# Development of the Thermo Scientific Dionex IonPac AS26 Column for Haloacetic Acid Analysis

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## Introduction

Haloacetic acids are a group of disinfection byproducts resulting from the reaction between the naturally occurring organic matters and the disinfectants used during water treatment. These disinfection byproducts pose potential health hazard due to long-term exposure and are currently regulated by EPA. The Stage 2 Disinfection/Disinfection Byproduct rule sets a maximum contamination level of 60 ppb for HAA5, which includes monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, dibromoacetic acid and trichloroacetic acid (Table 1).

The predominant method for HAA analysis is U.S. EPA Method 552.3, a GC/electron capture detection (ECD) method. It is a time-consuming and labor-intensive process, often resulting in operational errors. U.S. EPA Method 557 describes a suppressed ion chromatography (IC) MS or MS/MS detection method using direct injection and matrix elimination. The MS detection is required to selectively detect coeluting species.

The work presented here describes the development of a new IC separation column (Thermo Scientific Dionex IonPac™ AS26) for haloacetic acid analysis by utilizing amine-epoxide hyperbranch chemistry. Various synthesis strategies for improving the haloacetic acid resolution and quantitation are shown, and a two-dimensional (2D) method allowing sensitive conductivity detection is described.

**Table 1. What Are HAAs?**

| Acid | Abbreviation | Chemical Formula | pKa | Boiling Point °C |
|---|---|---|---|---|
| Monochloroacetic Acid | MCAA* | $ClCH_2CO_2H$ | 2.86 | 187.8 |
| Dichloroacetic Acid | DCAA* | $Cl_2CHCO_2H$ | 1.25 | 194 |
| Trichloroacetic Acid | TCAA* | $Cl_3CCO_2H$ | 0.63 | 197.5 |
| Monobromoacetic Acid | MBAA* | $BrCH_2CO_2H$ | 2.87 | 208 |
| Dibromoacetic Acid | DBAA* | $Br_2CHCO_2H$ | NA | 195 |
| Tribromoacetic Acid | TBAA | $Br_3CCO_2H$ | 0.66 | 245 |
| Bromochloroacetic Acid | BCAA | $BrClCHCO_2H$ | NA | 103.5 |
| Dibromochloroacetic Acid | DBCAA | $Br_2ClCCO_2H$ | NA | NA |
| Dichlorobromoacetic Acid | DCBAA | $Cl_2BrCCO_2H$ | NA | NA |

*MCAA, DCAA, TCAA, MBAA, DBAA are collectively referred to as HAA5

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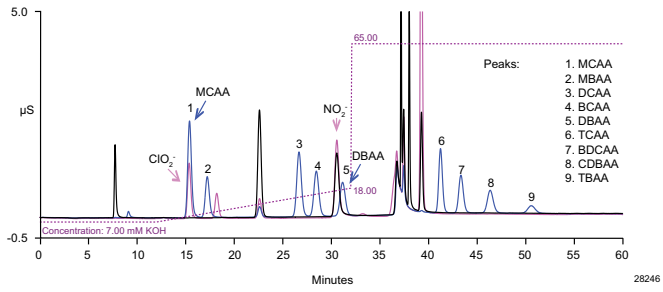
## Haloacetic Acid Methods

U.S. EPA Method 552.3 requires liquid-liquid microextraction and derivatization before GC/ECD analysis. A 40 mL sample is adjusted to pH 0.5, then extracted either with methyl *tert*-butyl ether (MTBE) or *tert*-amyl methyl ether. HAAs are converted to their methyl esters by adding acidic methanol and heating for two hours. The sample is separated from the acidic methanol by adding a concentrated aqueous solution of sodium sulfate, and is then neutralized with saturated solution of sodium bicarbonate. Analysis using GC/ECD requires 25–30 min. This method provides good selectivity, low Minimum Detection Limits (MDLs) from 0.021–0.2 µg/L for HAA5, and a wide applicable concentration range from 0.5–30 µg/L. However, it requires sample pretreatment that is time consuming, labor intensive, and subject to multiple procedural errors, with recoveries ranging from 81–105% for HAA5.

U.S. EPA Method 557 using suppressed ion chromatography with MS or MS-MS detection is a direct injection method, with no need for liquid-liquid extraction, sample pretreatment, or derivatization. It uses a fully automated matrix diversion setup to eliminate column overloading due to high-ionic-strength matrices, and coelution is not an issue since MS is a selective detector. Recoveries are more than 90%.

