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Chloride

(BY ION CHROMATOGRAPHY - EPA 300.0)

1. Application (Analyte and Matrices)

1.1 This method is applicable to the determination of chloride by ion chromatography. The matrices applicable to this method include drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, and solids (after extraction).

1.2 Method detection Limit (LOD) is 0.02 mg/L chloride.

2. Summary of Method

2.1 A small volume of sample, typically 2 to 3 mL, is introduced into an ion chromatograph. The anion of interest is separated and measured, using a system consisting of a guard column, separator column, suppressor device, and conductivity detector.

2.2 In order to use this method for solids an extraction procedure must be performed as described in section 8.1.2.

3. Sample Collection, Preservation, and Storage

3.1 Samples should be collected in clean glass of polyethylene bottles.

3.2 Sample preservation not required for chloride and holding time is 28 days.

4. Interferences

4.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems.

4.2 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 baseline in ion chromatograms.

5. Safety

5.1 All chemicals should be considered a potential health hazard. The 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 handling data sheets should be made available to all personnel involved in the chemical analysis.

5.2 Normal, accepted laboratory safety practices should be followed during reagent preparation and instrument operation. No known carcinogenic materials are used in this method.

6. Apparatus and Materials

6.1 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2 Ion chromatograph - Analytical system complete with ion chromatograph and all required accessories including auto-sampler, analytical column, guard columns, compressed helium gas, detectors and data system. The current system is the Dionex DX-500.

- 6.2.1 Anion guard column: A protector of the separator or analytical column. If omitted from the system the retention times will be shorter. Ag14-4mm guard column is currently utilized .
- 6.2.2 Anion separator (analytical) column: Separation is generated using a Dionex AS14A- 4mm column
- 6.2.3 Anion suppressor device: The Dionex ASRS-Ultra Anion Suppressor is used for this system.
- 6.2.4 Detector – 35oC Heated Conductivity cell: 25 µL loop.
- 6.2.5 Dionex Data Chromatography Software used to generate the data.
- 6.2.6 Thermo S3500 Autosampler.

7. Reagents and Standards

7.1 Sample bottles: Glass or polyethylene of sufficient volume to allow replicate analyses of the anion of interest.

7.2 Reagent water: Deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

7.3 Eluent solution: 50X concentrated eleuent solution is made. A working eleuent is made by diluting 1:50 to make a final concentration of sodium carbonate, 8.0 mM and sodium bicarbonate, 1.0 mM.

7.4 Stock standard solutions, 1000 mg/L (1 mg/mL): Stock standard solution may be purchased as certified solutions from ERA. Working standard solutions are made from stock by serial dilution to give the following concentrations: 200, 100, 50, 20, 10, 5, 1, 0.5 , 0.1 and 0 (blank) mg Cl/L. Quality control standards are made from stock purchased from another supplier.

8. Procedure

8.1 Sample Preparation

- 8.1.1 Water: Clear water samples are to be filtered through a 0.45 um filter prior to analysis.
- 8.1.2 Solid materials: The following extraction should be used for solid materials. Add an amount of reagent water equal to ten times the weight of dry solid material taken as a sample. This slurry is mixed together for ten minutes using a magnetic stirring device. Filter the resulting slurry before

injecting using a 0.45 μm membrane type filter. This can be the type that attaches directly to the end of the syringe. Care should be taken to show that good recovery and identification of peaks is obtained. A matrix spike should be performed.

8.2 Instrument Operating Conditions: Instrument operating conditions are controlled by the Data System and a copy of the instrument operating parameters is presented in the Dionex Operator's Manual.

8.3 Calibration

8.3.1 Ion chromatographic operating parameters should be established which are equivalent to parameters in the Operator's Manual of the instrument.

8.3.2 Calibration standards at 10 concentration levels consisting of a blank, and 9 standards ranging from the method detection limit to the established upper limit. Each attenuation range of the instrument used to analyze a sample must be calibrated individually.

8.3.3 Tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure retention times must also be recorded. These steps are done by the Data System which displays the peak height and area, the calibration curves and the linearity of the calibrations at the different concentrations.

