Perchlorate Analysis Using Ion Chromatography and Suppressed Conductivity Detection

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Executive Summary

Ion chromatography (IC) is recognized as an effective tool for the determination of perchlorate in drinking water and other sources. U.S. EPA Methods 314.0, 314.1, and 314.2 describe the determination of trace perchlorate in drinking water using IC with suppressed conductivity detection.

Keywords

Suppressed Conductivity Detection, Perchlorate Contamination Prevention Act, Perchlorate Best Management Practices, Capillary IC, 2D-IC

Perchlorate has been found in drinking water and surface waters. Consequently, it has attracted widespread attention within the environmental community over the last decade due to concerns that it poses a risk to public health. At high concentrations, perchlorate can interfere with iodide uptake in the human thyroid, which plays a central function in regulation of various hormones. Disruption of the thyroid can result in developmental disabilities and impair development, especially among infants and children.

On February 11, 2011, under the Safe Drinking Water Act (SDWA) the U.S. Environmental Protection Agency (EPA) decided to regulate perchlorate levels. Specifically, the EPA determined that perchlorate meets SDWA's criteria for regulating a contaminant—that is, perchlorate may have an adverse effect on the health of persons. Perchlorate is known to occur or there is a substantial likelihood that perchlorate will occur in public water systems at levels that are of concern to public health. As a result, regulation of perchlorate in drinking water systems presents a meaningful opportunity for health risk reduction for persons served by public water systems.

Several states have enacted drinking water standards for perchlorate including Massachusetts in 2006. California's legislature enacted AB 826, the Perchlorate Contamination Prevention Act directing the State Department of Toxic Substance Control (DTSC) to develop regulations specifying the best management practices for managing perchlorate materials. DTSC adopted the Perchlorate Best Management Practices (BMP) regulations on December 31, 2005, and the regulations became effective July 1, 2006. Several other states, including Arizona, Maryland, Nevada, New Mexico, New York, and Texas have established non-enforceable, advisory levels for perchlorate.

While perchlorate is not officially regulated in European countries, European and International Standardization committees have recently started working on standardizing ion chromatographic methods that monitor perchlorate, based on the previously mentioned EPA methods. Their scope is not only drinking water, but also surface water and swimming pool water samples. Currently, public European interest is driven by recent findings of significant concentrations of perchlorate in vegetables and fruit juices.

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Perchlorate analysis using ion chromatography

Ion chromatography is recognized as an effective tool for the determination of perchlorate in drinking water and other sources. U.S. EPA Methods 314.0, 314.1, and 314.2 describe the determination of trace perchlorate in drinking water using IC with suppressed conductivity detection. The method detection limits (MDLs) of U.S. EPA Methods 314.0 and 314.1 are 0.53 µg/L and 0.03 µg/L, respectively. These methods are also described in Thermo Scientific Application Update (AU) 148[1] and Application Note (AN) 176[2], which demonstrate MDLs of 0.10 µg/L and 0.02 µg/L, respectively.

U.S. EPA Method 314.0 is subject to interferences and loss of sensitivity caused by the presence of high concentrations of the common matrix ions chloride, sulfate, and carbonate. This is illustrated in Figure 1, which shows the effects of increased matrix anions on the perchlorate peak. For this reason, U.S. EPA Method 314.0 recommends determining the sample conductivity prior to analysis, and shows an 86% recovery for a 4-µg/L spike in a high-ionic-strength synthetic inorganic water with a conductivity of 4200 µs/cm. The method provides two options for samples with high total dissolved solids (TDS): dilution and the use of trap columns. Though both strategies are effective, dilution will result in an increased method reporting level (MRL), while trap columns add a sample preparation step. In addition to high-concentration matrix anions, some anionic compounds, such as chlorobenzene sulfonates, are known to elute at a similar retention time as perchlorate, and can therefore lead to a false positive result.

