the calibration standards by carefully adding measured volumes of the stock standard (Section 7.3) to a volumetric flask and diluting to volume with reagent water.

10.2.4 Inject 1.0 mL of each calibration standard. Tabulate peak area responses against the perchlorate concentration. The results are used to prepare a calibration curve. Acceptable calibration is confirmed after reviewing the curve for linearity (second order fits are also acceptable) and passing the criteria for the initial calibration check standard in Section 10.3.1. Alternately, if the ratio of area to concentration (response factor) is constant over the LCR (indicated by <

15% relative standard deviation), linearity through the origin can be assumed and the average ratio or response factor can be used in place of a calibration curve.

10.2.4.1 Peak areas must be used as a measure of response since they have been found to be more consistent, in terms of quantitation, than peak heights. Peak height can tend to be suppressed as a result of high levels of common anions in a given matrix which can compete for exchange sites leading to peak broadening. Using peak areas, it is the analyst's responsibility to review all chromatograms to insure accurate baseline integration of target analyte peaks, since poorly drawn baselines will significantly influence peak areas.

10.2.5 After establishing or reestablishing calibration curves, the accuracy of this calibration must be verified through the analysis of a QCS or externally prepared second source. The QCS should be prepared at a concentration near the middle of the calibration curve. As specified in Section 9.2.5, determined concentrations must fall within ± 10% of the stated values.

10.3 CONTINUING CALIBRATION VERIFICATION -- Initial calibrations may be stable for extended periods of time. Once the calibration curve has been established it MUST be verified for each analysis batch, prior to conducting any field sample analysis using an Initial Calibration Check Standard. Continuing Calibration Check Standards and End Calibration Check Standards are also required as described in the sections below.

10.3.1 INITIAL CALIBRATION CHECK STANDARD (ICCS) – For each analysis batch the calibration must initially be verified prior to analyzing any samples. The lowest level standard used to prepare the linear calibration curve must be used. In cases where the analyst has chosen to set the MRL above the lowest standard, a standard at a concentration equal to the MRL is acceptable. Percent recovery for the ICCS must be in the range or 75 - 125% before continuing the analysis batch and conducting any sample analyses.

10.3.2 CONTINUING CALIBRATION CHECK/END CALIBRATION CHECK STANDARDS (CCCS/ECCS) -- Continuing calibration check standards MUST be analyzed after every tenth field sample analysis and at the end of the analysis batch as an end calibration check standard. If more than 10 field samples are included in an analysis batch, the analyst must alternate between the middle and high continuing calibration check standard levels.

10.3.2.1 The percent recovery for perchlorate in the CCCS/ECCS must be between 85 - 115%.

10.3.2.2 If during the analysis batch, the measured concentration for perchlorate

in the CCCS or ECCS differs by more than the calibration verification criteria shown above, or if the perchlorate peak retention time shifts outside the retention time window (as defined in Section 11.2.4), all samples analyzed after the last acceptable check standard are considered invalid and must be reanalyzed. The source of the problem must be identified and resolved before reanalyzing the samples or continuing analyses.

10.3.2.3 In the case where the end calibration fails to meet performance criteria, but the initial and middle calibration checks are acceptable, the samples bracketed by the acceptable calibrations may be reported. However, all field samples between the middle and end calibration checks MUST be reanalyzed.

10.4 CONDUCTIVITY METER CALIBRATION -- Prior to conducting the MCT and coinciding with each analysis batch, conductivity meter calibration must be verified or established using a standard KCl solution (Section 7.5).

10.4.1 Thoroughly rinse the conductivity electrode with reagent water. Place the electrode in the reagent water, turn on the meter and confirm the conductance of this blank is < 1 uS/cm.

10.4.2 Pour approximately 15 mL of the standard KCl solution (Section 7.5) into a plastic disposable micro beaker (Section 6.7) and place the electrode into the solution. The reference conductance for this solution is 1410 uS/cm at 25 °C.[16] The conductivity meter must yield a conductance between 1380 uS/cm and 1440 uS/cm to be in calibration.

10.4.3 If the conductivity meter fails calibration, recalibrate the unit per manufacture's instruction and repeat the procedure in 10.4.2 as if the standard solution were an unknown matrix.

11. PROCEDURE

11.1 SAMPLE PREPARATION

11.1.1 Samples do not need to be refrigerated but if samples are held refrigerated as a standard practice for sample control, ensure the samples have come to room temperature prior to conducting sample analysis.

11.1.2 MATRIX CONDUCTANCE VERIFICATION - Prior to conducting the analysis of a field sample matrix, the conductance of that matrix must be measured. Matrix conductivity is directly related to the common anion levels

which, at high concentrations, can influence the integrity of the perchlorate analysis.

11.1.2.1 Verify conductivity detector calibration by following the procedure outlined in Section 10.4.

11.1.2.2 Pour approximately 15 mL of sample into a plastic disposable micro beaker (Section 6.7) and reseal the sample bottle to protect the sample integrity.

11.1.2.3 Place the electrode into the matrix and measure the conductivity.

11.1.2.4 If the conductance is less than the MCT, continue to Section 11.1.5.

11.1.2.5 If the conductance is greater than the MCT, the matrix requires dilution or pretreatment prior to analysis. The dilution procedure is found in Section 11.1.3. Pretreatment is described in Section 11.1.4.

11.1.2.6 Discard this aliquot of sample and be certain to thoroughly rinse the electrode with reagent water between each matrix conductivity measurement.

11.1.3 MATRIX DILUTION - If matrix conductivity is less than the MCT, go to Section 11.1.5.

11.1.3.1 A sample can be analyzed once diluted with reagent water to a conductance below the MCT. The exact magnitude of this dilution will adversely increase the MRL by an equivalent proportion.

11.1.3.2 Knowing the matrix conductance exceeds the MCT, estimate the proportion required for the dilution by dividing the measured matrix conductance by the MCT. Round up to the next whole number and dilute the sample by a proportion equivalent to this value. For example, if the established MCT is 6100 uS/cm and a sample reflecting a conductance of 8000 uS/cm was measured, dilute the sample with reagent water by a factor of 2.

11.1.3.3 Measure the conductance of the diluted sample to confirm it is now below the MCT. Analyze the sample as specified in Section 11.1.5 with the understanding that the MRL has now been elevated by a proportion equivalent to the dilution.

11.1.3.4 If perchlorate is measured above the elevated MRL, back calculate

actual field sample concentration and report. If no perchlorate is measured above the elevated MRL and analysis or project objectives required monitoring below the concentration of the elevated MRL, proceed to Section 11.1.4 and pretreat the matrix.

11.1.4 PRETREATMENT FOR MATRICES WHICH EXCEED THE MCT – If matrix conductivity is less than the MCT, go to Section 11.1.5. If sample dilution did not yield the required results, sample pretreatment should be employed. When the MCT is exceeded, it is most often due to a high levels of common anions (chloride, sulfate, and carbonate) in a particular matrix. If the analyst were to attempt the IC analysis of this particular matrix, the common anions present in the sample would distort the baseline and negatively affect the accurate quantitation of perchlorate. To effectively reduce a significant amount of these anions which contribute to the high conductivity reading, a series of pretreatment cartridges must be employed. For this pretreatment, three cartridges are attached in series in the following order: Ba, Ag, and H. It is recommended that all three cartridges be employed unless the analyst has specific knowledge that a matrix primarily has high levels of a specific common anion.

