CASE STUDY 73618

Fast, direct analysis of disinfection byproducts, including nine haloacetic acids (HAA9), bromate, and dalapon using IC–MS/MS per U.S. EPA Method 557

Ensuring safe drinking water—rapidly and cost-effectively

Clean drinking water is critically important to human health. Typically, both mechanical and chemical processes are needed to ensure drinking water quality; however, the by-products of chemical processes can include chlorinated to halogenated acids (HAAs) and bromate among others. Because excessive consumption of these compounds can result in severe health issues, drinking water regulations require determination of the concentrations of disinfection by-products (DBPs) prior to release to the public.

Depending on the analytical method chosen, analysis and quantitation of DBPs can pose several challenges including time-consuming and tedious sample preparation and poor recoveries. The Erie County Public Health Laboratory has addressed these challenges with the adoption of a direct-injection ion chromatography-tandem mass spectrometry (IC–MS/MS) method that uses the Thermo Scientific™ Dionex™ ICS-5000 HPIC™ System coupled to the Thermo Scientific™ Quantiva™ triple quadrupole mass spectrometer (equivalent to the Thermo Scientific™ Dionex™ ICS-6000 HPIC™ system and Thermo Scientific™ TSQ Fortis™ triple quadrupole mass spectrometer). Quantitation of target DBPs in drinking water per U.S. EPA Method 557 is robust, reliable, reproducible, and requires no sample preparation, allowing significant time, hazardous waste, and cost savings. Most significantly, Erie County Public Health Laboratory has reduced HAA determination time from approximately four hours to about 45 min per sample.

"We use IC–MS/MS over GC-ECD for HAAs determination, because the GC-ECD method is very labor intensive and fraught with recovery issues."

— Gerhard Paluca, BA, Senior Sanitary Chemist, Erie County Public Health Laboratory

ThermoFisher SCIENTIFIC

> "By going from a GC-ECD to an IC–MS/MS method, we've saved substantial analyst time performing extractions. We used to need four hours to extract a sample batch."
>
> — Gerhard Paluca

Disinfection by-product formation

HAAs, bromate, and dalapon are formed when chlorine disinfectant reacts with naturally occurring organic and inorganic matter in water. The U.S. EPA Unregulated Contaminant Monitoring Rule (UCMR 4) specifies Assessment Monitoring for three haloacetic acid (HAA) disinfection by-products groups, which cover the nine species of HAAs referred to as HAA9. Of the nine species of HAAs, five are currently regulated by the U.S. EPA and require compulsory testing: monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA). The remaining four are bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), and tribromoacetic acid (TBAA). Bromate can arise as a by-product of the ozonation of bromide-containing water depending on the conditions (pH, temperature, etc.) at the treatment site.

Analytical methods

The most established method for the and charged of HAAs in drinking water uses gas chromatography with electron capture detection (GC-ECD) per U.S. EPA Method 552.3, which is limited to HAAs only. However, GC-ECD methods require time-consuming derivatization and multiple extraction steps. GC-ECD run times are typically 25 to 30 min, but with sample preparation, the total analysis time per sample can be up to four hours. In contrast, U.S. EPA Method 557 is a direct IC–MS/MS method for the determination of HAAs that eliminates sample preparation and associated solvents for significant time and cost savings. In addition, U.S. EPA method 557 covers more compounds than U.S. EPA Method 552.3: HAA9, as well as bromate and dalapon (regulated herbicide).

Benefits of IC–MS/MS

IC offers significant benefits for the determination of HAAs owing to its ability to separate polar and charged molecules, while MS detection provides the sensitivity and selectivity required to achieve reliable analytical results. Compared to GC-ECD methods, IC–MS/MS methods provide better recoveries, making it easier to meet proficiency standards. Most importantly, according to Gerhard Paluca, Senior Sanitary Chemist, Erie County Public Health Laboratory, "IC–MS/MS has the advantage of eliminating labor-intensive sample extraction. We freed up chemists' time to perform other analyses, improving our efficiency with limited number of staff. In addition, the extraction time associated with the GC-ECD method limited the number of samples that we were able to run to only 10 to 12 per day. Now we easily run 20 samples over 24 hours. This matches the U.S. EPA recommendation to run 20-sample batch sizes, which includes calibration standards and QC samples."

"GC-ECD method recoveries aren't great, making it more difficult to pass required biannual drinking-water proficiency tests. IC–MS/MS provides reliably improved recoveries, increasing our confidence in results and reducing our repeats."