Figure 1 shows the typical separation of nine haloacetic acid anions using a Dionex IonPac AS24 column. MBAA, CDBAA, and TBAA degrade readily at high pH, so to minimize degradation, the separation is performed at 15 °C. Chlorite and MCAA coelute under these conditions.

**FIGURE 1. Analysis of HAA9 using the Dionex IonPac AS24 column at 15 °C.**




## Results and Discussion

### Polmer Formation

Figure 2 illustrates the schematics of the step-growth electrostatic-graft porous polymeric substrate. The ion-exchange site is highlighted.

**FIGURE 2. Step-growth electrostatic-graft porous polymeric substrate.**

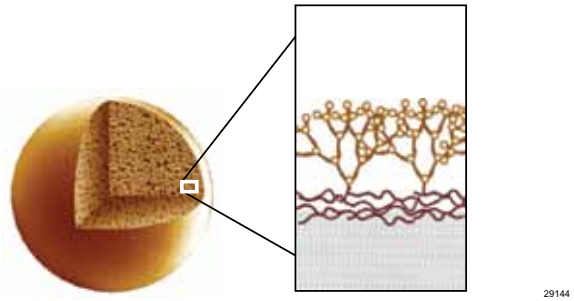



Figure 3 illustrates the basic chemistry behind amine-epoxide condensation polymer chemistry. By using a 1:1 molar ratio of primary amine and a diepoxide, it is possible to synthesize a predominantly linear polymer with residual tertiary amine functionality. If the condensation polymer is formed in the presence of an anionic surface, the resulting polymer will form a coating over the entire surface. The residual tertiary amine sites can be used for growth of hyperbranched polymer chains with anion-exchange groups located at regular distances along the growing chain.

**FIGURE 3. Hypothetical product of 1:1 ratio (diepoxide:amine).**

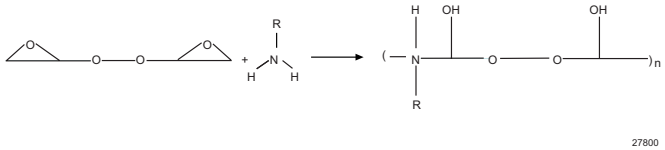
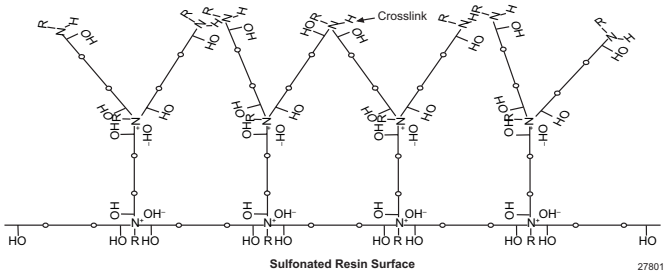


Figure 4 illustrates a representative section of the stationary phase substrate surface after the initial reaction in the presence of the substrate, forming the basement layer followed by two subsequent reaction cycles of a diepoxide followed by a primary amine. This alternates in the following sequence: diepoxide, water rinse, primary amine, water rinse, diepoxide, water rinse, primary amine, and a final water rinse. With each reaction cycle (each cycle consisting of diepoxide followed by primary amine), the number of quaternary sites in the growing polymer doubles. Substantial capacity can be created with three and four reaction cycles. At the end of each reaction cycle, residual secondary amine groups remain available for further reactions.

**FIGURE 4. Layer 2 after diepoxide and amine treatment.**




A new in-vial synthesis strategy was used for the Dionex IonPac AS26 columns. A basement layer was applied to the sulfonated resin by mixing the diepoxide/amine solution mixture (1:1 mole ratio of epoxide to amine) with the resin (sulfonated) at 70 °C for 60 min. This was functionalized by reacting the diepoxide with the resulting resin at 76 °C for 2 h then treating the resin with the same amine mixture solution at 76 °C for 1 h.

## Selectivity

Figure 5 illustrates the effect of epoxide concentration on the column selectivity. As the epoxide concentration increases, the resolution between bromate and MBAA, nitrite and DBAA improves.