11.1.4.1 Individually and thoroughly rinse each pretreatment cartridge with reagent water in order to insure all residual background contaminants are removed from the cartridge. Perform this rinse per manufacturer's instructions.

11.1.4.2 Prior to pretreating any field samples, prepare and pretreat both an LRB and an LFB. These pretreated quality control samples are required when an analysis batch contains a matrix which must be pretreated. This pretreatment is conducted by placing the cartridges in the following prescribed series (–>Ba–>Ag–>H). The pretreated LRB and LFB are used to verify that no background interference or bias is contributed by the pretreatment. If a response is observed in the pretreated LRB, triple or quadruple the volume of reagent water rinse suggested by the manufacturer in Section 11.1.4.1 and repeat until a blank measures no more than ½ the MRL. If this additional rinsing procedure is required, it must be consistently applied to all the cartridges prior to conducting any matrix pretreatment.

11.1.4.3 Filter 3 mL of sample through the series of rinsed, stacked cartridges as an initial sample rinse (Ba, Ag and H) at a flow rate of 1.0 mL/ min or less (approximately one drop every 3 to 4 seconds). This flow rate is critical to the pretreatment and must be carefully followed. Discard this fraction and begin collecting the pretreated sample aliquot of

collected sample.

11.1.4.4 When sufficient volume has been collected, measure the conductance of the pretreated sample aliquot being certain the conductivity meter's probe has been thoroughly rinsed and excess water has been shaken from the tip. If the conductance is now below the MCT, the sample is ready for analysis. If the conductance is still above the MCT, the flow rate through the pretreatment cartridge is likely too fast and the pretreatment should be repeated with new cartridges. In some instances, double pretreatment cartridges may need to be applied. When this pretreatment is performed properly, U.S.EPA has found 70% to 95% reduction in matrix conductance with good recoveries for perchlorate.

11.1.4.5 Place this aliquot of pretreated sample into an autosampler vial as described in Section 11.1.3.

11.1.4.6 In order to ensure data quality, all samples which fail the MCT and have been selected for pretreatment, as described in Section 11.1.4, must also be used to prepare an LFM. This LFM must be fortified with perchlorate at concentrations close to, but greater than, the level determined in the native sample prior to the pretreatment. Initially, the pretreated sample is analyzed and perchlorate level is determined. Then, a second aliquot of sample must be fortified with perchlorate, pretreated to reduce the high common anion levels, and analyzed to assess perchlorate recovery from that matrix. This additional QC is required to rule out matrix effects and to confirm that the laboratory performed the pretreatment step appropriately. **If the perchlorate recovery falls outside the acceptance range of 80 - 120% (Section 9.4.1.4), that particular sample should be reported as suspect/matrix.**

11.1.4.7 The pretreatments prescribed above are effective at reducing the chloride and sulfate content of a sample matrix but will not reduce matrix concentrations of other anions such as nitrate or phosphate.

11.1.5 Pour approximately 15 mL of sample into a micro beaker (Section 6.7) and reseal the sample bottle to protect the sample integrity. Using a Luer lock, plastic 10 mL syringe, withdraw approximately 10 mL of sample from the micro beaker and attach a 0.45 μm particulate filter (Section 6.11), which has been demonstrated to be free of ionic contaminants, directly to the syringe. Filter the sample into an autosampler vial or manually load the injection loop injecting a fixed amount of filtered, well mixed sample. If using a manually

loaded injection loop, flush the loop thoroughly between sample analysis using sufficient volumes of each new sample matrix.

11.1.5.1 If the autosampler vials or vial caps are designed to automatically filter the sample matrix as the sample is loaded on the IC system, this filtration procedure can be omitted and the sample can be directly transferred to the autosampler vial.

11.2 SAMPLE ANALYSIS

11.2.1 Table 1 summarizes the recommended operating conditions for the ion chromatograph. Included in this table is the estimated retention time for perchlorate which has been achieved by this method. Other columns, chromatographic conditions or detectors may be used if the requirements of Sections 1.2.1, 6.1.2.2 and 9.2 are met.

11.2.2 Establish a valid initial calibration and verify this calibration by conducting a QCS as described in Section 10.2 and complete the IDC (Section 9.2). Initially, analyze the IPC solution, followed by the LRB. Then confirm the IC system calibration by analyzing an ICCS (Section 10.3.1) and, if required, recalibrate as described in Section 10.2. Lastly, analyze the LFB.

11.2.3 Inject 1.0 mL of each filtered sample. Use the same size loop for standards and samples. An automated constant volume injection system may also be used. Record the resulting peak size in area units and retention time for each analyte.

11.2.4 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards measured over several days. Three times the standard deviation of retention time may be used as a suggested window size but the retention time window should not extend beyond ± 5% of the retention time for perchlorate. The experience of the analyst should weigh heavily in the interpretation of these chromatograms.

11.2.5 If the response of a sample analyte exceeds the calibration range, the sample must be diluted with an appropriate amount of reagent water and reanalyzed. If this is not possible then three new calibration concentrations must be employed to create a separate high concentration calibration curve, one standard near the estimated concentration and the other two bracketing around an interval equivalent to approximately ± 25% the estimated concentration. The response generated by these three new high concentration calibration standards must not exceed the upper linear range for the conductivity detector. The latter procedure

involves significantly more time than a simple sample dilution therefore, it is advisable to collect sufficient sample to allow for sample dilution and sample reanalysis, if required.

11.2.6 Should more complete resolution be needed between perchlorate and a coeluting, shoulder peak, the eluent (Section 7.2) may be diluted. This will spread out the peaks, causing later elution of perchlorate. Analysts are advised to carefully evaluate any of these eluent dilutions since when these eluent changes are incorporated, other coelutions may be encountered which were not initially evident. Additionally, the analyst must verify that this dilution does not negatively affect performance by repeating and passing all the QC criteria in Section 9, and by reestablishing a valid initial calibration curve (Section 10.2).

11.2.6.1 Eluent dilution will reduce the overall response of an anion due to chromatographic band broadening which will be evident by shortened and broadened peaks. This will adversely effect the MDLs for each analyte.

11.3 AUTOMATED ANALYSIS WITH METHOD 314.0

11.3.1 Laboratories conducting analyses on large numbers of samples often prepare large analysis batches that are run in an automated manner. When conducting automated analyses, careful attention must be paid to ensure sufficient volume of eluent in the reservoir is available to sustain extended operation. In order to ensure their data are of acceptable quality, laboratories must ensure that all QC performance criteria are met throughout the analysis batch through subsequent careful inspection of the data.

11.3.2 Analysis sequences must be carefully constructed to meet required QC specifications and frequency (Table 6). To help with this task, an acceptable sequence for a sample analysis batch, with all the method-required QC, is shown in Table 7. This schedule is included only as an example of a hypothetical analysis batch which contains normal sample matrices as well as samples which have failed the MCT. Within this analysis batch, references to exact concentrations for the ICCS, CCCS and ECCS are for illustrative purposes only.

11.3.3 Table 7 may be used as a guide when preparing analysis batches. Additional batches may be added sequentially on to the end of these types of schedules as long as all QC samples, which define an individual batch (IPC, LRB, ICCS, LFB, LFM, etc.) are individually reanalyzed with each successive serial batch and the QC criteria for these analyses are continually met (from the IPC through ECCS).