— Gerhard Paluca

Thermo Scientific solution saves time, reduces costs

The IC system used by the Erie County Public Health Laboratory is the Thermo Scientific™ Dionex™ Reagent-free IC (RFIC) system with eluent generation (RFIC-EG). With automated creation of IC eluents and regenerants, the laboratory further reduces labor and solvent costs, while achieving highly reproducible separations. In addition, the new stationary phase of the Thermo Scientific™ Dionex™ IonPac™ AS31 column reduces U.S. EPA Method 557 run times compared to the Thermo Scientific™ Dionex™ IonPac™ AS24 column, further increasing laboratory efficiency. According to Paluca, "the AS31 column shortened our analysis time, shaving off about 15 min compared to the AS24 column." Overall, by eliminating lengthy extractions, shortening chromatographic separations, and using eluent generation, the Thermo Fisher Scientific total solution enables the laboratory to analyze 20 samples per day, meeting U.S. EPA batch size recommendations.

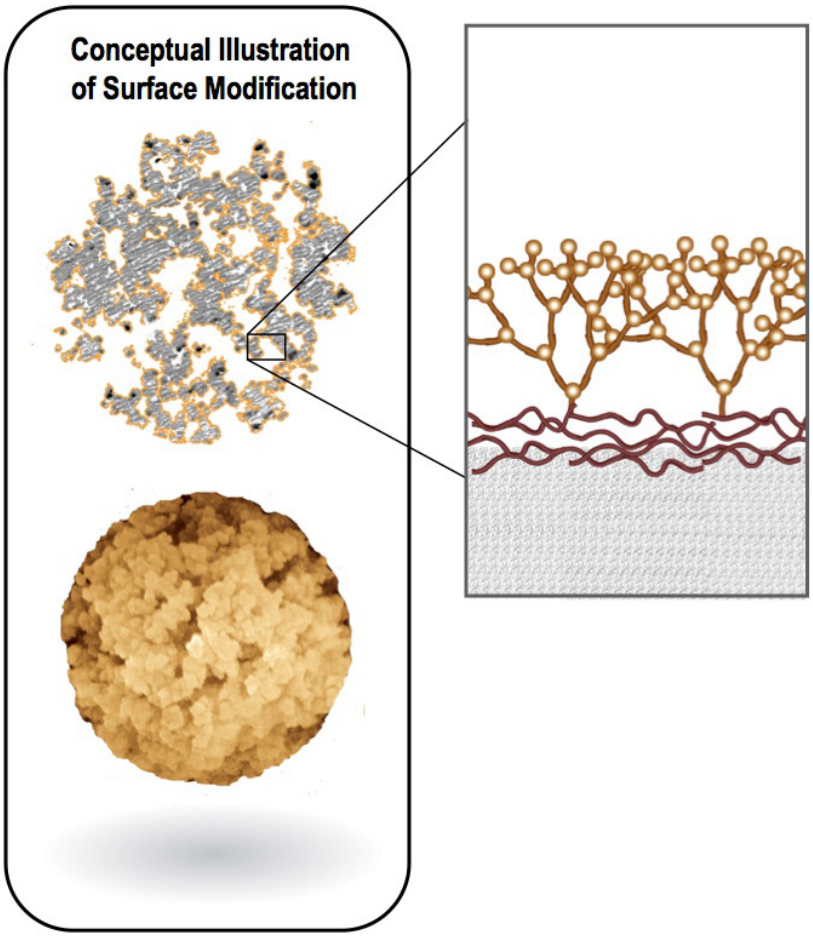
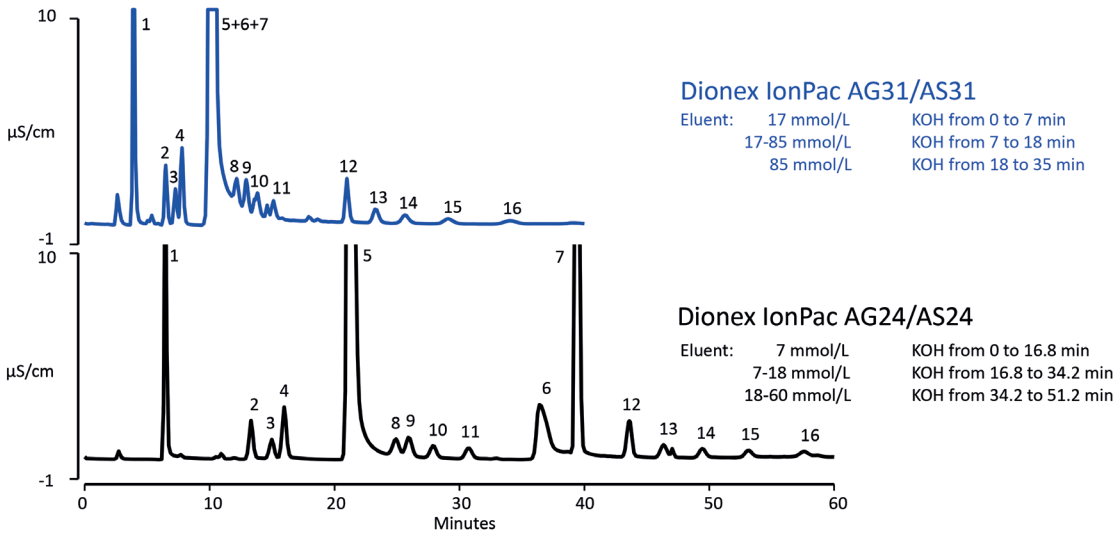


