Introduction

Trihalomethane (THM) disinfection by-products are formed when either chlorine or bromine is used as a drinking water disinfectant to control microbial contamination. These four compounds; chloroform, bromodichloromethane, dibromochloromethane, and bromoform, are produced when chlorine or bromine reacts with organic material present in the water. With prolonged exposure, THMs are known to be carcinogenic and are therefore regulated by the USEPA to maintain safe levels.

> ## 2011 Edition of the Drinking Water Standards and Health Advisories
>
> Limit of 80 ppb for each individual THM and Total THMs

Objective

Since continuously fluctuating levels of organic material cause the concentration of THMs to vary, frequent THM monitoring of finished water is necessary to ensure consistent compliance with USEPA standards.

Figure 1: CMS5000 configured for continuous water monitoring

Materials & Methods

A fully automated, quantitative method was developed for the INFICON CMS5000 Continuous Monitoring System to monitor THMs in water.

Figure 2: Water sampling vessel with purge tube for argon bubbling

- **Purge & Trap Sampling System**
  Argon is bubbled into the water sample, volatilizing the THMs into the sample headspace where they are then drawn into the instrument using a sample pump.

- **Tri-Bed Carbon Concentrator**
  A three bed carbon packed ceramic concentrator collects the volatile sample for a method specific period of time. Heat is applied to the concentrator to desorb the sample. The sample is then diverted to the GC column module.

- **GC Column Module**
  The sample is separated using a 30m, 0.25mm ID, 4.0µm df GC column with a DB-1 stationary phase and argon carrier gas.

- **Micro Argon Ionization Detector (MAID)**
  The MAID is sensitive to organic compounds having an ionization potential of 11.7 eV or lower. When argon flows over a Ni-63 source, argon atoms are energized to an excited, metastable state. Organic molecules enter the detector and collide with the metastable argon, becoming charged and releasing electrons. High voltage applied across the detector produces a current, which is amplified and measured to produce a chromatogram.