8.3.4 The calibration curve must be verified on each working day, or whenever the anion eluent is changed, and after every 10-15 samples. A certified reference standard at a concentration near the mid-range of the curve must be used to verify the calibration curve. The standard must be purchased from a different vendor than the working standard. If the response or retention time of the analyte varies from the expected values by more than +10%, the test must be repeated, using fresh calibration standards. If the results are still more than +10%, a new calibration curve must be prepared for that analyte.

8.4 Analysis

8.4.2 Check system calibration daily, if required, recalibrate as described in Section 8.3.

8.4.3 Load standards, blanks, and samples by filling polyethylene autosampler vials and inserting cap/filter into the vials.

8.4.4 Begin analysis.

8.5 Data Review and Reporting

8.5.1 After the standards have been analyzed review the calibration curves using the data system. The calibration curves should be reviewed for response and linearity ($r > 0.995$). If a problem is observed the run should be stopped and corrective action should be taken prior to restarting the run. The standards may need to be prepared and analyzed again.

8.5.2 For the blank, a response less than the MDL should be observed for the analyte. If there is a positive response for the blank the run should be stopped and corrective action should be taken prior to restarting the run. The blank should be prepared again and reanalyzed.

8.5.3 All results should be reported in mg/L.

9. Quality Assurance/Quality Control and Acceptance Criteria

9.1 The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of fortified samples as a continuing check on performance. The laboratory should maintain records to define and document the quality of data that are generated.

9.1.1 If any changes or modifications are made to this procedure due to improvements in technology the analyst is required to repeat the procedure in Section 9.2.

9.1.2 The laboratory should fortify and analyze a minimum of 5% of all samples to monitor continuing laboratory performance. A minimum of 5% of all samples should be run in duplicate.

9.2 Before performing any analyses, the analyst should demonstrate the ability to generate acceptable accuracy and precision with this method, using a laboratory performance standard.

9.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each fortified concentration of analyte being measured.

9.5 Before processing any samples, the analyst must demonstrate through the analysis of an aliquot of reagent water that all glassware and reagent interferences are under control. Each time there is a change in reagents, a laboratory reagent blank must be processed as a safeguard against laboratory contamination.

9.6 Additional quality assurance practices have been adopted by the laboratory to be used with this method. The analysis of field duplicates when they are submitted to monitor the precision of the sampling technique. When doubt exists over the identification of a peak in the chromatogram, confirmatory techniques such as sample dilution and fortification, must be used. Whenever possible, the laboratory should perform analysis of quality control check samples and participate in relevant performance evaluation sample studies.

9.7 In order to verify that standards have been prepared correctly and have not degraded, a reference standard check should be performed using a standard of known concentration prepared by an independent source with each set of samples. Results must be within the listed acceptance limits of the control sample or + 10% if no limit is listed.

9.8 With each batch of samples processed analyze a single laboratory fortified blank (LFB) or matrix spike containing each analyte of concern at a concentration at or near those used in Section 9.2. If more than 20 samples are run in a batch analyze one LFB or matrix spike for every 20 samples. Evaluate the accuracy by If acceptable data cannot be obtained, locate the problem and correct it.

9.9 A replicate LFBs and matrix spikes should be analyzed to determine the precision of the laboratory measurements for every 5% of the sample batch. Add these results to the ongoing control charts to document data quality.

9.10 One sample should be analyzed in duplicate for every 20 samples analyzed or for each batch of samples and duplicate results should be within + 10%. If the duplicate results do not fall within this range the duplicates should be reanalyzed.

10 Method Performance

10.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.

11. Reporting

11.1 All results are reported in mg/L

11.2 All results will be reported using three significant figures. If a target analyte is detected between the MDL and the RL, the result will be reported as detected not quantified (DNQ) and if the result is detected below the MDL the result will be reported as ND (not detected) and be followed by the MDL value.

12. References

12.1 U.S. Environmental Protection Agency, The Determination of Inorganic Anions in Water by Ion Chromatography, Method 300.0. August 1991. Environmental Monitoring and Systems Laboratory, Cincinnati, OH 45268.