12. DATA ANALYSIS AND CALCULATIONS

12.1 Identify perchlorate in the sample chromatogram by comparing the retention time of a suspect peak within the retention time window to the actual retention time of a known analyte peak in a calibration standard. If the perchlorate retention time has slightly shifted (generally towards shorter times) since the initial calibration, but is still within acceptance criteria and are reproducible during the analysis batch, the analyst should use the retention time in the daily calibration check standards to confirm the presence or absence of perchlorate anion.

12.1.1 If a low concentration of perchlorate is suspected in an unknown sample, but the retention time has drifted to the edge of the retention time window, a low level perchlorate LFM, prepared at nearly the same concentration as the suspect peak, should be prepared from this sample matrix to confirm the matrix induced retention time shift. If the fortified sample reveals a split or shouldering peak response, the low concentration in the unfortified sample is likely an interferant and should not be reported as perchlorate.

12.2 Compute sample concentration using the initial calibration curve generated in Section 10.2.

12.3 Report ONLY those values that fall between the MRL and the highest calibration standards. Samples with a perchlorate response which exceeds the highest calibration standard concentration must be diluted and reanalyzed. When this is not possible the alternate calibration procedures described in Section 11.2.5 must be followed. Samples with perchlorate identified but quantitated below the concentration established by the lowest calibration standard, may be reported as "trace present" above the MDL but below the minimum reporting limit (MRL) and therefore not reported as a quantitated concentration.

12.4 Report results in μg/L.

13. METHODS PERFORMANCE

13.1 Table 1 gives the standard conditions, typical retention time, single laboratory MCT and single laboratory MDL in reagent water, as determined for perchlorate. This retention time is graphically indicated in the chromatograms in Figures 1 through 4.

13.2 Table 2 shows the precision and accuracy of the perchlorate measurement at two fortified concentrations, in reagent water, simulated high ionic strength water (HIW), simulated high organic content water (HOW), ground water, untreated surface water and treated surface water. The mean perchlorate recovered concentration (accuracy relative to the fortified level) and the precision (expressed as %RSD of the replicate analysis) are tabulated. The HIW was designed to simulate a high ionic strength field

sample and the HOW designed to simulate a high organic content field sample. The HIW was prepared from reagent water which was fortified with the common anions of chloride at 400 mg/L, carbonate at 600 mg/L, and sulfate at 500 mg/L. The HOW was prepared from reagent water fortified with 10.0 mg/L fulvic acid.

13.3 Table 3 shows the stability data for perchlorate held for 35 days and stored under various conditions. Conditions investigated included sample bottle construction (HDPE plastic vs. glass), storage condition (refrigerated vs. held at room temperature) and various matrices including some with a measured perchlorate concentration assumed to contain microbiological constituents acclimated to the presence of the anion. Matrices without perchlorate were fortified at 25 ug/L. Each data point in this table represents the mean percent recovery following triplicate analyses. These data were used to formulate the holding times shown in Section 8.3.

13.4 Table 4, in conjunction with the chromatograms overlaid in Figure 4 as well as the linear regression plots in Figure 5, show the results of the single laboratory MCT determination. The data presented in Table 4 and graphically illustrated in Figure 5, show results for not only the AS16 but also the AS11 and AS5. The chromatogram shown in Figure 4 were generated using the AS16 column.

14. POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasiblely reduced at the source, the Agency recommends recycling as the next best option.

14.2 Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W., Washington D.C. 20036, (202) 872-4477.

15. WASTE MANAGEMENT

15.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. Excess

reagents, samples and method process wastes should be 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, 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 at the address listed in Section 14.3.

16. REFERENCES

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17. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS IN REAGENT WATER FOR PERCHLORATE.

Standard Conditions and Equipment[a]:

Ion Chromatograph:	Dionex DX500
Sample Loop:	1000 μL
Eluent:	50 mM NaOH
Eluent Flow:	1.5 mL/min
Columns :	Dionex AG16, 4 mm / AS16, 4 mm
Typical System Backpressure:	2600 psi
Suppressor:	ASRS ULTRA (P/N 53946), external water mode, 300 mA current
Detectors:	Suppressed Conductivity Detector, Dionex CD20 Background Conductivity: 2 - 3 μS
Determined MCT[b]:	6100 uS/cm

Recommended method total analysis time: 15 minutes (may be shortened to 12 minutes)

Analyte Retention Times and Method Detection Limits (MDLs):

		MDL DETERMINATION		
Analyte	Retention Time [c] (min.)	Fortified Conc. (μg/L)	# of Reps.	MDL (μg/L)
Perchlorate	10.1 ± 0.2	2.0	7	0.53

(a) Mention of trade names or commercial products does not necessarily constitute endorsement or recommendation for use.
(b) This was the single laboratory MCT determined for these conditions listed (See Table 4 and Figure 5 for more detail as well as data pertaining to the AS11 and AS5).
(c) Reference to chromatograms in Figure 1 through 4.

TABLE 2. SINGLE LABORATORY PRECISION AND RECOVERY FOR PERCHLORATE IN VARIOUS MATRICES

Matrix	Matrix Conductivity uS/cm	Unfortified Conc. (µg/L)	Fortified Conc. (µg/L)	# of Reps.	Mean (µg/L)	Mean %REC	SD(n-1)	%RSD
Reagent Water	~ 1	<MRL[a]	4.00	8	4.04	101%	0.43	10.6%
			25.0	8	26.2	105%	0.89	3.4%
Synthetic High Inorganic Water [b]	4200	<MRL	4.00	8	3.42	86%	0.27	7.9%
			25.0	8	24.1	96%	0.46	1.9%
Synthetic High Organic Water [c]	5.0	<MRL	4.00	8	3.84	96%	0.38	10.0%
			25.0	8	25.7	103%	1.12	4.4%
Ground Water (high TDS)	710	<MRL	4.00	8	4.22	106%	0.54	12.8%
			25.0	8	26.5	106%	0.62	2.3%
Untreated Surface Water	460	<MRL	4.00	8	4.46	112%	0.24	5.4%
			25.0	8	28.3	113%	0.29	1.0%
Chlorinated Surface Water	460	<MRL	4.00	8	4.18	105%	0.23	5.6%
			25.0	8	28.0	112%	0.63	2.3%

(a) <MRL = analyte was not detected above the laboratory minimum reporting level (MRL) of 4.0 ug/L.
(b) Synthetic High Inorganic Water was prepared from reagent water and contained synthetic high TDS or common anion levels of 400 mg/L chloride, 500 mg/L sulfate and 600 mg/L carbonate.
(c) Synthetic High Organic Water contained 10 mg/L fulvic acid (extracted and crystallized from untreated surface water) fortified into reagent water.

Note: These data were collected using the equipment and conditions listed in Table 1.

