Water Analysis



PerkinElmer Partners with Weld County to Optimize Their Water Testing to Include Over 60 Organic Contaminants and a New Method for Methane

Weld County, Colorado, with a population of approximately 250,000 people covering over 4000 square miles, is the third largest by area and the ninth most populous of the 64 counties in Colorado. However, it's only when you read its mission statement on the Department of Public Health website do you begin to fully understand the importance it puts on the well-being of its residents¹.

Their public health laboratory is a strong indicator of the importance that Weld County puts on scientific research to achieve this goal. It works in conjunction with both the Environmental Health and the Public Health Education divisions to provide support for a variety of testing programs.

Maintaining the quality of the drinking water is one of the most critical functions of the laboratory. Currently it has nearly 50 drinking water and five waste water contracts for municipalities



"In partnership with the communities we serve, Weld County Department of Public Health and Environment preserves, promotes and protects the health and environment of the residents of Weld County, Colorado"

in and outside of Weld County. In addition, the laboratory acts as a regional laboratory in Northern Colorado by conducting bacteriological and chemical drinking water compliance testing for the adjoining counties. Their recent partnership with PerkinElmer exemplifies the importance they put on making sure that county water supplies are safe for its residents.



Safety Concerns of the Residents

As the result of a substantial increase in oil and gas development, and amid resident concerns over hydraulic fracturing activities, the Health Department submitted a request to County Commissioners to fund instrumentation to reassure residents that their well water was safe. Mark Thomas the chemist in charge of the evaluation had visited another customer's site to see a PerkinElmer Clarus® GC/MS system being used for EPA Method 524.2. He was very impressed with what he saw, and summed up the reasons why they decided to go with PerkinElmer:

"We were not certified to run Method 524.2 - The Measurement of Purgeable Organic Compounds in Water Using Capillary Column GC/MS; and only had very limited experience in running purge and trap methodology with GC. So we were looking for a vendor with a wealth of experience in this type of application, who was going to take care of us. Personal relationships are very important to us and I knew, based on past experiences working with PerkinElmer atomic spectroscopy instrumentation and currently in our own lab, that their application and service support people were the best in the business."



Mark Thomas, a Chemist with Weld County's Department of Public Health and Environment, running the Clarus GC mass spectrometer

EPA Method 524.2 Certification

Weld County Public Health Lab invested in a Clarus GC/MS system fitted with a purge and trap sample introduction system and entered into a three-phase collaboration project with PerkinElmer. The first phase of the collaboration was to install PerkinElmer's Turnkey system to run EPA Method 524.2², to ensure it met the criteria; and establish standard operating procedures (SOPs) for the laboratory. In this technique an aliquot of sample is purged of its volatile components by bubbling an inert gas through the sample. These volatile compounds are then trapped on a sorbent material, heated, and back-flushed into a GC column, where the analytes are separated and eluted into a mass spectrometer for detection.

Running this method was new for Mark, but with the help of the PerkinElmer team, including Tom Kwoka the local GC Sr. Product Specialist; Lee Marotta, the GC Field Application Specialist, and Mike Matovina, the GC service specialist, he quickly became an

expert. They were officially certified by the Colorado Department of Public Health and officially started testing samples under their certification. The certification process entails validating the method by running a three day Method Detection Limits (MDL) study and an Instrument Demonstration Study (IDS) involving the running of a group of checks for accuracy and precision. Additionally they also had to completed two Proficiency Testing (PT) samples from an outside source certification supplier. Certification was finally given upon an onsite inspection of personnel capability, method completeness, review of PT results, and the instrumentation being used for the analysis.

They currently test for 59 volatile organic compounds (VOCs), of which 28 are regulated by the State of Colorado primary drinking water regulations. Most of their customers are the residents of Weld County on private wells, but they have recently expanded the method to public water systems for the analysis of Total Trihalomethanes (TTHM) under EPA Method 524.2 (see later).

Testing Water Supplies for Contaminants from Oil and Natural Gas Drilling

The high visibility of fracking in the media has therefore resulted in property owners in those areas being concerned about the purity of their drinking water. For that reason, it has created an unprecedented demand for the testing of water samples for contamination components generated from "fracking". It is also possible that methane already exists at a low concentration in the aquifer from diffusion of the gas occurring naturally from the breakdown of biological materials.

EPA Method 524.2 came on line when the county began testing private well water for 59 organic compounds. Without this program, concerned residents who wanted to test their water for oil and gas drilling activity would have had to pay \$300 for a test. To date, in conjunction with the Colorado Oil and Gas Conservation Commission, over 200 private wells have been sampled and tested, and shown no signs of contamination.

