

LC-ESI-MS/MS Determination of Low-Level Perchlorate in Water and Produce

Michael Shelton, West Coast Analytical Service, Inc.

BACKGROUND

Perchlorate has been used for many years in solid rocket propellants, road flares, munitions, airbags, and other related materials. It is also found in some fertilizers.

One manufacturing facility in southern Nevada, which began operations in 1951, sits atop a perchlorate-contaminated plume of groundwater, estimated to contain over 20 million pounds of perchlorate in 9 billion gallons of water. This plume eventually discharges into the Las Vegas Wash, and then into Lake Mead. From there, it flows down the Colorado River, which feeds drinking and irrigation water supplies throughout the Southwest.¹



Specifically, this water is used for irrigation in the Imperial and Coachella Valleys in California, where a large portion of the nation's winter food crops are grown. These include alfalfa, squash, tomatoes, green beans, broccoli, cauliflower, dates and various types of lettuce. Tainted alfalfa may be linked to trace perchlorate contamination detected in milk.² Cities from San Diego to Las Vegas to Tucson draw on the Colorado River for portions of their drinking water supply.

The health effects of perchlorate are not well understood. It is known to inhibit thyroidal iodine uptake, but little data is available to suggest "safe" levels. In 2002, EPA proposed a health-protective standard of 1 ppb for perchlorate in drinking water. This limit is currently being reviewed. State limits range from 1 ppb upward. Data concerning perchlorate from foods is even scarcer.

¹ Hogue, C. Chemical and Engineering News, 2003, 33, 37-46.
² Kirk, A.; Smith, E.; Tian, K.; Anderson, T.; Dasgupta, P. Environ. Sci. Technol., 2003, 37(21), 4979-4981.

CONDITIONS

CHROMATOGRAPHY

IC Column	250 x 2mm AS-16 (Dionex)
Eluent	65mM KOH in 60/40 water/methanol
Flow Rate	0.3 mL/minute

The addition of methanol to the eluent was found to somewhat improve chromatography, but more importantly, it greatly improves MS response due to better nebulization. Potassium is removed using a chemical suppressor and sulfuric acid regenerant.

ELECTROSPRAY

Needle Voltage	-5500V
Shield Voltage	-600V
Dry Gas	Air, 300°C, 22 psi
Neb Gas	Air, 53 psi

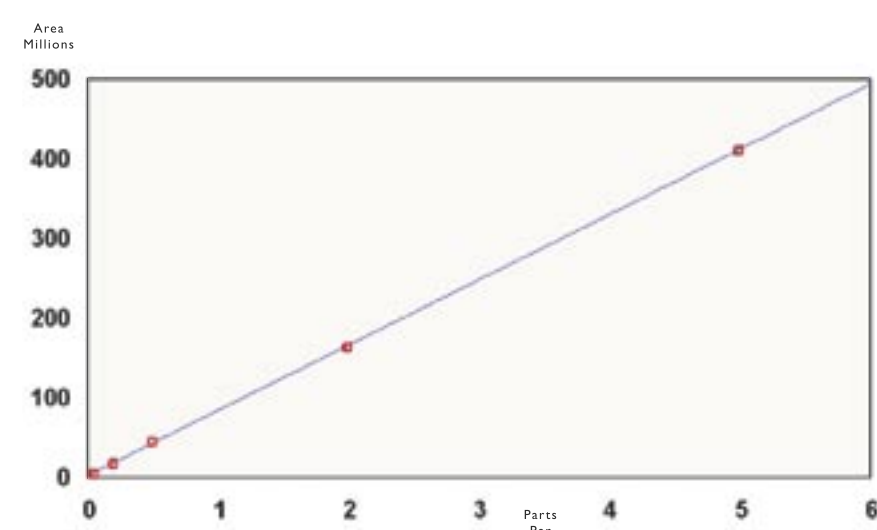
MASS SPECTROMETER

Capillary Voltage:	-40V
CID Gas	Ar, ~3.7 mTorr

TRANSITIONS MONITORED

m/z 99 → m/z 83	³⁵ ClO ₄ → ³⁵ ClO ₃
m/z 101 → m/z 85	³⁷ ClO ₄ → ³⁷ ClO ₃

Use of these masses enables confirmation of the perchlorate identity both by presence of each product ion and the natural chlorine isotope abundance.