$$Ar \rightarrow Ar^* \text{ (energized to excited state, exciton)}$$
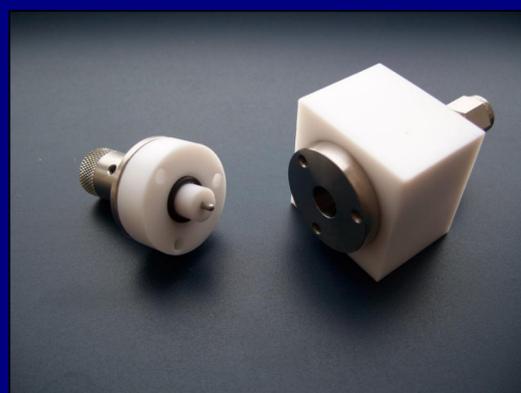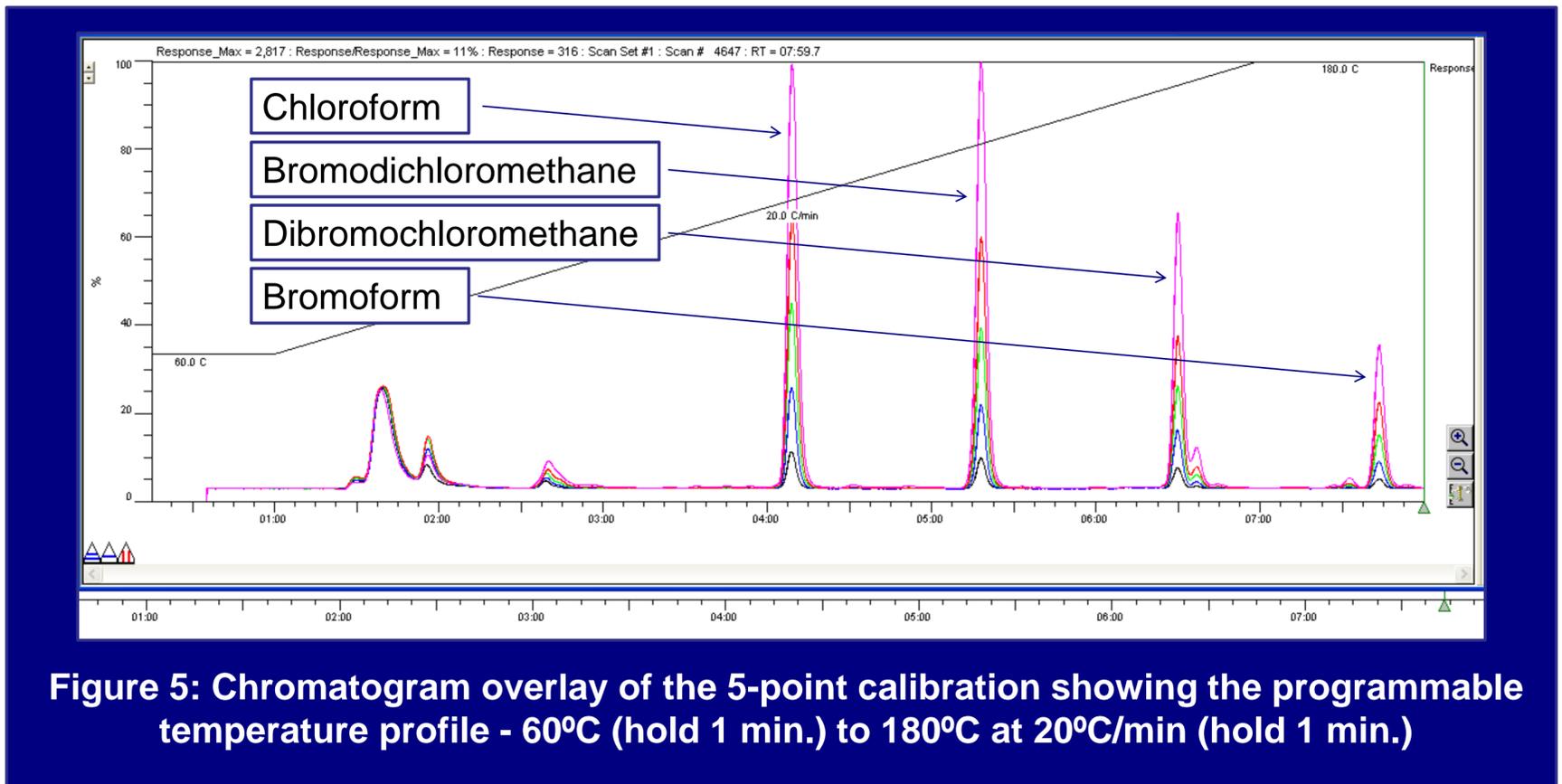$$Ar^* \text{ (exciton)} + R \text{ (organic molecule)} \rightarrow Ar + R^+ + e^-$$

Figure 3: GC Column Module
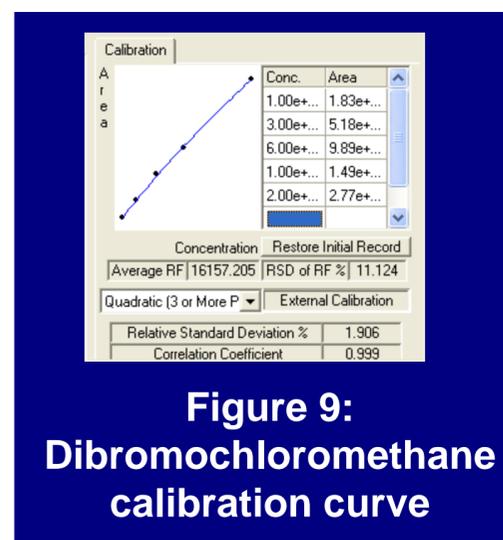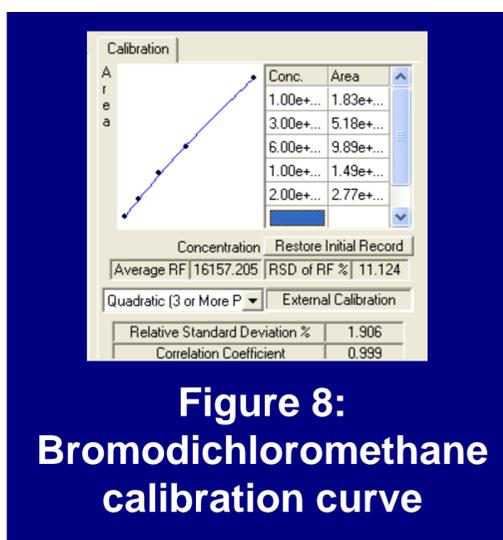

