

**14<sup>th</sup> ANNUAL GOOD LABORATORY PRACTICE CONFERENCE SCHEDULE**  
**August 5, 2008**

**MORNING:**

**Current Issues and Challenges**

**8:30-8:45      Welcome & Introduction**

*(Alicia Connelly, VA AWWA/VWEA LPC Chair)*

**8:45-9:30      Update of Current Activities in the USEPA CWA Methods Program**

*(Richard Reding, Ph. D, US EPA – Engineering and Analytical Support Branch)\**

We will provide an update of current activities in the CWA methods program. We have ongoing projects to refine analytical methods to measure contaminants of emerging concern, such as surfactants, OTC/Rx drugs, and steroids in wastewaters. We also are evaluating rapid qPCR methods for the determination of enterococci in recreational waters. We also are moving forward on implementing recommendations of the federal advisory committee for estimating laboratory detection and quantitation limits.

**9:30-10:15    Protecting our Water Supplies in National Capital Region (NCR) with a Contaminant Warning System\***

*(Jim Shell, Metropolitan Washington Council of Governments (COG) ) \**

The National Capital Region (NCR) has nearly 5 million inhabitants. Geopolitically, it is a complex region comprised of two states and the District of Columbia, 19 local governments and more than 23 public and independent drinking water utilities, authorities and commissions that treat and distribute drinking water. Public water systems in the NCR serve more than 4 million customers, approximately 670 government-owned and leased regional buildings, and prominent national “icon facilities” such as the U.S. Capitol, the Whitehouse, the world-class museums of the Smithsonian Institution, and memorials along Washington’s famed Mall. Consequently, water systems in the NCR face unique challenges related to both potential terrorist threats and natural disasters.

Shortly after September 11, 2001, water utilities, local governments, state, federal and regional public agencies convened a special Water Security Workgroup under the umbrella of the Metropolitan Washington Council of Governments (COG) and its ad hoc Work Group on Homeland Security for the National Capital Region. The goal of that Work Group is to insure the security, safety, and reliability of drinking water supplies and distribution systems in the NCR. Toward that end a number of projects have been implemented. One component of that comprehensive water security program was the development and implementation of a regional contaminant warning monitoring system using state-of-the-art technologies.

Nearly 90 percent of the drinking water supply comes from the Potomac River with the remainder obtained from other rivers, lakes, streams, and ground water sources in the Potomac River basin. As a result, implementation of a monitoring system that can provide reliable and timely data regarding the quality of the water supply is an essential element in helping insure that the region has sufficient warning time for local action in the event of an accidental or deliberate release of contaminants into the Potomac. A companion monitoring system for the various distribution systems is also of critical importance to water supply security. The presentation will cover the comprehensive water security

approaches that have been undertaken in the NCR and specifically the issues and challenges faced in creating a regional water security monitoring network.

10:15-10:45 **BREAK**

10:45-11:15 **The Detection and Removal of Endocrine Disruptor Compounds (EDCs) and Pharmaceuticals in Waste Water and Drinking Water: A Laboratory Challenge\***  
(Roy L. Williams, Ph. D., Professor Emeritus, ODU)

Over the past few months the American public has become increasingly aware of the presence of extremely low levels of a wide variety of natural and synthetic chemicals in many of the nation's drinking water sources. Many of these compounds, which have been detected in the ppb range, are often described as endocrine disruptor compounds or EDCs. Such compounds are quite capable of interacting and modulating hormonal activity in a variety of aquatic life and may pose some level of risk as a health issue to the drinking water industry. Although these EDCs and many of the pharmaceutical contaminants have undoubtedly found their way into some drinking water sources, the real question is what are the toxicological based limits for such chemicals in the water. The presence of these types of chemicals has only come to light as a result of our advanced analytical instrumentation and laboratory techniques. These new analytical methods now allow us to detect such compounds in the ppb range, and it has been suggested that presence or absence should not be considered as a toxicological endpoint in regards to health issues.

