

# Development of a Better Method to Identify and Measure Perchlorate in Drinking Water

Elizabeth Hedrick and Thomas Behymer

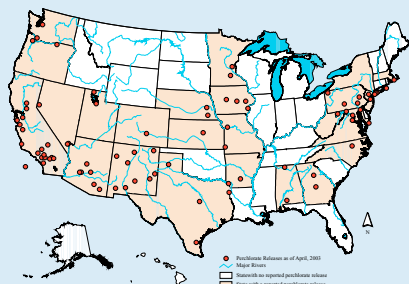
Chemical Exposure Research Branch, National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, 26 West Martin Luther King Drive, Cincinnati, Ohio 45268

EPA Science Forum

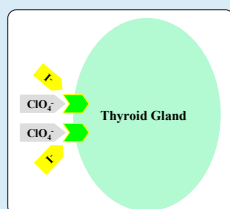
Healthy Communities and Ecosystems

## Environmental Issue

- Perchlorate ( $\text{ClO}_4^-$ ) is used primarily as an oxidant in solid propellant in rockets, pyrotechnics, air bag inflators, and highway safety flares.
- From accidental releases and improper disposal practices of the past,  $\text{ClO}_4^-$  has become a contaminant in surface and ground waters.
- It is highly mobile and, due to its chemical stability, can persist for decades.
- $\text{ClO}_4^-$  has been found in drinking water in 34 states.

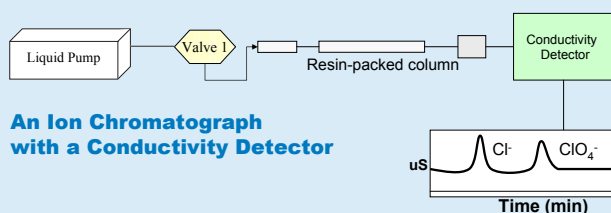


- $\text{ClO}_4^-$  interferes with thyroid hormone production by blocking iodine ( $\text{I}^-$ ) from entering the thyroid gland. Thyroid hormones play a crucial role in metabolism throughout life. They are also critical for proper prenatal brain development, making developing fetuses a sensitive subpopulation.
- Currently, the National Academy of Sciences is reviewing the health and toxicological studies used by the EPA to help assess the risk posed to humans by  $\text{ClO}_4^-$  in the environment and to determine the health endpoint of concern. At the EPA, research continues to better characterize the occurrence of  $\text{ClO}_4^-$  in the environment, assess human exposure pathways, and to refine treatments to remove  $\text{ClO}_4^-$  from drinking water.
- Methods for measuring low levels of  $\text{ClO}_4^-$  in drinking waters have improved dramatically in the past decade. However, the concentration of human health concern may be lower than the best methods of the past are capable of detecting. Scientists at the U.S. EPA in Cincinnati, Ohio, are working to develop better methods for identifying and quantifying  $\text{ClO}_4^-$  in drinking waters.



## The Analytical Problem

Currently,  $\text{ClO}_4^-$  is detected in drinking water by injecting a small volume into an instrument called an ion chromatograph. An ion chromatograph consists of a liquid pump (containing potassium hydroxide solution) and a narrow column packed with a special resin material that is capable of separating cations and anions. Anions, such as  $\text{ClO}_4^-$ , are small molecules having an overall negative charge. Common anions in drinking water are  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ , and  $\text{HCO}_3^-$ . The anions separate from each other based on their relative affinities for the resin and potassium hydroxide solution. The separated anions may then be detected by their conductance. Detection by conductivity is considered to be non-specific since there are potentially many conducting anions in water. The only manner in which to identify the separated anions is by their retention times on the resin-packed column.

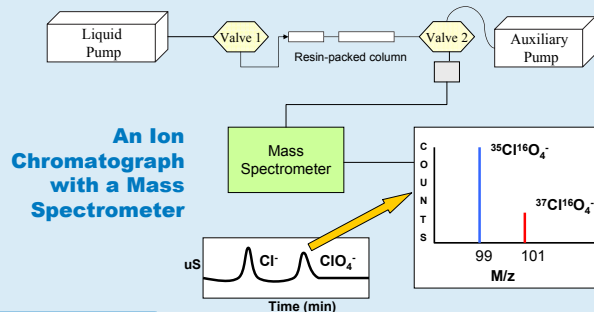


An Ion Chromatograph with a Conductivity Detector

Conductivity detection has been used to collect  $\text{ClO}_4^-$  occurrence data in the public U.S. water supply since 1999. The two major problems with conductivity detection are, (1) the inherent lack of sensitivity, and (2) the potential for interfering anions to elute at the same retention time as  $\text{ClO}_4^-$ . These problems may result in false negative and false positive results, respectively.

## The Analytical Solution

The Office of Research and Development in association with the Office of Water and Dionex Corporation, makers of ion chromatographs, have partnered to investigate the potential for definitive identification of  $\text{ClO}_4^-$  in drinking waters using a highly sensitive and specific detector called a mass spectrometer. A mass spectrometer utilizes specific information about the analyte i.e., the mass-to-charge ratio ( $m/z$ ) of the ion of interest. In the case of the  $\text{ClO}_4^-$  ion (with a single negative charge), the primary  $m/z$  of interest is 99 based on the 75.77% relative abundance of the chlorine-35 isotope.  $m/z$  101 is a secondary ion of interest based on the 24.23% abundance of chlorine-37. Coupled with ion chromatographic separation, mass spectrometry is by far the most promising analytical tool available today for low-level identification and quantitation of  $\text{ClO}_4^-$  in drinking water.

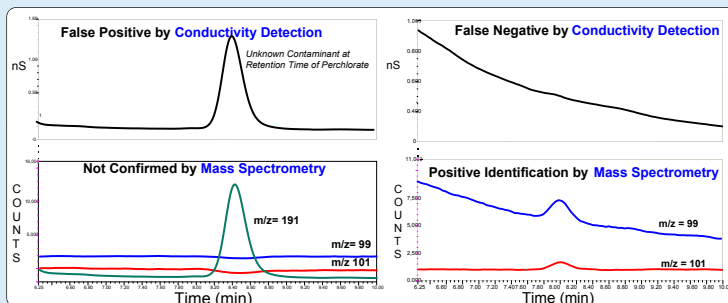


An Ion Chromatograph with a Mass Spectrometer

## Results

Below are examples of false positive and false negative detections (by conductivity detection) that are revealed by using mass spectrometric detection.

Using mass spectrometry,  $\text{ClO}_4^-$  has been found in hundreds of ground waters and source waters at concentrations less than 1 part per billion. This concentration is lower than any analytical method has been capable of detecting in the past.



## Impact

The development of a more sensitive and specific method for detecting  $\text{ClO}_4^-$  will allow regulators to better assess the extent of  $\text{ClO}_4^-$  contamination at concentrations of human health concern and to develop better strategies for treating  $\text{ClO}_4^-$  contaminated waters. Communities will also have greater confidence in the reported occurrence, or lack of occurrence, of  $\text{ClO}_4^-$  in their drinking waters.

Disclaimer: Mention of trade names does not constitute endorsement for use. Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.