TABLE 3. STABILITY STUDY RESULTS FOR PERCHLORATE IN VARIOUS MATRICES

A. Stability when stored in various sampling bottles - All stored at room temperature

Matrix	Bottle type	Unfortified Conc.(μg/L)	Fortified Conc.(μg/L)	Analyte % Recovery Day 0	Day 7	Day 14	Day 28	Day 35
Reagent Water	Clear Glass	<MRL[a]	25.0	108%	101%	88%	91%	109%
Reagent Water	Amber Glass	<MRL	25.0	108%	101%	91%	90%	107%
Reagent Water	Opaque HDPE Plastic	<MRL	25.0	108%	97%	92%	89%	107%
Reagent Water	Translucent HDPE Plastic	<MRL	25.0	108%	105%	93%	90%	108%

B. Stability in various matrices under different storage conditions -
All samples stored in HDPE, opaque sampling bottles and fortified with 25.0 ug/L perchlorate.

Matrix	Storage Condition	Unfortified Conc.(μg/L)	Matrix Cond.uS/cm	Analyte % Recovery Day 0	Day 7	Day 14	Day 28	Day 35
Reagent Water	Room Temp.	<MRL	< 1	104%	104%	95%	87%	107%
	Refrigerated	<MRL		104%	102%	94%	88%	107%
Treated Surface Water #1	Room Temp.	<MRL	520	109%	105%	101%	99%	111%
	Refrigerated	<MRL		109%	102%	100%	97%	108%
Treated Surface Water #2	Room Temp.	<MRL	510	107%	115%	102%	99%	113%
	Refrigerated	<MRL		107%	113%	103%	99%	111%
Untreated Surface Water #1	Room Temp.	<MRL	470	110%	115%	110%	106%	110%
	Refrigerated	<MRL		110%	114%	110%	105%	111%
Untreated Surface Water #2	Room Temp.	<MRL	700	105%	112%	110%	104%	107%
	Refrigerated	<MRL		105%	112%	111%	103%	107%
Untreated Surface Water #3	Room Temp.	<MRL	920	109%	109%	113%	104%	110%
	Refrigerated	<MRL		109%	105%	111%	103%	105%
Untreated Surface Water #4	Room Temp.	<MRL	930	107%	105%	110%	106%	105%
	Refrigerated	<MRL		107%	106%	107%	105%	106%
Ground Water #1	Room Temp.	<MRL	1900	110%	113%	103%	101%	107%
	Refrigerated	<MRL		110%	112%	105%	103%	107%

C. Stability of native perchlorate in matrices stored under different storage conditions -
All samples stored in HDPE, opaque sampling bottles.

Matrix	Storage Condition	Matrix Cond. uS/cm	Measured concentration, ug/L Day 0	Day 7	Day 14	Day 28	Day 35
Ground Water #2 (with native ClO_4^-)	Room Temp.	603	1090	1110	1080	990	1100
	Refrigerated		1090	1110	1080	1010	1110
Ground Water #3 (with native ClO_4^-)	Room Temp.	960	1010	1040	1010	950	1000
	Refrigerated		1010	1040	1020	940	1030
Ground Water #4 (with native ClO_4^-)	Room Temp.	750	439	450	427	407	434
	Refrigerated		439	441	427	400	434

(a) <MRL = analyte was not detected above the laboratory minimum reporting level (MRL) of 4.0 ug/L.
Note: Each data point represented the average from triplicate analysis.

TABLE 4. SINGLE LABORATORY RESULTS FOR THE DETERMINATION OF MCT - Determination on the AS16, AS11 and the AS5.

AS16 Studies - Perchlorate fortified at 25 ug/L								
Sample	Conductivity uS/cm	RT min.	Measured ClO4-, ug/L	%Rec	Area	Height	A/H ratio	$PD_{A/H}$
LFB	<1	10.3	25.3	101%	20268	1151	17.6	0.00%
MA(50)[a]	540	10.3	26.0	104%	20799	1135	18.3	4.07%
MA(100)	932	10.3	26.3	105%	21060	1144	18.4	4.54%
MA(200)	1770	10.2	26.2	105%	20998	1112	18.9	7.24%
MA(400)	3570	10.2	25.2	101%	20170	1028	19.6	11.4%
MA(600)	5010 [b]	10.2	24.2	97%	19307	954	20.2	14.9%
MA(800)	6450	10.1	25.1	100%	20038	932	21.5	22.1%
MA(1000)	7820	10.2	24.3	97%	19400	878	22.1	25.5%

AS11[c] Studies - Perchlorate fortified at 25 ug/L								
Sample	Conductivity uS/cm	RT min.	Measured ClO4-, ug/L	%Rec	Area	Height	A/H ratio	$PD_{A/H}$
LFB	< 1	8.9	25.0	100%	25213	1591	15.8	0.00%
MA(50)[a]	540	8.9	25.2	101%	25445	1515	16.8	5.98%
MA(100)	932	9.0	25.0	100%	25192	1486	17.0	6.98%
MA(200)	1770 [b]	9.0	24.1	96%	24340	1384	17.6	11.0%
MA(400)	3570	9.0	23.6	94%	23855	1243	19.2	21.1%
MA(600)	5010	9.0	22.7	91%	22922	1101	20.8	31.4%
MA(800)	6450	8.9	19.9	80%	20243	870	23.3	46.8%
MA(1000)	7820	8.8	17.0	68%	17407	678	25.7	62.0%

AS5[d] Studies - Perchlorate fortified at 25 ug/L								
Sample	Conductivity uS/cm	RT min.	Measured ClO4-, ug/L	%Rec	Area	Height	A/H ratio	$PD_{A/H}$
LFB	< 1	9.7	22.75	91.0%	30348	1780	17.0	0.00%
MA(50)[a]	540	9.7	24.89	99.6%	33505	1751	19.1	12.2%
MA(100)	932	9.7	23.72	94.9%	31776	1721	18.5	8.30%
MA(200)	1770 [b]	9.7	22.99	92.0%	30704	1591	19.3	13.2%
MA(400)	3570	9.6	23.51	94.0%	31474	1478	21.3	24.9%
MA(600)	5010	9.6	23.84	95.4%	31948	1441	22.2	30.0%
MA(800)	6450	9.6	21.01	84.0%	27792	1214	22.9	34.3%
MA(1000)	7820	9.6	22.95	91.8%	30650	1183	25.9	52.0%

(a) "MA" indicates mixed common anion solution with each anion (chloride, sulfate and carbonate) included in the sample matrix at the parenthetical mg/L concentration for each anion.

(b) If the regression analysis is not performed on these data, 5010 uS/cm, 1770 uS/cm and 1770 uS/cm would be the default MCT for the AS16, AS11 and AS5, respectively, as described in Section 9.2.8.10. See Figure 5 for a graphical representation of this data, applying a regression analysis of $PD_{A/H}$ vs matrix conductivity for the AS16, AS11 and AS5.

(c) AS11 conditions: See reference #2 and #3.

(d) AS5 conditions: See reference #1.