This paper will discuss the types of compounds that have now been categorized as potential EDCs; the current knowledge regarding effectiveness of water treatment processes in removing EDCs and pharmaceuticals from water sources; and a review of the current analytical methods used to detect the compounds in source waters and finished drinking water. To date, there are no regulations regarding the acceptable level of any of these environmental contaminants.

11:15-11:45 **Emerging Contaminants: The Science Behind the Headlines \***  
(Jamie Heisig-Mitchell, Hampton Roads Sanitation District)

Much media attention has been placed on occurrence of emerging contaminants in our nation's surface waters, with specific emphasis on the detection of pharmaceuticals and suspected endocrine disrupting compounds. Numerous questions exist concerning the potential for these compounds to impact aquatic life and human health. What is known and what research is necessary to address the gaps in the knowledge? What are the regulatory implications? This presentation will review the science behind the headlines and will address the potential impact on the wastewater treatment community.

## **AFTERNOON**

### **Session #1:**

1:15-1:45 **What a Cat Fight it Can Be: Free Chlorine vs. Chloramine: A DBP Formation Study at Fairfax Water\***  
(Melissa Billman, Fairfax Water)

Fairfax Water (FW), the largest drinking water utility in Virginia serving over 1.4 million residents in the Northern Virginia Metro area, has a long record in utilizing chloramine as a disinfectant. Chloramination at FW began in 1979, to combat the formation of a particular

group of DBPs, Total Trihalomethanes (TTHM). New DBP regulations were on the forefront in the late '70's which caused FW to re-think its disinfection strategy and ultimately make the switch. Again, in the 1990's and 2000's DBP regulations were being reviewed along with many other new regulations, thus creating a balancing act for most utilities to stay "above water" on all regulations.

Through the decades FW has been preparing for future regulations in many ways, the DBPs being one of the most concentrated areas of effort. Treatment plant upgrades and new-builds to add ozonation, enhance coagulation, and utilize granular activated carbon are the primary means by which these regulatory limits have been met.

FW's success in lowering the DBPs due to the combination of these treatment changes/additions prompted a decision making process to settle which type of disinfectant should be used in the future. Thus, the DBP Formation Study began.

The DBP Formation Study simulated the distribution system during the peak season for high DBP concentrations while disinfecting with Free Chlorine and then again under similar conditions with Chloramines. Timed aliquots were taken between zero and 168 hours to simulate the range of residence times in the distribution system. These samples were tested for TTHM's and Haloacetic Acids (HAA), as well as support analytes: pH, chlorine residual, Total Organic Carbon (TOC), and temperature.

In addition to the main study, a periphery study was performed on the FW distribution system and three wholesale customer distribution systems which purchase bulk water from FW. Due to FW's practice of supplying the best water quality available to the customers, it was important to research the effect of Free Chlorine on the wholesale customer system as well as the FW retail system. In some instances the wholesale customers have longer retention times than the FW distribution system. This study was performed on potential Maximum Initial Distribution System Evaluation (IDSE) sites, during the peak concentration season for DBPs while utilizing Free Chlorine as the primary disinfectant. The study was able to show real-time data under extreme conditions, thus giving a harbinger of whether future DBP regulations will be met.

The results of this research can aid management in making a very important decision: whether to use Chloramine or Free Chlorine as the primary disinfectant. Pros and cons for each of the disinfectants are evident, but having this type of research and facts to stand on will make decisions more clear cut.

1:45-2:15

### **New EPA Methods Using 2-D IC for Bromate (302.0) and Perchlorate (314.2) Determination for Enhanced Selectivity and Sensitivity\***

*(Richard Jack, Dionex)*

Bromate is commonly formed from the ozonation of bromide in drinking water and has determined to be a human carcinogen. Currently, bromate is regulated in drinking water at 10 ug/L. EPA Methods 300.1 B, 317.0, and 326.0 are approved by the US EPA for compliance monitoring. High concentrations of common anions, such as chloride, sulfate, and carbonate, can produce poor bromate peak shapes and lower recoveries. This often requires the analyst to either dilute the sample which raises the minimum reporting limit (MRL) or pre-treat the sample offline prior to analysis. Pretreatment of samples requires increased time and cost for each analysis. Therefore, the objective of this project was to develop a method that eliminates high concentrations of matrix ions and minimizes interferences. This paper describes two new EPA pending methods using two-dimensional