**FIGURE 5. Effect of the diepoxide concentration on selectivity.**

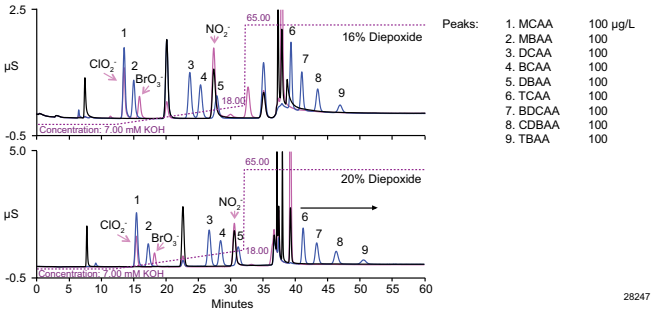



Figure 6 illustrates the effect of high concentration of epoxide on the column capacity and selectivity. This phase shows very high capacity and excellent separation for the early eluting peaks. However, the overall run time is too long.

**FIGURE 6. Example of high capacity phase and its impact on HAA separation.**

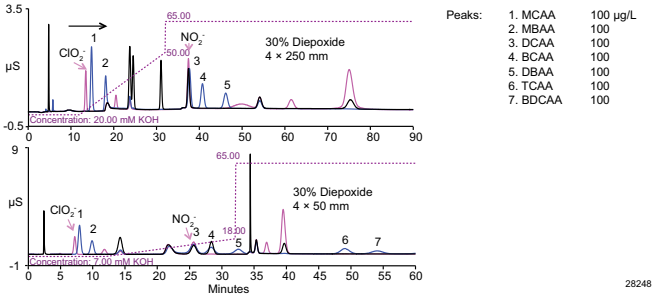



Figure 7 illustrates the effect of temperature during the basement layer synthesis on the separation of the early eluting peaks. The separation between bromate and MBAA improves when higher temperature is used. The separation between the chlorite and MCAA peak also improves at higher temperature.

**FIGURE 7. Selectivity optimization using different basement layer reaction conditions.**

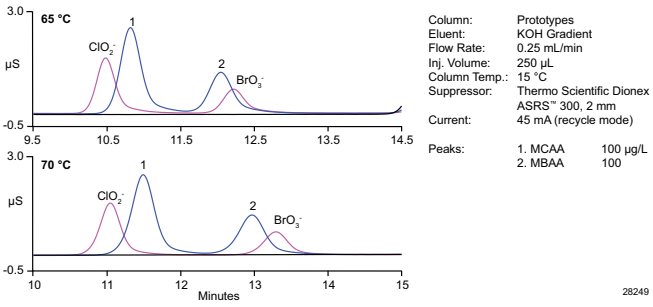
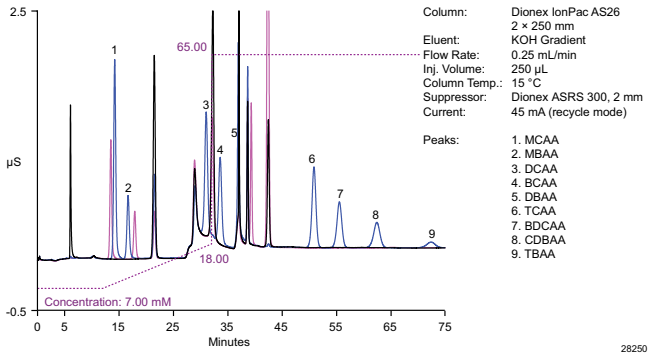


Figure 8 illustrates the separation using the new Dionex IonPac AS26 column. All nine haloacetic acid anions are separated from the matrix anions.

**FIGURE 8. Separation of HAAs using the new Dionex IonPac AS26 column.**




## Matrix Elimination Ion Chromatography (MEIC)

A variety of methods for determining trace levels of contaminants in water are commonly employed. Samples with low levels of matrix ions (e.g., ultrapure water [UPW]) are typically analyzed using preconcentration or large-volume direct injections. For samples with high levels of matrix ions (e.g., drinking water, wastewater), preconcentration or large-volume direct injection may not be possible because the matrix ions may coelute with species of interest or may elute species of interest, leading to recovery and integration issues due to band broadening. Sample pretreatment steps using solid-phase extraction (SPE) cartridges may be used to remove matrix interferences (e.g., a silver form cation-exchange resin used to remove high levels of chloride). Such off-line SPE methods are labor intensive, and multiple cartridges may be needed, adding cost.

Matrix elimination is an automated method in which the high-concentration matrix ions are separated from the analytes using a 4 mm first-dimension column and diverted to waste. A larger loop volume than the standard approach can be used because the capacity and selectivity of the analytical column in the first dimension dictates the recovery, and the analyte of interest is analyzed in the second dimension.

