Perchlorate Review and Update

August 17, 2004

Perchlorate Background

- Chemical Molecule
  - Tetrahedral array of 4 Oxygen Atoms around a central Chlorine Atom
  - Strong Oxidizer
  - Anion (negative charge)

- Usually found in salts with metals such as Aluminum, Ammonium, Calcium, Potassium, Sodium, etc.

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Perchlorate Background

- Naturally occurring and man-made chemical
- Primary ingredient of solid rocket/missile propellant
- Used in ammunitions of all types
- Contributes to the safe handling and use of munitions and rocket propellant

Perchlorate Background

- Other Uses
  - Airbags
  - Emergency Flares
  - Fireworks
  - Medication for thyroid conditions
  - Matches

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Perchlorate in the Environment

- Perchlorate salts have been widely used since the 1940's
- Perchlorate has a finite shelf life
- Therefore, large amounts of perchlorate were disposed of when missile and rocket inventories were upgraded with new perchlorate
- Releases also occurred during manufacturing, testing, disposal, or detonation of rockets and missiles

Perchlorate in the Environment

- Mobile in water
  - large plumes
  - large affected areas
- Treatability
  - not difficult, but development and optimization required
  - potentially very costly due to large volume of water required to treat

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Perchlorate in the Environment

- National Impact
  - Present in groundwater and/or surface water in 30 US States
  - Present in drinking water supply systems of over 20 million people in CA, NV, & AZ
  - In CA alone, over 300 wells with perchlorate levels of more than 4 ppb

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Perchlorate and Human Health

- Perchlorate interferes with iodide uptake in the thyroid gland

  - perchlorate and iodide are similar in size

  - the thyroid gland regulates metabolism in adults

  - the thyroid gland plays a major role in proper development in addition to metabolism in children

EPA Draft Toxicological and Risk Characterization for Perchlorate

- "Perchlorate Environmental Contamination: Toxicological and Risk Characterization External Review Draft (1/16/02)"
- 364 pages
- This report has undergone two previous external peer review and public comment processes
- EPA in conjunction with the DoD, DOE, and NASA requested that the National Academy of Sciences (NAS) conduct another review

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EPA Draft Toxicological and Risk Characterization for Perchlorate (2002)

- Conclusions

  - Potential human health risks of perchlorate exposure include metabolism problems, nervous system development issues, and thyroid tumors

  - A draft reference dose is included that is intended to be protective of human health

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Draft Reference Dose (RfD)

- The Draft RfD is 0.00003 milligrams/kilogram/day (mg/kg/day)
- Hypothetical conversion of the draft RfD to drinking water equivalent level (DWEL) – assuming a 70 kilogram body weight and 2 liters of water consumed per day would be 1 ug/L or ppb

EPA Draft Toxicity Assessment

- NAS is reviewing the assessment and will issue their findings by December 2004
- NAS input will have an effect on the future of perchlorate analysis and MCL establishment by EPA

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Draft Drinking Water Range

- EPAs current perchlorate range of concern is 4-18 ppb for children and 7-35 ppb for adults
- The range is based on 2 liters of water consumption per day and a provisional RfD range of 0.1-0.5 ug/kg
- No MCL or allowable level has been set by EPA to date (i.e. there is no current enforcement value)

Perchlorate and the CCL

- The Safe Drinking Water Act (SDWA), as amended in 1996, directs the EPA to publish a list of contaminants (referred to as the Contaminant Candidate List, or CCL) to assist in priority-setting efforts.
- Perchlorate was placed on the CCL in 1998.
- EPA developed regulations for monitoring certain unregulated contaminants in 1999. These contaminants are listed in the UCMR. The CCL Occurrence Priority list is the primary source of contaminants for the unregulated monitoring list, which must not exceed 30 contaminants.

Perchlorate and the UMCR

- Perchlorate was placed under the Unregulated Contaminant Monitoring Rule (UMCR) in 1999.
- The UMCR requires hundreds of large and small public water systems to monitor for perchlorate for several years.

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State Regulation

- Ten states have established “action levels”
- The action levels range from 1 to 35 ppb
- MA and CA have established Drinking Water Public Health Goals (PHGs)
  - CA is 6 ppb (March 2004)
  - MA is 1 ppb (May 2004)

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Perchlorate Detection in CA

County	Sources	Systems	Peak Value
LA	135	37	159 ug/L
San Bern.	82	17	820 ug/L
Riverside	65	8	65 ug/L
Orange	32	10	10.7 ug/L
Sacramento	13	3	400 ug/L
Santa Clara	9	6	8.5 ug/L
Totals	336	81	

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EPA Process

- Identify possible drinking water contaminants
- Gather specific information/Review UCMR Data
- Gather more information/Seek public and private expert input
- Decision on whether to regulate or not
- Propose a MCLG – gather more input
- Propose a MCL

Future of Perchlorate Analysis

- Significant toxicological decisions will be made in near future
- Expensive remediation projects may be required
- More published data concerning analytical method performance is needed