(2D) ion chromatographic (IC). In the first dimension, a large loop is injected on a 4-mm high capacity ion exchange column to separate bromate from matrix anions. Bromate is selectively removed using automated valve switching onto a concentrator column. In the second dimension, Bromate is separated a second time using a 2-mm anion exchange column followed by quantitation after suppressed conductivity detection. This strategy allows the ability to inject large sample volumes, focus bromate partially resolved in the first dimension onto a concentrator column and separate it on a second, higher resolution column. It also combines two different column chemistries to enhance selectivity and reduce the possibility of false positives and eliminates the need for second column confirmation. This method also improves upon EPA Method 314.0 and 314.1 for the determination of perchlorate in drinking water, even in the presence of high salt matrices (>1,000 mg/L for Cl<sup>-</sup>, SO<sub>4</sub> and NO<sub>3</sub>). The new method results in a 4-fold signal enhancement, which yields a lower detection limit (0.016 µg/L).

2:15-2:45 **BREAK**

2:45-3:15 **A New and Easy Gravimetric Approach to Basic Chemistry Kit Testing\***  
(*Frank Locrone II, Hawk Creek Laboratory, Aqua Phoenix Scientific*)

Hawk Creek Laboratory, Inc, established in 1980 is a division of AquaPhoenix Scientific, located in Hanover PA. The primary core of our business is producing quality analytical reagents and customized test kits. We have recently developed a new test kit called *The GraviTek*<sup>TM</sup> and would like to present it at one of the technical sessions. Please see the attached spec sheet providing additional information about kit.

This test kit was presented at last year's conference and received much enthusiasm. The downside was the lack of EPA compliance; which we are currently completing 40 CFR 136.6, Method Modifications requirements to have available for this year's meeting.

3:15-3:45 **How the USEPA Method Update Rule (MUR) Can Positively Affect and Benefit Your Laboratory\***  
(*Lynn Egan, LACHAT Instruments, HACH*)

Lachat Instruments, is a leader in wet chemistry analysis. Lachat is also known for their reliability and market proven applications/methods that come with assurances that these methods will work.

Lachat Instruments has been actively developing methods for analysis both in the regulatory environment and in other areas where wet chemistry methods are applicable.

The most recent EPA Methods Update Rule (MUR) modified the testing procedures approved for chemical analysis and sampling under the Clean Water Act and Safe Drinking Water Act. EPA proposed these changes for public comment on August 18, 2003 and April 6, 2004. Final Rule was promulgated March 12, 2007.

The changes made to the Clean Water and Safe Drinking Water Act, adopted in these final rules, provided increased flexibility to the regulated community as well as to laboratories. This flexibility applies to both the selection of analytical methods and to modifications to methods within the scope of these rules.

How does this affect your lab and how is Lachat Instruments helping your laboratory maximize the benefit with these changes? Learn how Lachat Instruments has helped many

laboratories with documentation and reporting, efficiency and throughput and above all meeting the Method Update Rulings requirements for EPA equivalency testing.

**Session #2:**

1:15-1:45

**Trace Level Analysis of Pesticides Residue and Emerging Contaminants in Drinking Water with ON-line SPE/LC/MS/MS \* (Claude Mallet, Waters)**

Many countries around the world have strict regulatory guide lines for drinking water quality. To satisfy legislative requirements, analytical methods have been developed to monitor a wide range of contaminants at trace levels using analytical techniques such as gas chromatography/mass spectrometry (GC/MS) or liquid chromatography/ mass spectrometry (LC/MS/MS). The US EPA is mandated by The Safe Drinking Water Act Amendments to publish a contamination candidate list every 5 years with the main objective to identify new health threats for regulation. Lately, pharmaceuticals, hormones and endocrine disruptors were categorized as emerging contaminants due to their detection in environmental waters. It is estimated that well over 3 000 chemicals, such as painkillers, antibiotics,  $\beta$ -blockers, antidepressants, illicit drugs and over-the-counter drugs (OTC's) are introduced in drinking water sources. Pharmaceuticals are not only introduced by human activities, but also through veterinary drugs used in livestock. The presence of those chemicals is causing a major concern regarding the creation of bacterial resistance and adverse health effects on human and wildlife.