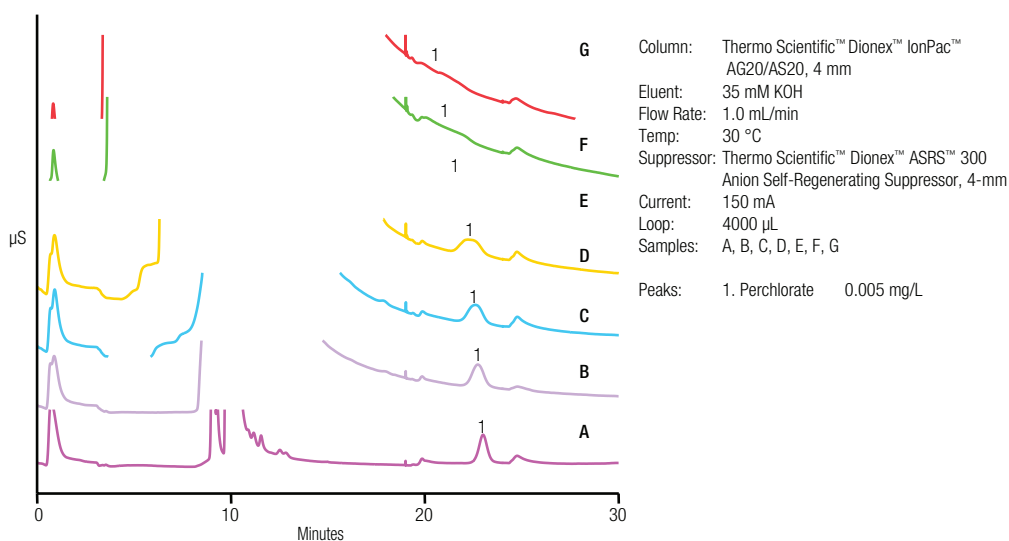| Column:	Thermo Scientific™ Dionex™ IonPac™ AG20/AS20, 4 mm
Eluent:	35 mM KOH
Flow Rate:	1.0 mL/min
Temp:	30 °C
Suppressor:	Thermo Scientific™ Dionex™ ASRS™ 300 Anion Self-Regenerating Suppressor, 4-mm
Current:	150 mA
Loop:	4000 µL
Samples:	A, B, C, D, E, F, G
Peaks:	1. Perchlorate 0.005 mg/L

Figure 1. Effect of matrix concentration on perchlorate peak shape.

To avoid these complications, Dionex Corporation (now part of Thermo Fisher Scientific) and the U.S. EPA collaborated to develop U.S. EPA Method 314.1. This method uses a preconcentration column to trap perchlorate from the matrix, followed by matrix elimination with 10 mM sodium hydroxide. Perchlorate is then separated using a 2-mm primary column. To minimize the identification of a false positive peak, a second analytical column (with a different selectivity that yields an improved separation of perchlorate from the chlorobenzene sulfonates) is used as the confirmatory column to verify the presence of perchlorate. Although the method is effective and can be used for compliance monitoring, the authors recommend the method described in Thermo Scientific AN 178[3] Improved Determination of Trace Concentrations of Perchlorate in Drinking Water Using Preconcentration with Two-Dimensional Ion Chromatography and Suppressed Conductivity Detection to determine trace concentrations of perchlorate in high-ionic-strength matrices. AN 178 was also produced during collaboration with the U.S. EPA on the development of U.S. EPA Method 314.2.

Method 314.2 improves on Methods 314.0 and 314.1, and was specifically developed for the determination of perchlorate in high-ionic-strength samples using a two-dimensional IC method. In this method, a portion of the first-dimension separation is diverted to a concentrator column, the contents of which are then eluted to a second-dimension column to separate perchlorate from the other ions in the diverted portion of the first dimension. There are several advantages of the 2-D matrix diversion method. First, initial sample loading onto the 4-mm column allows a large sample injection volume (large amount of sample) due to the high capacity of the analytical column and higher selectivity for analytes of interest relative to the matrix ions. Second, the analyte peak that is partially resolved in the first dimension is focused onto a concentrator column prior to the second dimension. The diverted portion of the first dimension has passed through a suppressor to convert the hydroxide eluent to water, which provides the ideal environment for retention and focusing on the anion concentrator. Third, the second-dimension column has a smaller cross-sectional area relative to the first dimension, thereby enhancing the detection sensitivity. Finally, this method allows the combination of two different chemistries in two dimensions, enabling selectivity not possible when using a single-chemistry dimension.

In Method 314.2 and AN 178, perchlorate is partially resolved on a 4-mm Dionex IonPac AS20 column in the first dimension, collected onto a concentrator column, and then resolved in the second dimension with a 2-mm Dionex IonPac AS16 column. Method 314.2 has a lower MDL compared to 314.1 and 314.0, ranging from 0.012 to 0.018 µg/L, depending on the sample volume analyzed. The improved selectivity eliminates the possibility of a false positive, such as a chlorobenzene sulfonate.