Calibration curve from 0.02-5.0 ppb
 $r^2=0.9998$

RESULTS

All of the tested produce samples contained measurable perchlorate, as did water both from El Centro and our lab in Santa Fe Springs. Only the bottled water sample was perchlorate-free.

The annual produce samples ranged from 4.81 ppb in celery up to 28.2 ppb in green beans, possibly due to their lower moisture content. These showed good precision, with RSD less than 10 % for all matrices.

PRECISION

Matrix	n	Parts per Billion	%RSD
Tap Water (El Centro)	4	4.20	4.4
Tap Water (Santa Fe Springs)	4	1.89	5.4
Bottled Water	4	<0.02	N/A
Zucchini	5	11.6	8.7
Celery	5	4.81	6.3
Green Beans	5	28.2	4.5
Dates	3	36.9	16
Date Sugar	5	27.4	14

ACCURACY

Matrix	Average Sample Result	Spike Level	Average Spike Result	Recovery
El Centro Tap Water	4.20	5.00	8.88	94%
Zucchini	11.6	40.0	54.4	107%
Celery	4.81	40.0	40.5	89%
Date Sugar	27.4	200	217	95%

All results are parts per billion.

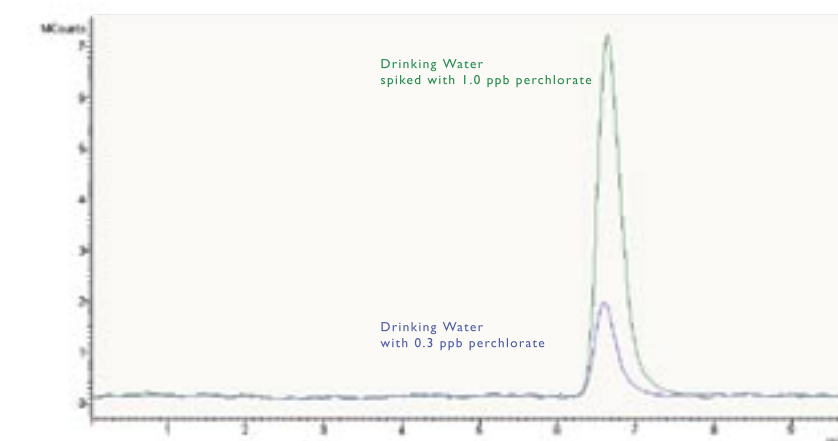
BAD DATES

The date samples had high levels of perchlorate, averaging 36.9 ppb for dates and 27.4 ppb for date sugar. (Date sugar consists of dried dates ground to a coarse meal.) These also exhibited poorer precision. This may be in part due to difficulty in homogenizing the dates, and the more complex matrix (especially increased sugar content).

CONCLUSIONS

Detection limits using existing IC methodology (1-2 ppb) are too high to accurately measure perchlorate at regulatory limits, which may be as low as 1 part per billion.

This method is an effective way of measuring low levels of perchlorate in water and produce. The detection limit is sufficiently low to permit accurate results at regulatory levels.