Ions of interest are diverted to a concentrator column after suppression in the first dimension and focused. The hydroxide eluent is converted to DI water by the suppressor, providing an ideal environment for focusing or concentrating the ions of interest. Analysis is performed in the second dimension using a column with a smaller cross-sectional area, yielding enhanced sensitivity. For example, the cross-sectional area of a 1 mm column is one sixteenth the area of a 4 mm column, providing a sensitivity enhancement factor of ~16. Analysis in the second dimension using a different chemistry provides complementary retention, leading to enhanced selectivity.

This method can be automated easily using the Dionex ICS-3000/ICS-5000 systems (Figure 9).

**FIGURE 9. Instrumental setup for the matrix elimination ion chromatography (MEIC).**

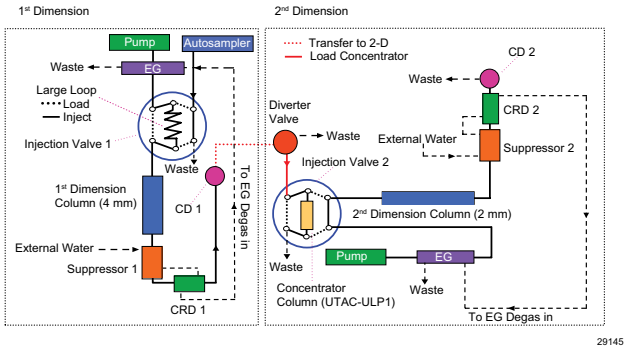
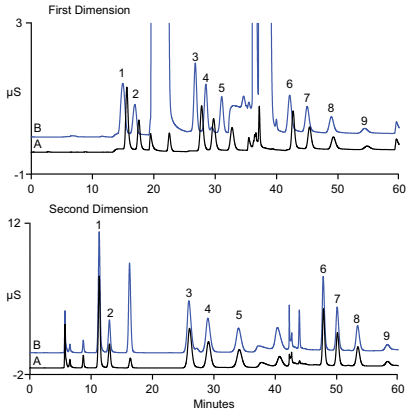


Figure 10 shows the analysis of nine haloacetic acid anions using the two-dimensional matrix-elimination ion chromatography, both in the reagent water (black trace, A) and the high ionic water (HIW, blue trace, B), containing 100 mg/L each of Cl-, $HCO_3^-$, and $SO_4^{2-}$ and 10 mg/L each of N as $NO_3^-$ and P as $PO_4^{3-}$. The top chromatograms show the first-dimension analysis using a Dionex IonPac AS24A 4 mm column and the bottom chromatograms show the second-dimension analysis using a Dionex IonPac AS26 2 mm column. Retention time shifts and peak broadening observed in the first-dimensional HIW sample are absent in the second dimension. Excellent recovery is observed for all 9 HAAs.

**FIGURE 10. MEIC analysis of HAA9 in reagent water and high ionic water (HIW).**




**First Dimension**

| | |
|---|---|
| Column: | Dionex IonPac AS24A, 4 mm |
| Flow Rate: | 1.0 mL/min |
| Column Temp.: | 15 °C |
| Inj. Volume: | 1000 µL |
| Suppressor: | Dionex ASRS 300, 4 mm |
| Current: | 161 mA (Recycle) |

**Second Dimension**

| | |
|---|---|
| Column: | Dionex IonPac AS26, 2 mm |
| Flow Rate: | 0.25 mL/min |
| Suppressor: | Dionex ASRS 300, 2 mm |
| Current: | 41 mA (Recycle) |
| Column Temp.: | 15 °C |
| Concentrator: | Dionex IonPac UTAC-LP2 |
| Samples: | A) HAA9 in DI water<br>B) HAA9 in HIW |

| Peaks: | | |
|---|---|---|
| | 1. MCAA | 100 µg/L |
| | 2. MBAA | 100 |
| | 3. DCAA | 100 |
| | 4. BCAA | 100 |
| | 5. DBAA | 100 |
| | 6. TCAA | 100 |
| | 7. BDCAA | 100 |
| | 8. CDBAA | 100 |
| | 9. TBAA | 100 |

**Recovery >90% for 9 HAAs**

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## Conclusion

- The Dionex IonPac AS26 column was developed by optimizing amine epoxide reaction conditions
- Excellent resolution of 9 HAAs was achieved in the presence of inorganic matrix ions
- Preliminary studies with the MEIC methodology allowed analysis of HAA9 in the presence of matrix ions with suppressed conductivity detection
  - Matrix diversion and selective concentration of HAA species in the first dimension
  - Separation and enhanced detection by suppressed conductivity detection in the second dimension



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