TABLE 5. INITIAL DEMONSTRATION OF CAPABILITY QC REQUIREMENTS.
Requirements prior to beginning any analysis batch

Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sect. 9.2.2 9.3.1	Initial Demonstration of Low System Background	Analyze a method blank (LRB) and determine that all target analytes are below ½ of the proposed MRL prior to performing the IDC.	The LRB concentration must be ≤½ of the proposed MRL.
Sect. 9.2.3	Initial Demonstration of Accuracy (IDA)	Analyze 7 replicate LFBs fortified with perchlorate at 25 ug/L. Calculate the mean recovered concentration ($C_{\bar{x}}$) See Equation in Section 9.2.3.	The $C_{\bar{x}}$ must be ± 10% of true value.
Sect. 9.2.4	Initial Demonstration of Precision (IDP)	Calculate percent relative standard deviation (%RSD)of IDA replicates. See Equation in Section 9.2.4.	The %RSD must be ≤10%
Sect. 9.2.5	Quality Control Sample (QCS)	Initially, upon reestablishing calibration or at least quarterly analyze a QCS from an external/second source.	The QCS must be ± 10% of the true value.
Sect. 9.2.6	Method Detection Limit (MDL) Determination	Select a fortifying level at 3-5 times the estimated instrument detection limit. Analyze 7 replicate LFBs over multiple days and calculate MDL using equation in Section 9.2.6 - do not subtract blank	
Sect. 9.2.7	Minimum Reporting Level (MRL)	An MRL should be established for perchlorate during the IDC.	The low CAL standard can be lower than the MRL, but the MRL MUST be no lower than the low CAL standard
Sect. 9.2.8	Matrix Conductivity Threshold (MCT)	Prepare a series of LFB samples, each containing a suggested perchlorate concentration of 25 ug/L, at sequentially increasing fortified levels of common anions. Measure sample conductance and analyze each, calculate average A/H ratios and $PD_{A/H}$ (using equation in Section 9.2.8.8). Perform linear regression to calculate MCT (using equation in Section 9.2.8.9) or follow step outlined in Section 9.2.8.10.	MCT, based upon linear regression, is point where $PD_{A/H}$ equals 20%. Alternatively, the MCT is set at the highest measured conductance observed in the last fortified MCT sample to yield a $PD_{A/H}$ value below 20%.
Sect. 9.2.8.11	MRL verification	Verify the MRL in a solution prepared at the MCT.	Prepared within ±10% of the MCT. Perchlorate recovery must be 70- 130% of the MRL.

TABLE 6. QUALITY CONTROL REQUIREMENTS (SUMMARY).

Requirements specific for each analysis batch

Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sect. 8.3	Sample Holding Time / Preservation / Storage	Perchlorate 28 days No Preservation technique required. Room Temperature adequate for shipping and storage.	Holding time must not be exceeded.
Sect. 10.2	Initial Calibration	Generate calibration curve. At least 5 calibration standards are recommended.	MRL MUST be no lower than the lowest calibration standard
Sect. 9.3.2	Instrument Performance Check (IPC)	Designed to verify Matrix Conductivity Threshold (MCT). Prepare mixed common anion solution at the MCT (prepared consistent with procedures in Section 9.2.8). Confirm the sample's conductance and analyze at the beginning of each analysis batch.	Prepared within ±10% of the MCT. IPC solution conductance verified to within ± 10% of original measured value (when originally prepared) $PD_{A/H}$, (when compared to the A/H_{LFB}) must be < 25%. Perchlorate quantitated between 80 -120% of fortified level. <5% shift in perchlorate retention time.
Sect. 10.3.1	Initial Calibration Check (ICCS)	With each analysis batch, initially verify calibration at the MRL by analyzing an initial low-level continuing calibration check standard (ICCS).	Recovery must be 75-125% of the true value.
Sect. 10.3.2	Continuing Calibration (CCCS) and End Calibration Checks (ECCS)	Alternately analyze separate mid and high level CCCS/ECCS after every 10 samples and after the last sample in an analysis batch.	Recoveries must fall between 85 - 115%
Sect. 9.3.1	Laboratory Reagent Blank (LRB)	Include LRB with every analysis batch (up to 20 samples) Analyze prior to analyzing field samples	Perchlorate must be ≤ ½ MRL
Sect. 9.3.1.1	PRETREATED Laboratory Reagent Blank (LRB)	REQUIRED in any analysis batch which includes samples which have exceeded the MCT and have been pretreated in any way to reduce the common anion levels.	Perchlorate must be ≤ ½ MRL

TABLE 6. QUALITY CONTROL REQUIREMENTS (SUMMARY CONTINUED). Requirements specific for each analysis batch

Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sect. 9.3.3	Laboratory Fortified Blank (LFB)	Laboratory must analyze LFB in each analysis batch following the ICCS. Calculate %REC prior to analyzing samples. The concentration selected for the LFB in subsequent analysis batches should be varied throughout the calibration range.	Recovery for LFB MUST be 85 - 115% prior to analyzing samples. Sample results from batches that fail LFB are invalid.
Sect. 9.3.3.1	PRETREATED Laboratory Fortified Blank (LFB)	REQUIRED in any analysis batch which includes samples which have exceeded the MCT and have been pretreated in any way to reduce the common anion levels. Fortification must be made prior to pretreatment	Recovery for pretreated LFB MUST be 85 - 115% prior to analyzing samples. Sample results from batches that fail a pretreated LFB are invalid.
Sect. 9.4.1	Laboratory Fortified Sample Matrix (LFM)	Must add known amount of perchlorate to a minimum of 5% of field samples or at least one within each analysis batch. LFM must be fortified above the native level and at no greater than 10 x the highest field sample concentration. Calculate target analyte recovery using formula (Sect. 9.4.1.3).	Recovery must be 80 - 120% If fortified sample fails the recovery criteria, label both as suspect/matrix.
Sect. 11.1.4.6	SPECIAL LFM for matrices requiring pretreatment	When a sample exceeds the MCT and pretreatment is employed to reduce the common anion levels, an additional LFM must be prepared from this matrix and subsequently pretreated exactly as the unfortified matrix.	Same criteria, recoveries must be 80 -120%.
Sect. 9.4.2	Field or Laboratory Duplicates or LFM Duplicate	Analyze either a field, laboratory or LFM duplicate for a minimum of 5% of field samples or at least one within each analysis batch. Calculate the relative percent difference (RPD) using formula in Section 9.4.2.1.	RPD must be ± 15%.
Sect. 6.1.2.2	ALTERNATE IC analytical column performance criteria	If a laboratory chooses an alternate analytical column for this analysis, it must be hydrophilic and pass the criteria for Peak Gaussian Factor (PGF) using equation (Sect. 6.1.2.2).	PGF must fall between 0.80 and 1.15.

TABLE 7. EXAMPLE SAMPLE ANALYSIS BATCH WITH QUALITY CONTROL REQUIREMENTS

Injection #	Sample Description	Acceptance Criteria
1	Instrument Performance Check Standard at MCT	$PD_{A/H}$ for IPC < 25%
2	Laboratory Reagent Blank (LRB)	≤ ½ MRL
3	ICCS at the MRL (4.0 µg/L)	3.00 to 5.00 µg/L
4	Laboratory Fortified Blank (LFB)	Recovery of 85 - 115%
5	Sample 1	normal analysis
6	Sample 1 - Laboratory Duplicate (LD) [a]	± 15 % RPD
7	Sample 2	normal analysis
8	Sample 2 - Laboratory Fortified Matrix (LFM) [a]	Recovery of 80 - 120%
9	Sample 3	normal analysis
10	Sample 4	normal analysis
11	Sample 5	normal analysis
12	Sample 6	normal analysis
13	Sample 7	normal analysis
14	Sample 8	normal analysis
15	Sample 9	normal analysis
16	Sample 10	normal analysis
17	CCCS (25.0 ug/L)	21.3 to 28.8 ug/L
18	Sample 11 (failed MCT, matrix conductance = 8000 uS/cm) - Analyzed diluted (Section 11.1.3) by factor of 2 or by 50% with reagent water (diluted matrix conductance = 3800 uS/cm).	MRL increases from 4 to 8 ug/L, noted in analysis report - sample found to contain 50 ug/L (measured at 25 ug/L in diluted sample)
19	Sample 12	normal analysis
20	Sample 13	normal analysis