Figure 1. Thermo Scientific™ Dionex™ IonPac™ AS31 columns are packed with an anion exchange resin developed specifically for faster analysis of HAAs, bromate, and dalapon. The Dionex IonPac AS31 stationary phase consists of a novel, hyper-branched anion-exchange condensation polymer, electrostatically attached to the surface of a sulfonated wide-pore polymeric substrate. With the Thermo Scientific Dionex ICS-6000 System and the Dionex IonPac AS31 column held to 15 °C, sample integrity throughout the run is ensured.

"Since switching from the AS24, to the AS31 column, separation time has dropped sufficiently below one hour with our Dionex 5000 system."

— Gerhard Paluca



Peak		mg/L
1	Fluoride	NQ
2	MCAA	1.0
3	MBAA	1.0
4	Bromate	1.0
5	Chloride	NQ
6	Sulfate	NQ
7	Carbonate	NQ
8	Dalapon	1.0
9	DCAA	1.0
10	BCAA	1.0
11	DBAA	1.0
12	Nitrate	NQ
13	TCAA	1.0
14	BDCAA	1.0
15	DBAA	1.0
16	TBAA	1.0

Figure 2. Comparison of chromatographic selectivity of the Dionex IonPac AS31 and Thermo Scientific™ Dionex™ IonPac™ AS24 column sets using the Thermo Scientific Dionex ICS-6000 with suppressed conductivity detection

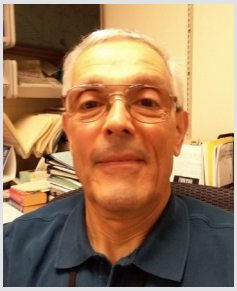
Table 1. The Dionex IonPac AS31 column reduces separation time to about 25 min compared to the Dionex IonPac AS24 column (60 min separation), increasing throughput by 39%. With 60 minute runs, laboratories are limited to 24 injections per day, which allows analysis of roughly 15 samples per day considering the need to run blanks, calibration curves, and suitability runs.

Column	Number of samples/ batch (day)	Estimated revenue/ day at $200/sample	Estimated revenue at 260 work days/year
Dionex IonPac AS24	15	$3,000	$780,000
Dionex IonPac AS31	20	$4,000	$1,092,000

IC–MS/MS is preferred when there are:

- Limited time and personnel to perform all analyses required of the laboratory and thus need to reduce labor-intensive tasks
- Other ionic, ionizable, or polar contaminants need to be included
- Glyphosate, Glufosinate, AMPA, Diquat, Paraquat and other Polar Pesticides (both Anionic and Cationic) may need to be added to the list of analytes
- Concerns about solvent use and costs
- Needs for a reliable technique to reduce repeat analyses
- Multiple organic and inorganic analytes that need testing
- Limited GCs to perform organic analysis (volatiles, pesticides, disinfection by-products, etc.)

thermo scientific



About Gerhard Paluca

Gerhard Paluca is a Senior Sanitary Chemist with over 37 years experience at the Erie County Public Health Laboratory. Prior to joining Erie County, he earned his Bachelors of Arts (B.A.) in Chemistry from the University of New York College at Buffalo.

About the Erie County, NY Department of Health

The mission of the Erie County Department of Health (ECDOH) is to promote and protect the health, safety, and well being of Erie County residents through active prevention, education, enforcement, advocacy, and partnerships. In support of this mission, the Erie County Department of Health is responsible for overseeing and regulating public drinking water supplies' compliance with State and Federal standards. All public water supplies are required to test for a variety of contaminants.

Find out more at **thermofisher.com/icms**

ThermoFisher SCIENTIFIC