In order to achieve trace level analysis, large sample volumes are usually extracted using various OFF-Line extraction methods (ex: solid-phase extraction (SPE), liquid-liquid ...etc) and concentrated into a smaller volume. A typical extraction method usually starts with a 500 mL of sample and ending up with a final volume of a 100  $\mu$ L (5 000: 1 enrichment ratio). If higher sensitivity is required, the only alternative left is to process larger sample volume, but will require an increase in manual labor. Manual extraction protocols have reached the end of their limited range. A few years ago, SPE cartridges were reformatted into an extraction column. By combining the extraction column, analytical separation column, LC, MS and software, a system is created known as "ON-Line SPE/LC/MS/MS". A major advantage of this integrated platform is the elimination of the labor intense evaporation and reconstitution steps in favor of a direct elution into the mass spectrometer.

This research will discuss the performance of ON-line SPE/LC/MS/MS for the analysis of pesticides residues and emerging contaminants in drinking water. Two major advantages are the reduction of sample volume from 1 liter to a 20 mL sample and sub ppt detection limits. Overall, the extraction protocol was reduced from 3-5 hours to less than 5 minutes. Various pharmaceuticals were analyzed in drinking water sample such as tricyclic antidepressants, illicit drugs and benzodiazepines. Also, over-the-counter drugs, such as anti-allergy, anti-acid, cough suppressants and anti-fungal were screen in drinking water sample from local towns and privately own wells.

1:45-2:15

**Non-Hazardous Automated Colorimetric Method for Nitrate Analysis \* (Craig R. Chinchilla, Syntea Scientific LLC)**

Several methods exist for the determination of Nitrate in aqueous solutions; however, the most commonly performed automated colorimetric methods utilize toxic substances and generate hazardous waste (Nitrate reduction by Hydrazine and Cadmium). Since there is

no hazardous waste generated when performing the method, disposal costs are minimized or eliminated. The method has been specifically developed for discrete analysis which enables it to truly run unattended, thus greatly reducing labor and improving laboratory productivity.

The procedure for the determination of Nitrate utilizes the reaction in which Nitrate is reduced to Nitrite by a proprietary Reagent "R1". The reaction is slow and requires greater than 12 minutes for 100% reduction of Nitrate to Nitrite at 50°C. The reduced Nitrate is then treated with Sulfanilamide and N-1-naptylethylenediamine dihydrochloride under acidic conditions to form a highly colored soluble dye which is measured colorimetrically between 520-550nm. The final product measured represents the Nitrite ion originally present, plus that formed from the reduction of Nitrate (Nitrate+Nitrite). In order to determine the true Nitrate concentration, the sample must also be analyzed separately for Nitrite to determine the amount originally present in the sample. The value obtained for Nitrite is, then, subtracted from the Nitrate+Nitrite value to determine the true value for Nitrate.

The method utilizes automated discrete analysis. Discrete analysis is rapidly becoming the preferred technique for environmental ion analysis in laboratories throughout the United States. The advantages of using discrete technology for the analysis of nutrients is significant compared to the traditional continuous flow, and flow injection analysis methods. Some examples include: ease of use, waste minimization, reduced reagent consumption, and true unattended operation. The USEPA has recently accepted the use of discrete technology for environmental ion analysis.