CONTINUED TO NEXT PAGE

Injection #	Sample Description	Acceptance Criteria
21	Sample 14 (failed MCT, matrix conductance=15000 uS/cm) Analyzed diluted (Section 11.1.3) by a factor of 3 or by 33% with reagent water (Diluted matrix conductance = 4600 uS/cm)	MRL increases from 4 to 12 ug/L, noted in analysis report - No perchlorate > 12ug/L measured - project required monitoring to MRL - sample pretreatment is therefore required
22	Ba/Ag/H Pretreated LRB (Section 9.3.1.1)	≤ ½ MRL
23	Ba/Ag/H Pretreated LFB (Section 9.3.3.1)	Recovery of 85 - 115%
24	Sample 14 - Ba/Ag/H pretreated (Section 11.1.4), following pretreatment the matrix conductance = 230 uS/cm.	normal pretreated analysis perchlorate < MRL of 4.0 ug/L
25	Sample 14 [b] - pretreated LFM (Section 11.1.4.6)	Recovery of 80 - 120%
26	Sample 15	normal analysis
27	Sample 16	normal analysis
28	Sample 17	normal analysis
29	Sample 18	normal analysis
30	Sample 19[b]	normal analysis
31	ECCS (100 μg/L)	85.0 to 125 μg/L

[a] If no analytes are observed above the MRL for a sample, an alternate sample which contains reportable values should be selected as the laboratory duplicate. Alternately, the LFM can be selected and reanalyzed as the laboratory duplicate ensuring the collection of QC data for precision.

[b] Sample #19 (inj #30) was the final field sample permitted in this batch but 20 total field samples were analyzed. Sample #14 (inj #21 and #24) was analyzed both initially as a diluted sample and subsequently as a pretreated sample, therefore it accounted for two "field sample analyses" toward the maximum of twenty in an analysis batch (Section 3.1).

Note: Sample #11 and #14 illustrate examples of proper ways to handle sample matrices which exceed the MCT.

FIGURE 1. CHROMATOGRAM OF LOW LEVEL PERCHLORATE (4.0 ug/L) IN REAGENT WATER (Conditions as indicated in Table 1)

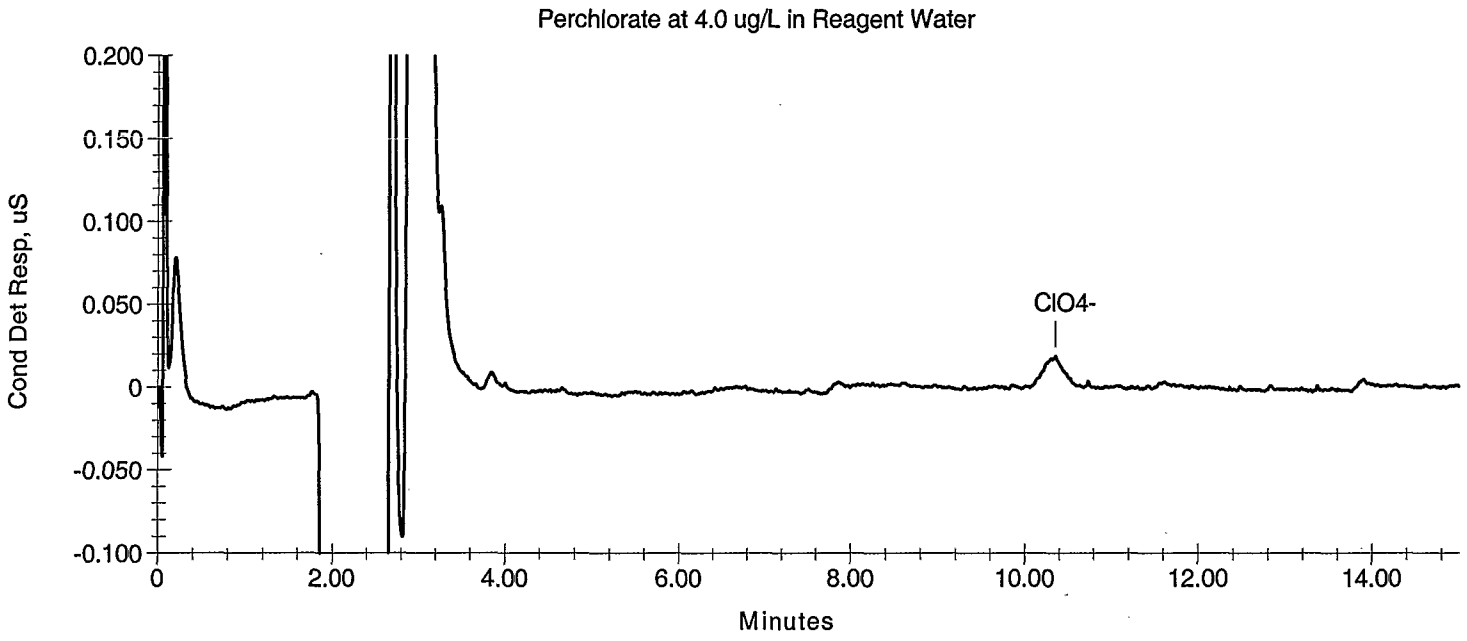

FIGURE 2. CHROMATOGRAM OF 25 ug/L PERCHLORATE IN REAGENT WATER (Conditions as indicated in Table 1)