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Current Analytical Method

- EPA Method 314.0
- Drinking water method
- Single Column - Ion chromatography
- There are interference problems with high TDS samples
- There can be false positive/negative results due to interferences

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Other Analytical Methods

- Draft EPA Method 314.1
- Drinking water method
- Dual Column - Ion chromatography
- Column concentrator
- Additional preparation work required (sample clean-up and spiking)
- This method is under development by EPA

Other Analytical Methods

- Draft EPA Method 331.0
- Liquid Chromatography/Mass Spectrometry
- LC/MS
- Under development by several different groups including EPA, FBI, & USAF
- Similar technique under SW-846 Method 8321 for non-drinking water samples

Other Analytical Methods

- Draft EPA Method 330.0
- Ion Chromatography/Mass Spectrometry/Mass Spectrometry
- IC/MS/MS
- Under development by several different groups including EPA, FBI, & USAF
- Similar technique under SW-846 Method 8321 for non-drinking water samples

Other Analytical Methods

- SW-846 Draft Method 8321
- IC/MS/MS
- LC/MS
- LC/MS/MS
- Various techniques could be used for non-drinking water samples

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EPA Method 314.0

- This method is currently the only EPA approved technique
- BUT, it is only validated for drinking water
- This leaves out groundwater, surface water, waste water, soil, and biota
- Therefore, a large number of samples may be currently analyzed by an invalid method
- SW-846 Method 9058 is not yet promulgated

Better Methods

- Required characteristics
  - Accuracy
  - Linearity
  - Precision
  - Sensitivity
  - Selectivity

Accuracy

- Accuracy must be measured in each sample
- False positives may occur using EPA Method 314.0
- Why? Conductivity detector is sensitive to any substance that can carry an electric current in water
- More complex methods (MS/MS) require an internal standard (O-18 labeled perchlorate) and calculation by isotope dilution technique

Precision

2003 GW Method Validation Study

	IC	LC/MS/MS
Precision (RSD)	7-17%	6-22%

Relatively similar results for precision

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Linearity

2003 GW Method Validation Study

	IC	LC/MS/MS
Linear Range (ug/L)	1-40	0.1-10

Lower calibration window for LC/MS/MS

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Sensitivity

- Current action levels vary from 1 to 35 ppb
- EPA Draft Risk Assessment may lead to a new MCL of 1 ppb (adults) and lower for children
- EPA Method 314.0 can not reach the sensitivity required to provide results below 1 ppb

Sensitivity Difference

IC versus IC/MS/MS

Separation – Interface – Detection

Step 1 – same in both – perchlorate separated from other chemical species by ion exchange

Step 2 – similar concept – chemical filter at the interface to the detector

Step 3 – difference – conductivity detector versus tandem MS detectors

Sensitivity Advantages

- MS/MS is used in lieu of MS because:

  1. with MS, only analyzing molecular ions

  2. MS/MS provides structural information from fragmentation

  3. Quieter background and better chromatography (separation) for difficult samples

- There have been no reports of false positive results using this technique

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Estimated Reporting Limits

Analysis	Reporting Limit (ug/L)
Colorimetric	500
Ion-Selective Electrode	100
IC (EPA 314.0)	~4
LC/MS (Not approved)	0.2
LC/MS/MS (Not approved)	0.2
IC/MS/MS (Not approved)	0.01

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Summary of Methods

- There are several options available for perchlorate analysis
- The IC-Cond method has the appropriate sensitivity to meet the most of the current requirements
- More sensitive methods will be needed in the near future if a MCLG or MCL is proposed for perchlorate

New Method Timeline

EPA Method/Instrument		Peer Review	Final Pub.
314.1	IC-Cond (DC)	10/04	12/04
330.0	IC/MS/MS	8/04	10/04
331.0	LC/MS	8/04	10/04

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EPA Method 314.0 Issues

- Method is not always reliable
  - False Positives
  - False Negatives
  - Extra analytical work can help but it will add cost and not always be successful
  - EPA working on new methods
- Cannot meet some of the current State PHGs

New Methods

- More accurate
- Equal in precision
- Much more sensitive
- Much more selective – no false positives
- Can be used for several matrices
- Will be more costly

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Summary

- Decisions will be made on the best available analytical techniques based on regulatory thresholds
- The better the method, the better the data
- EPA Method 314.0 can be used in preliminary investigations to determine if perchlorate is a compound of concern at a given site
- The new methods will hopefully be reviewed and approved in time for any regulatory threshold decisions

Summary

- New EPA methods should be available by 2005 in time to meet any new regulatory threshold values
- AFCEE QAPP Version 4.0 contains SW-846 Method 8321 options for perchlorate analysis
- This version of the QAPP will be out in the very near future…draft is available on AFCEE website

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DoD EDQW

- Environmental Data Quality Workgroup
- Will form sub-group to conduct round robin method validation studies for perchlorate methods
- Will use ASTM format to conduct method validation study
- This will assist in the development of the non-drinking water methods

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