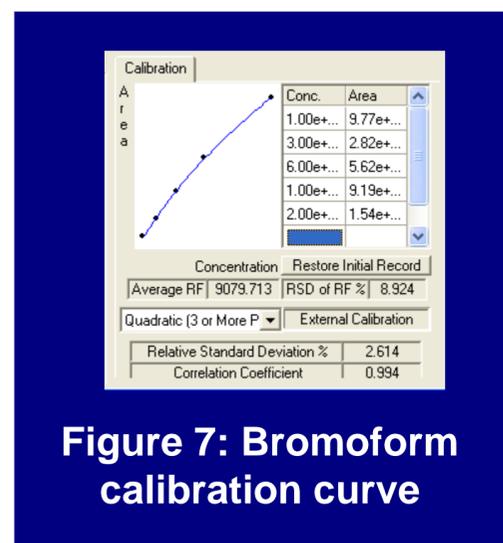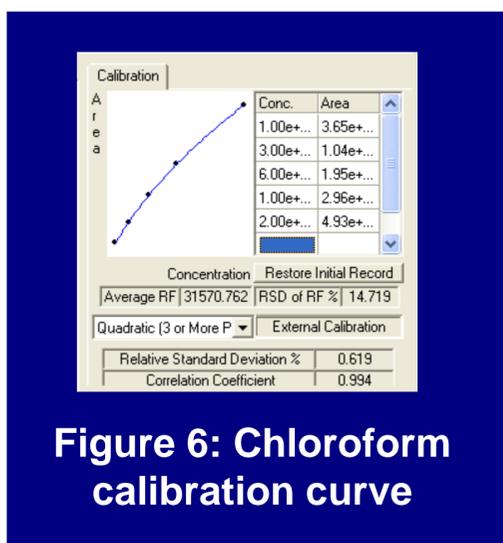
Figure 4: MAID detector assembly

Method Calibration

Five standards of a THM mixture were prepared and analyzed at the following concentrations: 1, 3, 6, 10, and 20 ppb. Sample was collected onto the Tri-Bed concentrator for 1 minute. The analysis time is 8 minutes.

Figure 5: Chromatogram overlay of the 5-point calibration showing the programmable temperature profile - 60ºC (hold 1 min.) to 180ºC at 20ºC/min (hold 1 min.)

Quadratic Calibration Fit

The instrument produces calibration curves which follow a quadratic fit pattern.

Figure 6: Chloroform calibration curve

Figure 7: Bromoform calibration curve

Figure 8: Bromodichloromethane calibration curve

Figure 9: Dibromochloromethane calibration curve

Internal Check Standard

The instrument contains an on-board toluene permeation tube, which emits toluene at a consistent rate. With each check standard run a correction factor is established, and applied to subsequent data, to compensate for slight instrument drift.
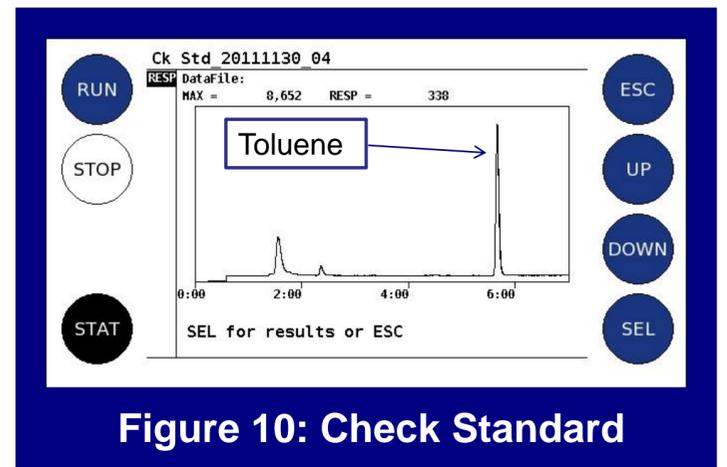