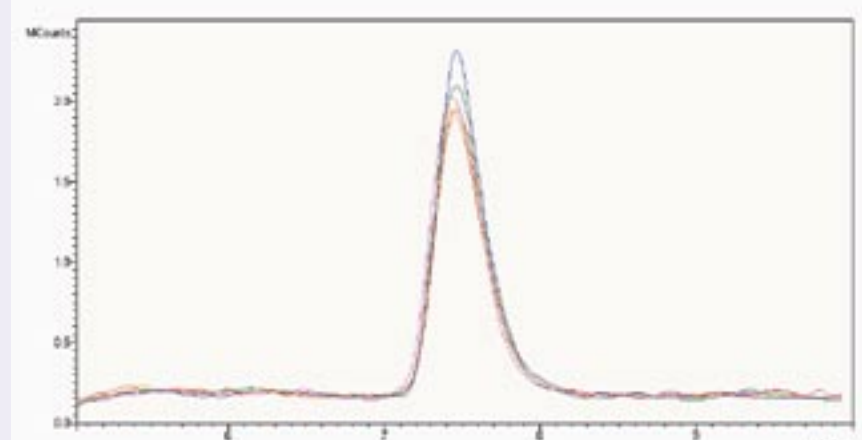
Bottled Water

FUTURE WORK

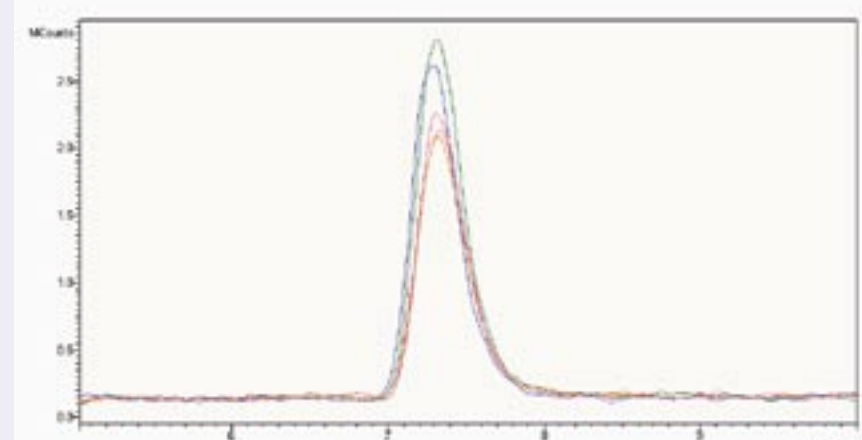
In the near future, we will be incorporating ¹⁸O-labelled perchlorate as an internal standard in order to improve the precision and accuracy of the analysis. We will also be investigating new chromatographic conditions which would eliminate the use of a hydroxide eluent, simplifying the system for electrospray use.

ACKNOWLEDGEMENTS

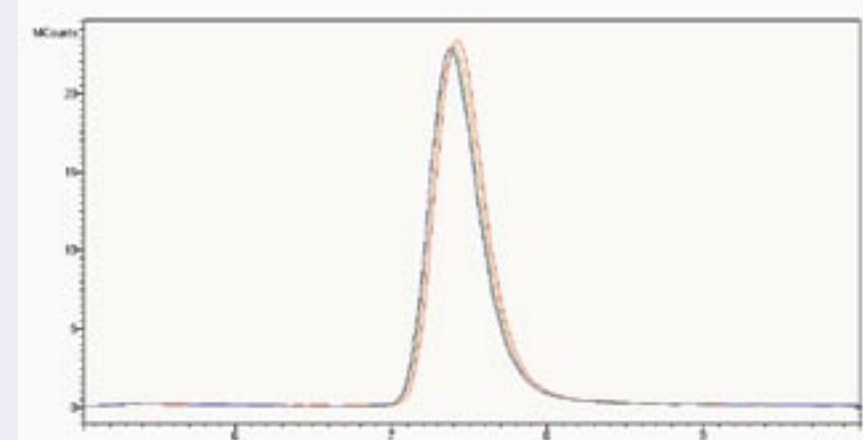
I would like to thank Dr. Jack Northington and WCAS for providing the facilities to carry out this work. Thanks also to Dewey Northington for Graphic Design of this poster.



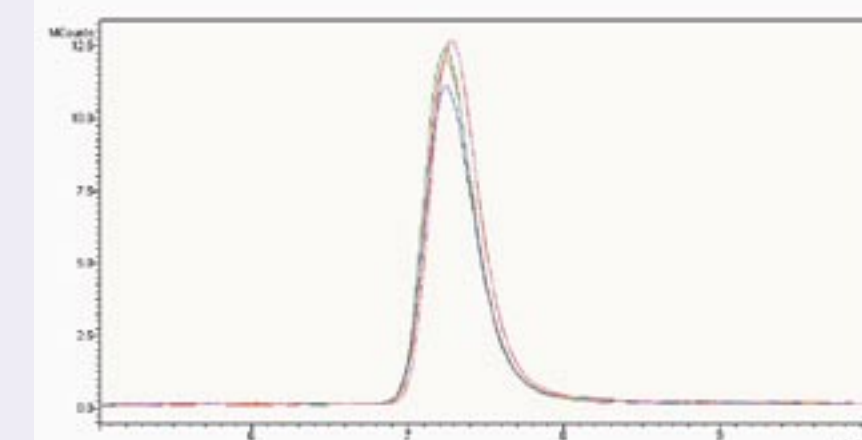
Celery



Date Sugar



El Centro Tap Water



Green Beans

These chromatograms show overlays of multiple preparations of each sample type. The precision, expressed as % RSD, is summarized in the Table above.