Second Phase of Collaboration

The second phase of the collaboration involved developing a method for the measurement of the hydrocarbon gases (methane, ethylene, ethane and propane etc) in drinking water using headspace coupled with gas chromatography, which was adapted from EPA RSK-175, the analysis of dissolved gases in drinking water³. Headspace is a term used to describe the gas space above the sample in a headspace vial, where the volatile components diffuse into the gas phase, forming the headspace gas⁴. The hydrocarbon gases including methane are very efficiently partitioned into the headspace gas volume above the liquid sample⁵. However, the main challenge with this application was to use the same instrument to run both the purge and trap procedure for Method 524.2 together with headspace method, and yet also be able to carry out a liquid-liquid injection for other types of samples and analytes. This point was emphasized by Mark:

"Other vendors wanted to sell us two GCs' one for GC-MS solely and another one for the headspace work. Our budget wasn't that open ended and lab space was also limited. The benefit of going with the PerkinElmer system and particularly with Lee's and Tom's expertise, and experience, was that we were able to develop methodology for all sample types on the same instrument."

Third Phase – Determination of Halo Acetic Acids in Drinking Water

Developing a method for the determination of Halo acetic acids (HAA) in drinking water will be the third phase of the collaboration. Together with the TTHMs, halo acetic acids are a group of chemicals that are formed along with other disinfection by-products when chlorine or other disinfectants are used to control microbial contaminants in drinking water, react with naturally occurring organic and inorganic matter in water. The regulated halo acetic acids (known as HAA5), are monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid. If there is too much chlorination, these target analytes will be at a level that can impact human health and our environment. Weld County Health Department and PerkinElmer will collaborate to develop this method using MS detection instead of the traditional Electron Capture Detection (ECD) used in EPA Method 552.3 - The Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-Liquid Extraction, Derivatization and Gas Chromatography Coupled with ECD6.

The plan is therefore to utilize the liquid autosampler connected to their GC system for this analysis in addition to the purge and trap autosampler for the volatile organic compounds and the Headspace autosampler for methane. Once the HAA5 method has been developed, the advantage of using MS detection instead of ECD is that you have identification of the target compounds and do not need to use the more complicated dual column approach needed when using an ECD. The other advantage is that it will not only allow Weld County to streamline its analytical methods for these components in drinking water, but it will also help other water authorities save money and realize a faster ROI, since they will only need to invest in one GC with FID and MS system instead of three to run all three applications.

All this testing has given residents of Weld County added peace of mind. It won't quell all the fears, but it does provide an important measure of confidence that their drinking water supplies are safe. And with all the samples being run in-house, as opposed to sending the work out to contract labs, analytical turnaround times have been literally cut in half. Furthermore, not many labs in the state are capable of testing for methane, ethane and propane. Mark Thomas summed up the benefits of this increased testing:

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"Every time we offer the testing to a resident of the County who is not aware of the testing program, the excitement and gratitude in their voice captures the essence of what we have accomplished. There is no question that our collaboration with PerkinElmer has made a significant contribution to this fact. I

just want to emphasize that we have enormous respect for the company, but it is the credibility of the people who have made this partnership so successful. Every person we have worked with is personable and an absolute pleasure to work with."

We feel very much the same towards Mark Thomas and Weld County Public Health Laboratory and are very proud to call them one of our most valued customers.

Further Reading

- Weld County Department of Public Health and the Environment Website: http://www.co.weld.co.us/Departments/ HealthEnvironment/AbouttheHealthDepartment/index.html
- EPA Method 524.2 The Measurement of Purgeable Organic Compounds in Water Using Capillary Column GC/ MS: http://water.epa.gov/scitech/methods/cwa/bioindicators/ upload/2007_11_27_methods_method_524_2.pdf
- Analysis of Dissolved Methane, Ethane, and Ethylene in Ground Water by a Standard Gas Chromatographic Technique; D. H. Kampbell and S. A. Vandegrift, Journal of Chromatographic Science, Vol. 36, 253256, May 1998
- 4. The Determination of Low Level Benzene, Toluene, Ethyl Benzene and Xylenes (BTEX) in Drinking Water by Headspace Trap GC/MS; Lee Marotta, PerkinElmer Application Note: http://www.perkinelmer.com/CMSResources/Images/44 131604APP_HeadSpaceTrapGCMSLowBenzine.pdf
- Methane, Ethylene, and Ethane in Water by Headspace-Gas Chromatography (HS-GC) with Flame Ionization Detection (FID); Lee Marotta and Dennis Yates, PerkinElmer Application Note: http://www.perkinelmer.com/CMSResources/Images/ 44-131604APP_HeadSpaceTrapGCMSLowBenzine.pdf
- EPA Method 552.3 The Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-Liquid Extraction, Derivatization and Gas Chromatography Coupled with Electron Capture Detection: http://www.epa.gov/ogwdw/methods/pdfs/ methods/met552_3.pdf

