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Perchlorate in Ground Water: Update on the Application of an Ion-Selective Electrode Analytical Method

Through the Measurement and Monitoring Technologies for the 21st Century ($21M^2$) initiative, EPA's Office of Solid Waste and Emergency Response (OSWER) is identifying and supporting deployment of promising measurement and monitoring technologies by matching existing and emerging technologies with OSWER program and client needs in the fields of waste management and site cleanup. OSWER has identified a number of "needs areas" as the focus of $21M^2$. These needs reflect evolving requirements across all waste programs. A recent list and description of needs is available at the $21M^2$ Internet site at http://www.cluin.org/programs/21m2/needs.cfm.

Background

EPA developed this fact sheet to summarize the recent study of a field analytical method for measuring perchlorate that was funded under the $21M^2$ program. This study resulted in a new protocol for analyzing ground water samples for perchlorate using ion-selective electrodes (ISE).

Project Objectives

EPA's goal was to develop an accurate and reliable field method for measuring perchlorate in ground water at concentrations as low as 15 µg/L. Specific study objectives included:

- determination of the suitability of both membrane and solid state electrodes;
- collection of information on the performance of the method in terms of accuracy and reliability;
- evaluation of the effect of common environmental anions on the accuracy of perchlorate data;
- development of protocols to handle interferences; and
- development of a standard operating procedure.

Project Results

Suitability of Ion Specific Electrode Designs. The study evaluated an ISE that uses a plastic membrane half-cell with a double junction reference electrode and a solid state ISE with a built-in reference element. The solid state ISE does not require any filling solution or maintenance and can be stored dry. The membrane ISE uses a reference electrode that requires maintenance of both the inner and outer chamber filling solutions and must be stored in a special solution or dismantled, cleaned, and stored dry. It was found that the 18 µg/L California Action Limit concentration that had to be achieved for the method to be of use in the field, could not be met by the membrane ISE, but could be met by the solid state one.

Method Detection Limit Study. A method detection limit study showed that the solid state ISE system could consistently detect perchlorate concentrations at 3 µg/L when no interferents were present. This allowed the project to set a practical quantitation limit (PQL) or reporting limit of 15 µg/L, which is 5 times the detection limit and 20 percent lower than the target concentration of 18 µg/L. Periodic tests of method blanks and 5 µg/L and 10 µg/L perchlorate standards indicated acceptable differentiation of

millivolt readings at 5-10 µg/L for a distilled water matrix. Although the MDLs were 3 µg/L, results for standards less than 5 µg/L could not generally be considered differentiable from results for blanks. The method was found to be linear over a 5 to 100 µg/L range.

Results reported as non-detects (ND) at the PQL or MDL indicate the absence of perchlorate at that concentration. If results are to be reported as detections between the PQL and MDL, they should be considered quantiatively and qualitatively uncertain due to possible matrix effects. However, results below the PQL of 15 µg/L should not be reported as detections unless the matrix is demonstrated to be free of positive interferences.

Interferences. A direct relationship between false positive readings and conductivity was noted with some samples causing significant loss of electrode sensitivity as well. From background information on the sampling locations, the most likely significant interferents were determined to be carbonate/bicarbonate, chloride, and nitrate. Bromide, fluoride, iodide, phosphate, and other anions such as thiocyanate were also identified as interferents in the ISE manufacturer's specifications. The project developed correction factors for matrices containing concentrations in excess of 50 mg/L chloride, 0.12 mg/L NO_3-N, or 1.2 mg/L bromide. Interference due to carbonate and bicarbonate is eliminated by the acidification of all standards and samples to pH 4.0 (± 0.1) with sulfuric acid. The electrode must be reconditioned after analyzing any sample containing concentrations of nitrate greater than 0.2 mg/L NO_3-N. Reconditioning consists of placing the ISE module in an acidified blank and an acidified 100-2,000 µg/L perchlorate solution (depending upon the concentration of nitrate) to maintain adequate sensitivity to meet ±20% accuracy criteria.

Standard Operating Procedure. A standard operating procedure (SOP) was developed for using ISE to analyze perchlorate in ground water. The SOP can be found in *Perchlorate Screening Study: Low Concentration Method For the Determination of Perchlorate in Aqueous Samples Using Ion Selective Electrodes* at http://clu-in.org/programs/21m2/letter_of_findings.pdf. It was suggested that matrices with very high concentrations of interfering anions be evaluated before going into the field to determine if this method will meet project objectives.

Recommendation for Further Studies. Further studies are recommended to reconfirm the accuracy of the correction factors and to study the effects of other potential interferents, including mixtures of interfering anions. Possible methods to mitigate nitrate interference should be explored to make the method more versatile. Further studies to determine and maximize the effectiveness of the method of standard additions are required. The study also determined that further improvements in cleanup technology, such as ion exchange cartridges, needed to be investigated to make the method more robust.

Project Information

For more information on this study, contact Joe Eidelberg, U.S. EPA Region IX, 415-972-3809, Eidelberg.Joseph@epa.gov.

Additional Information

Also, more information can be found at the following locations:

- Earthtech Inc., San Jose, CA, Chris Davis, (408) 232-2829, Chris.Davis@earthtech.com
- $21M^2$ program. *http://cluin.org/programs/21m2/* or
- Dan Powell, U.S.EPA, 703-603-7196, powell.dan@epa.gov