Improved perchlorate analysis: 2D-IC in a capillary format

Since the development of Reagent-Free™ Ion Chromatography (RFIC™) systems and their utility for 2D-IC, the need to improve performance, resolution, and sensitivity has led to the evolution of smaller-scale, capillary IC systems. Capillary IC scales down traditional IC from 10-fold to 100-fold by using 0.4-mm columns and 10-µL/min flow rates. The benefits of scaling down are the ability to use less eluent and the option of leaving the system constantly running, which is much more efficient and economical. With a capillary RFIC system continuously on, there is no need for startup or equilibration time; less calibration is required; and there is no eluent preparation for those unplanned, last-minute samples. Capillary IC falls under the scope of the U.S. EPA's flexibility rule, and is therefore accepted for compliance monitoring.
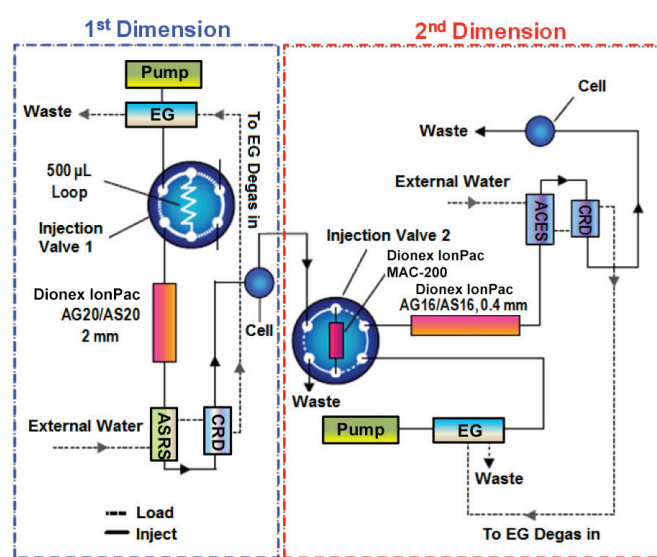

Figure 2. Schematic diagram of the analytical/capillary 2D system: perchlorate is resolved from the matrix on a 2 mm Dionex IonPac AS20 column set, concentrated on a monolithic capillary concentrator, separated on a 0.4 mm Dionex IonPac AS16 column set, and detected by suppressed conductivity detection.

Thermo Scientific AN 1024[4] demonstrates the improved determination of perchlorate using a capillary format in the second dimension of a 2D-IC system. Figure 2 shows the schematic of a 2D-IC system for trace determinations of perchlorate. The 4-mm and 2-mm columns used in AN 178 are replaced with 2-mm and 0.4-mm columns, respectively. The system with a smaller-diameter column is operated at a lower flow rate, thus requiring much less reagent consumption and reducing system maintenance. In this method (as compared to U.S. EPA Method 314.2), there is a much greater decrease in cross-sectional area from the first dimension to the second dimension, and therefore improved sensitivity can be obtained (i.e., there is a 25-fold increase from a 2-mm column to a 0.4-mm column as compared to a fourfold increase from a 4-mm column to a 2-mm column using the flow rates in U.S. EPA Method 314.2). AN 1024 demonstrates an MDL of 0.005 µg/L, and good recovery results for perchlorate were obtained with different sample matrices. The results of a 2-D separation on a capillary format from a high-ionic-strength (matrix) sample are shown in Figure 3.
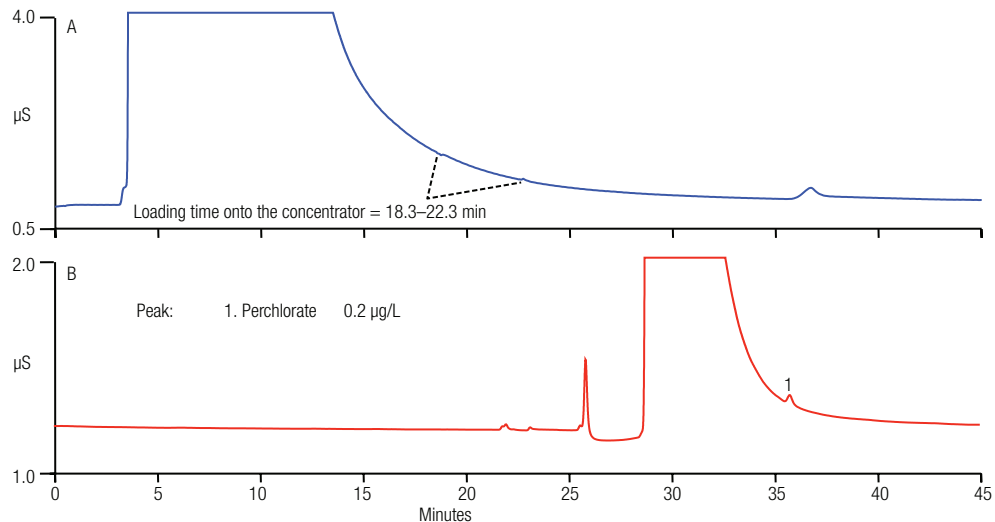

Figure 3. Chromatograms of synthetic high inorganic water containing 1000 mg/L each of chloride, sulfate, and bicarbonate fortified with 0.2 µg/L perchlorate in (A) first dimension and (B) second dimension.

Conclusion

IC with suppressed conductivity is the preferred method for the determination of perchlorate in drinking and high-ionic-strength waters. RFIC systems provide the sensitivity and ease of use for samples with moderate ionic strength. For more complex, high-ionic-strength samples, the use of validated 2D-IC provides many benefits, including on-line matrix elimination, increased sensitivity, and elimination of false positives. An even further improvement has been the evolution of capillary IC, which, when executed on a RFIC system in 2-D format, can achieve ppt-level detection.

References

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