Figure 10: Check Standard

Results

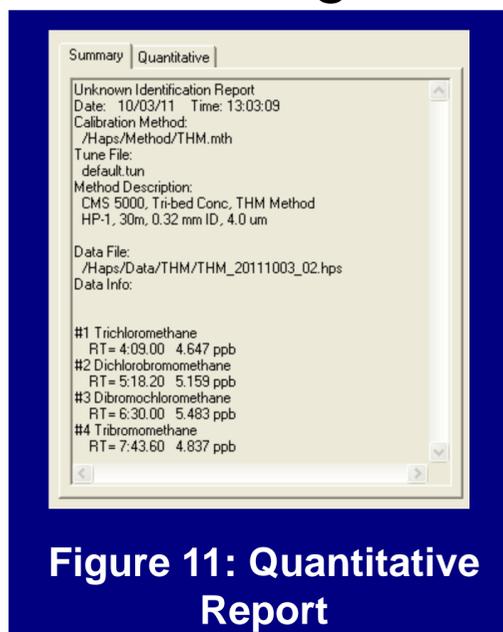Instrument accuracy is ±20%. A quantitative report is accessible through the software and instrument front panel.
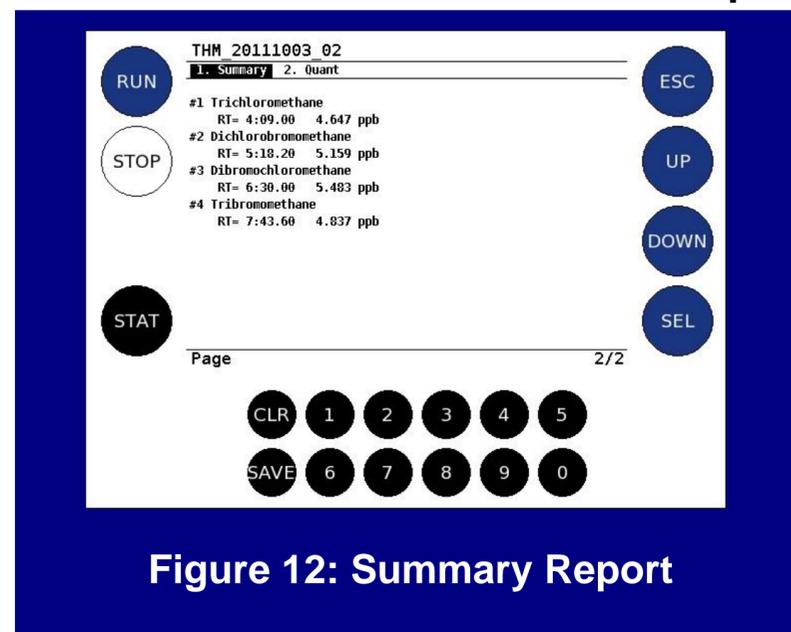

Figure 11: Quantitative Report

Figure 12: Summary Report

Compound	Expected	Actual	Recovery
Chloroform	5 ppb	4.6 ppb	92 %
Bromodichloromethane	5 ppb	5.2 ppb	104 %
Dibromochloromethane	5 ppb	5.5 ppb	110 %
Bromoform	5 ppb	4.8 ppb	96 %

Table 1: Analyte Recovery – 92 to 110%

Conclusion

The INFICON CMS5000 has the ability to collect, analyze, quantify, and report THM concentrations in water - multiple times per day, over an extended period of time with virtually no human intervention. The instrument is an excellent option for continuous on-site monitoring of THM levels in treated drinking water. Continually monitoring finished water to be certain THM levels are within acceptable USEPA limits will help to ensure the safety of consumers and the environment.