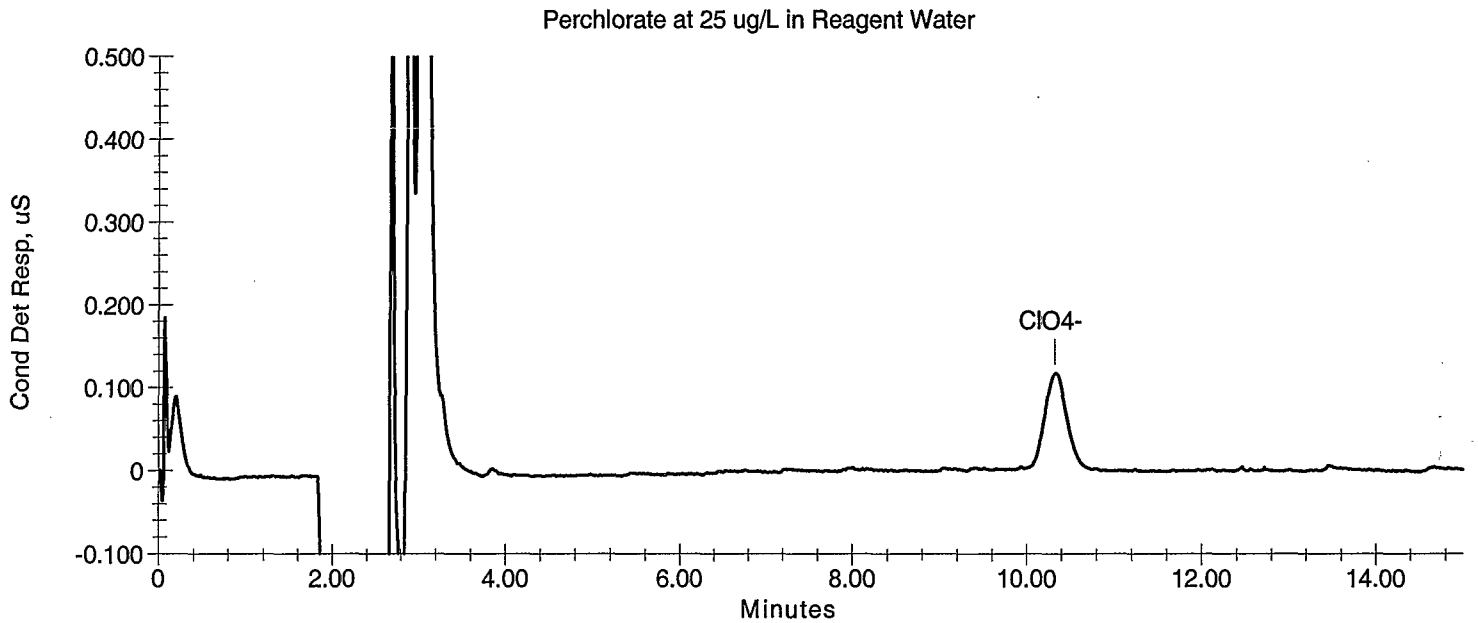

FIGURE 3. STACKED CHROMATOGRAMS INDICATING INFLUENCE OF HIGH CONCENTRATIONS OF COMMON ANIONS ON LOW CONCENTRATION MEASUREMENT OF PERCHLORATE AT 4.0 ug/L (Conditions as indicated in Table 1)

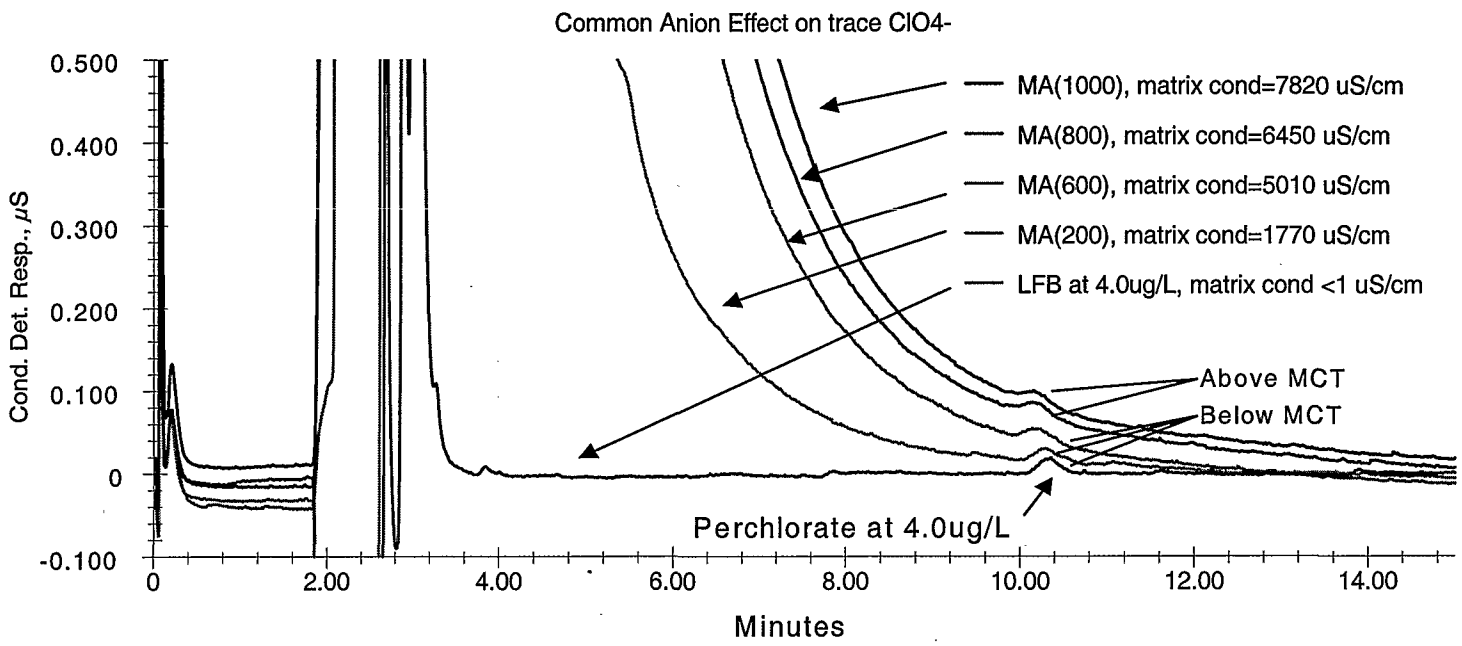

FIGURE 4. STACKED CHROMATOGRAMS INDICATING INFLUENCE OF HIGH CONCENTRATIONS OF COMMON ANIONS ON PERCHLORATE AT 25 ug/L DURING THE MCT DETERMINATION (Conditions as indicated in Table 1)