The method has several advantages over USEPA methods 353.1 Nitrate Hydrazine Reduction, and 353.2 Nitrate Cadmium Reduction. Perhaps the most significant advantage is the elimination of hazardous waste generation and exposure of cadmium and hydrazine to laboratory personnel. The method utilizes a non-hazardous reducing agent. The traditional EPA methods mentioned above, use chemicals that are carcinogenic and highly toxic. Thus, by switching to a method that uses a non-hazardous reducing agent, personnel and the environment are protected. Performing the method on a discrete analyzer further reduces the amount of chemicals used and waste generated. Discrete analysis usually reduces waste generation to 1/3 - 1/6 over traditional flow analysis techniques.

Analytical performance is also dramatically improved over traditional methods. Regardless of the sample matrix, recovery of Nitrate to Nitrite is consistently between 95% and 105%. In the cadmium reduction method of Nitrate, the reduction efficiency consistently changes over time. Depending on the matrix, efficiency of the cadmium reduction can change rather quickly. Charging and recharging of the cadmium coil or column used in the method, can also be uncertain from procedure to procedure. The introduction of air into a cadmium coil or column can also reduce the efficiency of the reduction. With the use of hydrazine, adjustments to the reagent quantity must be made for proper reduction. Thus, by using the method which consistently reduces Nitrate to Nitrite, analytical performance is greatly improved.

The Method Detection Limit (MDL) for the method is equivalent or better than using the USEPA methods 353.1 Nitrate Hydrazine Reduction and 353.2 Nitrate Cadmium Reduction. Thus, performance is not compromised by switching to the new method.

Analytical costs associated with performing the new Systea Easy (1 – Reagent) Nitrate method are also greatly reduced. Waste disposal charges are becoming a greater expense

for analytical laboratories. Since there is no hazardous waste generated when performing the proposed method, disposal costs are minimized or eliminated. Also, since there are no cadmium coils to be recharged or hydrazine reagent concentrations to adjusted, less labor is involved. Finally, since the method has been developed for the discrete analyzer, the method can truly run unattended; therefore, greatly reducing labor and improving laboratory productivity.

The method also eliminates matrix interference problems. In the traditional method utilizing cadmium as a reducing agent, high organics and surfactants such as Brij-35 can alter the effectiveness of the reduction. Oils and grease commonly found in waste water can also reduces the efficiency of the reduction by coating the surface of the cadmium. When using the hydrazine method, high chlorides are known to interfere with the reduction. After extensive testing on various matrices, no matrix interference problems have been observed when using reducing agent "R1".

In conclusion, the method has several advantages over traditional Nitrate methodology. Exposure of personnel to hazardous substances, and the generation of hazardous waste are eliminated. Performing the method by discrete analysis greatly reduces labor costs and improves laboratory productivity. After extensive testing, no matrix interference problems have been observed, and recovery is consistently between 95% and 105%. The method is a dramatic improvement over traditional automated colorimetric methods.

2:15-2:45 **BREAK**

2:45-3:15 **Biochemical Oxygen Demand Part I: Preparation and Planting\***  
*(Kerri Williams, Hampton Roads Sanitation District)*

This talk will provide an introduction to Biochemical Oxygen Demand (BOD), including an overview of the method, application and environmental impact with regard to treatment plant effluent. In addition, examples of sample preparation, pH adjustment, dechlorination, and planting techniques will be covered with details of how to troubleshoot errors attributed to these key elements. The importance of proper preparation and handling of dilution water and seed material will also be covered.

3:15-3:45 **BOD Part II: Initial and Final Dissolved Oxygen\***  
*(Reginald Morgan, Hampton Roads Sanitation District)*

This talk will begin with a brief summary of the topics covered in the preceding presentation: Biochemical Oxygen Demand Part I. Aspects of Dissolved Oxygen measurement will be covered including calibration and use of dissolved oxygen meters and probes. Proper technique for obtaining initial and final dissolved oxygen readings will be covered including suggestions on how to improve and or troubleshoot common problems associated with dissolved oxygen readings related to BOD. Additional aspects of the test to be discussed include automation, Winkler titrations, introduction of seed material to samples, incubation of bottles and calculations of BOD results.

