Perchlorate Analysis

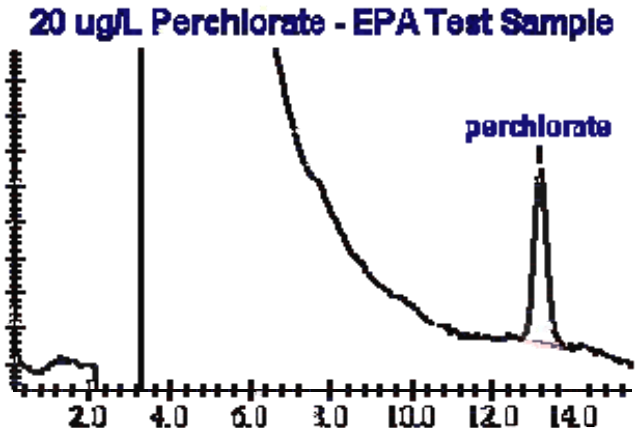
Perchlorate has been used in solid rocket propellants. It has now found it's way into drinking water supplies, and foods such as lettuce and milk. California has an action limit of 4 ug/L as an unregulated chemical requiring monitoring in ground water. On March 11, 2004 OEHHA announced a PHG of 6 ug/L.

The Environmental Working Group and Texas Tech University have reported finding perchlorate in lettuce and milk.

Perchlorate by EPA 314

Perchlorate binds tightly to many ion exchange columns. The chromatogram below shows the chromatography on a Dionex AS16 column with 35 mM sodium hydroxide. This sample is the EPA PT test sample having a conductivity of 470 uS/cm. Most common anions are not retained in this system, and elute in the large peak at 3-8 min. The detection limit is 2 ug/L in drinking water. Samples with high conductivity need dilution prior to analysis. Perchlorate has become an important environmental contaminant. A by-product of the explosive industry, it has been detected in groundwater in numerous locales. Currently EPA is especially interested in monitoring perchlorate in drinking water supplies.

We passed the first perchlorate PT study conducted in the spring of 2000 and are currently accredited by CA ELAP for perchlorate by EPA Method 314.0.



Perchlorate by IC-MS/MS

EPA 314 can be subject to matrix interferences, especially in the presence of high amounts of other anions. Contamination in foods which were irrigated with perchlorate-tainted water has become important, as reports have surfaced of contaminated lettuce and milk (presumably from cows fed alfalfa containing perchlorate). IC has difficulty with this type of complex matrix. Also pCBSA has been noted as an interference near the retention time for perchlorate by EPA 314.

We have developed an IC-MS/MS method to determine perchlorate. Due to the extreme specificity of MS/MS, matrix problems can be greatly reduced, and false positives essentially eliminated. Also, very low detection limits can be achieved due to the reduction in chemical noise. We can routinely detect sub-parts per billion levels in water.

Use of this method will allow us to greatly improve our perchlorate analytical capabilities. IC-MS/MS can be used to confirm IC results, to analyze for lower levels in important in-site assessments and remediations, and to detect low levels in foods and other complex matrices where EPA 314 simply cannot meet desired detection limits. Lettuce, spinach, and onions have been analyzed with detection limits of ~ 1 ng/g.

CA DTSC has approved Exova for projects which require IC-MS/MS confirmation of perchlorate.

The chromatogram below demonstrates detection of 0.1 ug/L perchlorate under chromatographic conditions similar to EPA 314, however using MS/MS in the negative ion mode as the detector. In this case the molecular ion for ClO^{4-}, 99 amu, is focused through the

first quadrupole, loses a single oxygen in the reaction cell, and the daughter ion ClO^{3-} 83 amu is focused through the second quadrupole, and onto the detector. This type of detection makes this analysis more sensitive and very specific.

This test has been used on the following sample types:

- water and wastewater
- soil
- produce (lettuce, zucchini, celery, green beans, and dates)
- milk and dairy products
- soy milk and other baby foods

EPA has now published methods like this for perchlorate. They distinguish an LC-MS/MS method, EPA Method 331, from an IC-MS/MS method, EPA Method 332, based upon the use of a suppressor. Our method complies with the latter.

IC-MS/MS of Perchlorate