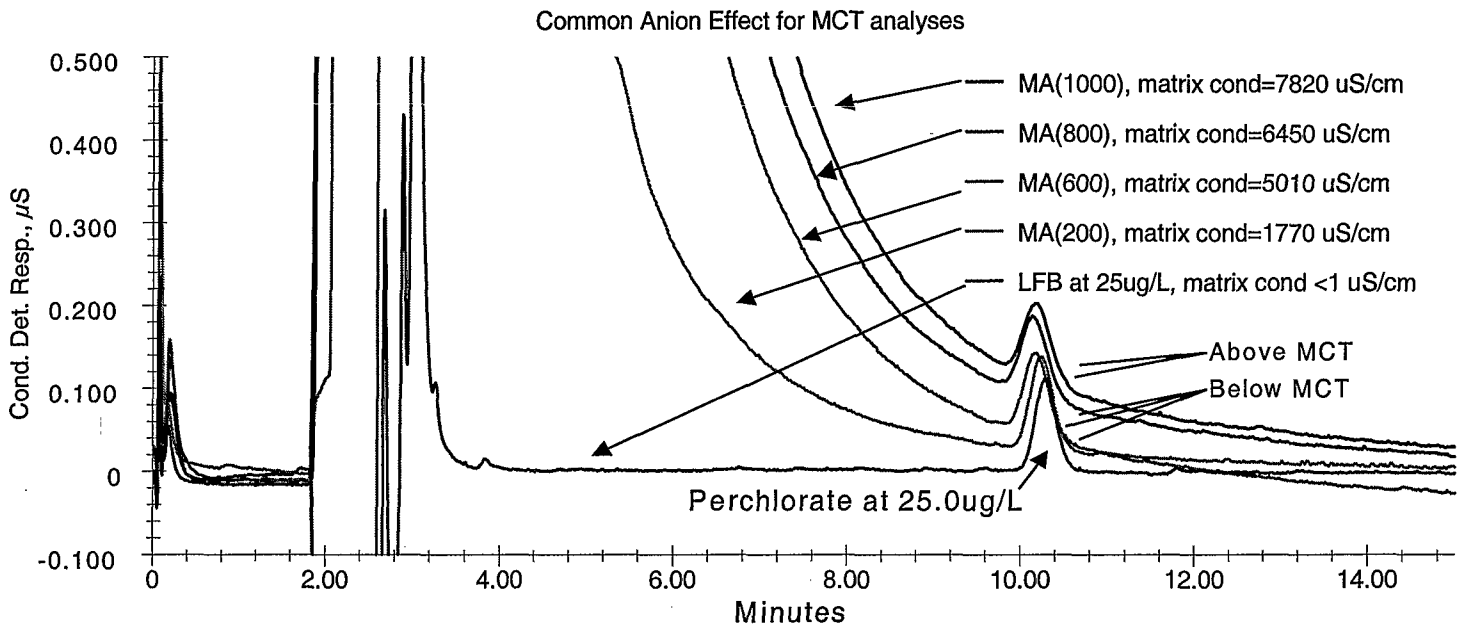
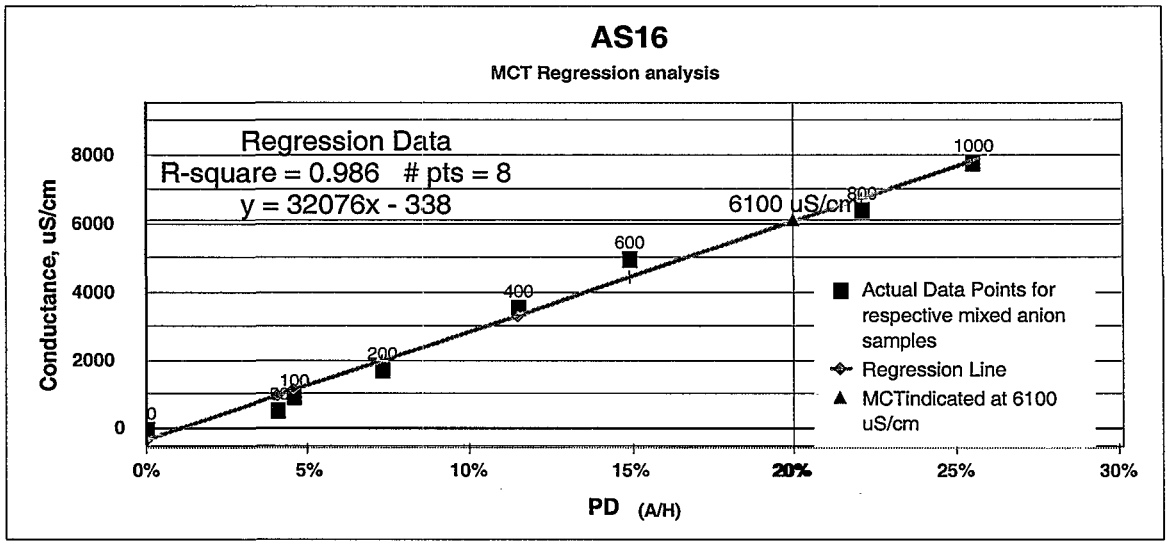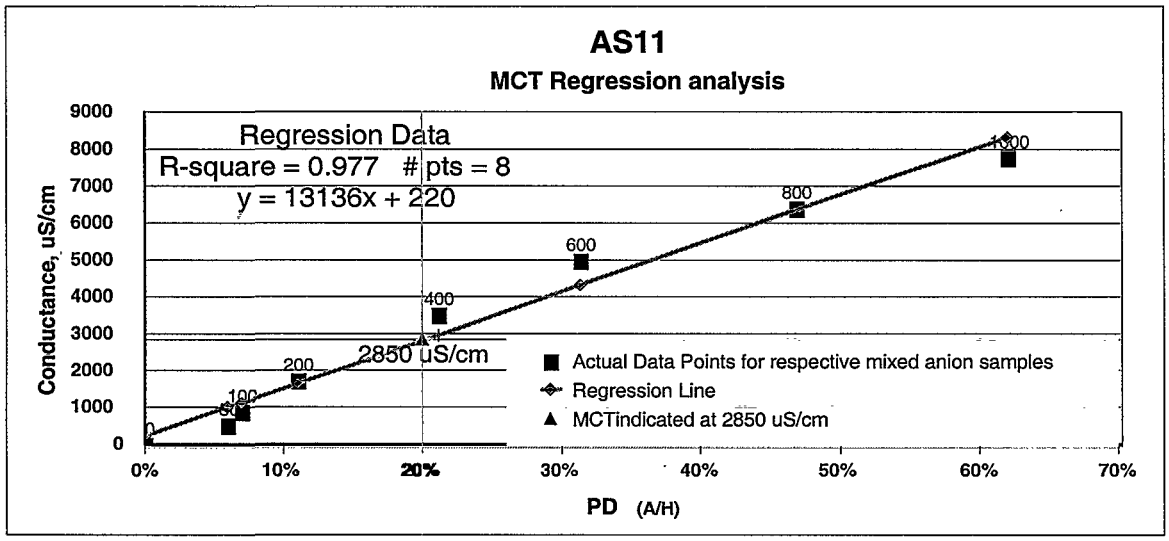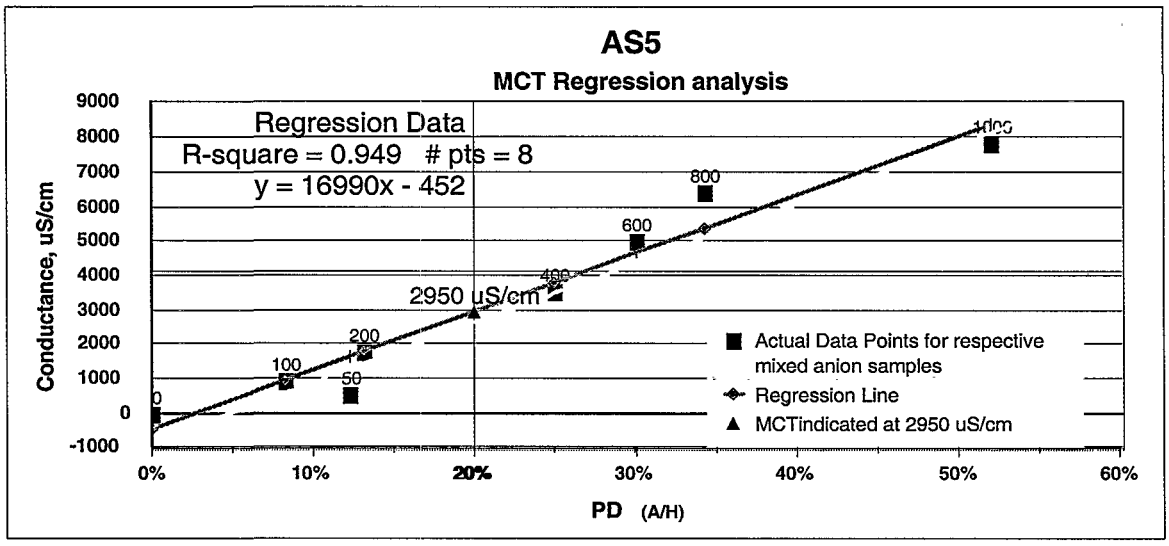
FIGURE 5. REGRESSION ANALYSIS OF THE MCT DETERMINATION DATA