### **Session #3**

1:15-1:45 **Stage 2 Disinfectant By-Product Rule: Laboratory Issues\***  
*(Sherry Williams, Newport News Waterworks)*

Utilities across the state have either submitted or will be submitting monitoring plans to conduct the required Initial Distribution System Evaluation (IDSE) under Stage 2 of the Disinfection/Disinfectant By-Product Rule (Stage 2 DBPR). Laboratories will not only be impacted by the increase workload of analyzing many more THM and HAA samples but also by additional and more stringent quality control requirements of Stage 2 DBPR. These changes include Performance Evaluation (PE) sample approval criteria, Minimum Reporting Limit check samples, and modifications to holding times of samples and analytical methods. This presentation will review these changes and briefly compare new approved analytical methods under Stage 2 DBPR.

1:45-2:15 **Using Commercial Laboratories for Important Compliance Data Prudent Assessment Practices in the Quest for High Quality Data**

*(Rock J. Vitale, CPC, CEAC, Environmental Standards Inc.)*

Even with national accreditation, the commercial environmental laboratory marketplace is fiercely competitive, continues to undergo consolidation and results in highly variable data quality. Accordingly, many industrial entities have found it prudent to install quality metrics when contracting with commercial environmental laboratories as a measure to gauge their environmental liabilities and in some cases to actually comply with administrative consent orders. On-site audits by qualified representatives is an excellent method of gauging data quality

During the performance of a number of commercial laboratory audits, a full spectrum ranging from “best practices” to questionable practices were observed. Other interesting observations which will be presented include a variety of pitfalls with respect to generating internal limits for quality control samples, the roles and responsibilities of a QA Manager and variety of approaches to the corrective action process.

2:15-2:45 **BREAK**

2:45-3:15 **Student Program To Reach Out To Our Next Generation**

*(Susan Miller, Fairfax Water)*

Drinking water providers have an obligation to reach children and teach them about the importance of source water protection and drinking water quality. This paper will discuss the importance of connecting with our young customers in the community and Fairfax Water’s experience working with students. We have found most students to be thirsty for knowledge about drinking water quality and very willing to learn. Fairfax Water formally implemented a student project program in the 1990’s. In this program, members of Fairfax Water laboratory staff mentor and assist students with projects related to water quality. Laboratory space, time, supplies and training from analysts are also supplied by the utility. Many students and parents also seek assistance with science fair project ideas, research and assistance with utilizing the Scientific Method. We have found our website and referrals from parents and teachers can greatly help to spread the word about the ways our utility can be of assistance to students. In January of 2006 a home owner’s association in northern Virginia, approached Fairfax Water with a request to set up an interactive visit to our laboratory for science camp participants. Over a period of five days, sixty-five campers ranging in age from eight to twelve visited Fairfax Water’s new laboratory facility and experienced the life of a lab analyst in training. Through the years, student interest in this program has skyrocketed and we have seen science fair projects increase in technical

difficulty as well. The successes of this program will be discussed along with aspects we have learned along the way. Fairfax Water's student project program has proven to be successful in extending our utility's outreach in the community.

3:15-3:45

**The Rewards of Sewer Science Outreach Program for HS Students**

*(Judy Fincham, Wastewater Management, Fairfax County)*

Fairfax County Wastewater Management is increasing water quality awareness in local high schools through the Sewer Science Program. Sewer Science is an educational initiative of the Water Environment Federation that simulates the wastewater treatment process through a week long laboratory class. Fairfax County Wastewater Management provides the laboratory equipment, supplies and workbooks for students and teachers. The week long program simulates wastewater treatment processes such as primary clarification, biological secondary treatment, disinfection, filtration and ammonia reduction. Students prepare simulated wastewater and analyze the treatment process while learning about basic water quality parameters such as pH, ammonia, chemical oxygen demand and turbidity. Sewer Science is in alignment with the Virginia Standards of Learning (SOLs) for biology and chemistry. Employees of wastewater management serve as mentors and assist the teacher and students to facilitate the program. The program was introduced into Fairfax County high schools in 2005. As of June 2008, approximately 4,615 students and 18 schools will have participated in the Sewer Science Program.

**\* 0.5 CPE Credits available for presentation**