

D/DBPR

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An evaluation of the accuracy of on-line THM monitoring

The US Environmental Protection Agency (USEPA) has estimated that public water systems will need to spend \$4.2 billion (in 2011 dollars) to upgrade their water treatment infrastructures (CBO, 1995) and achieve compliance with the Stage 2 Disinfectants/Disinfection Byproducts Rule (D/DBPR). Infrastructure upgrades could include improvements to coagulation, filtration, and disinfection systems and supplemental trihalomethane (THM) remediation in storage and distribution systems. To maintain THM levels within regulatory limits, these utilities will also incur significant additional operating expenses—on the order of hundreds of thousands to millions of dollars—in chemicals, membranes, and energy to operate these new systems. Without real-time, accurate THM measurements of their processed water at both the plant and in distribution systems, THM safety margins must be factored into their processes, making it difficult to optimize THM levels in the face of other resource constraints. As Stage 2 D/DBPR compliance adds a locational component, not only is better and more frequent information necessary for efficient plant operation, but the same level of information from across the network is required to ensure compliance.

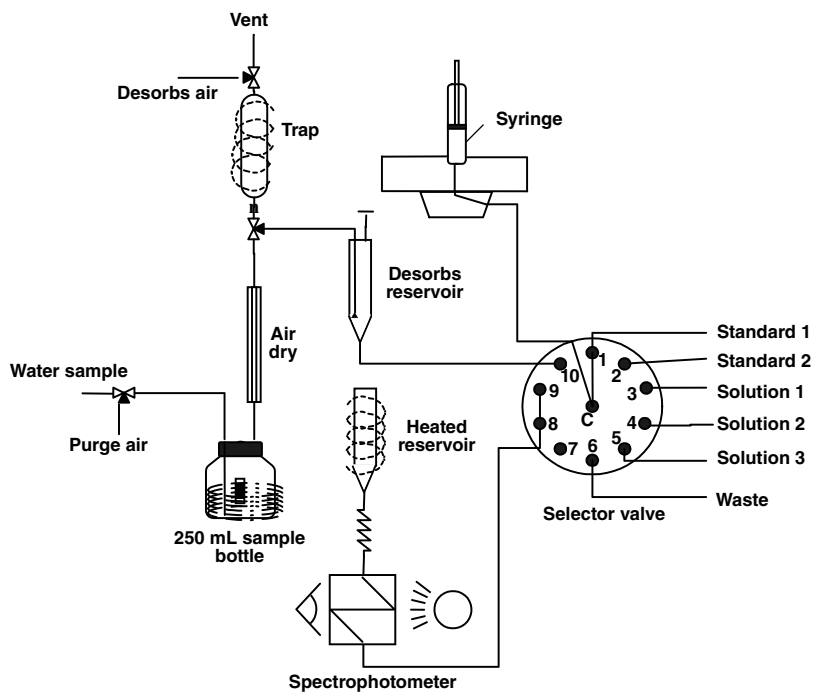
THIS STUDY SHOWS THAT THE PERFORMANCE OF AN ON-LINE, AUTOMATED TRIHALOMETHANE MONITOR IS AS ACCURATE AND PRECISE AS OFF-LINE COMMERCIAL LABORATORIES.

A recently developed on-line THM monitor¹ provides automated, unattended measurement of THM levels in finished drinking water. This monitor therefore enables a proactive utility to take immediate action to optimize the treatment process. To validate the accuracy of the monitor, its manufacturer conducted a study comparing results reported from three of its on-line monitors with five laboratories²⁻⁶ accredited by either the California National Environmental Laboratory Accreditation Program and/or the Environmental Laboratory Approval Program. (The names of the laboratories are not given in the sequence of the reported results.)

EXPERIMENTAL PROTOCOL

Sunnyvale, Calif., tap water was purged with clean, dry air for 48 hours in 10-L batches to remove volatile THMs. Next, 52.5 L of this THM-free tap water were spiked with 79.5 µg/L of total-THM (TTHM) as a mixture of 49.5 µg/L of chloroform (CHCl₃) and 30.0 µg/L of the three brominated THMs (Br-THMs: 18.3 µg/L of CHBrCl₂, 9.7 µg/L of CHBr₂Cl, and 2.0 µg/L of CHBr₃). The spiked water sample was measured on three automated, on-line THM monitors in the manufacturer's laboratory. Each instrument performed 20 analyses, continuously on the same day, simulating on-line analysis mode. The same spiked water sample was added with no head space and quenching agents were pre-added to sample vials provided from each laboratory and stored in a

FIGURE 1 Protocol of analytical method for on-line monitor*



C—common port of the selector valve, THM—trihalomethane

*THM-100, Aqua Metrology Systems, Sunnyvale, Calif.

refrigerator at 4°C. Every three days one sample was shipped overnight following standard USEPA protocol to each of the five laboratories.

This study reports a comparison of the on-line monitor results and those from the five laboratories. The study also evaluates the repeatability and dynamic range of THM analysis for the automated, on-line monitor methodology.

DESCRIPTION OF ANALYTICAL METHOD

During this study the on-line monitors were set up in their standard unattended configurations. Figure 1 shows the protocol of this analytical method.

(1) A 250-mL sample is abstracted from the on-line water supply (in this study a chain of bottles containing the spiked sample).

(2) The THMs are extracted from this water sample via purge-and-trap.

(3) The THMs are desorbed from the trap into a proprietary chemical mixture.

(4) The solution is heated and generates a red color, whose intensity is measured spectrophotometrically. Each of the four THMs has a unique kinetic profile in the formation and decomposition of the colored reaction-intermediate.

(5) The absorbance of the reaction mixture is measured at two different times, and a proprietary algorithm calculates the concentration of THMs (specifically CHCl_3 and Br-THMs), and their sum provides the TTHM value.

BIAS OF INDIVIDUAL METHODS/INSTRUMENTS

The average bias of the 85 measurements conducted by the outside laboratories and the three on-line instruments was better than $\pm 1\%$ for total THMs, $\pm 6\%$ for the sum of the Br-THMs, and $\pm 3\%$ for CHCl_3 , indicating no problems with the spike preparation (Table 1).

The on-line monitor accuracy specification is $\pm 10\%$. Results of individual analyses from this study (Table 1), at less than $\pm 5\%$, were all well within this specification for all 15 measurements for both TTHM and the CHCl_3 and Br-THMs. For TTHMs, all measurements were between 77.4 and 81.6 $\mu\text{g/L}$, compared with a nominal spiked value of 79.5 $\mu\text{g/L}$. However, this represents only a single concentration of THMs, so it is not necessarily indicative of the performance over the entire instrument range.

The specified bias for USEPA methods 524.2 and 551.1 for THMs and individual compounds is

TABLE 1 Accuracy of mean THM values

Analyzer Identification	Accuracy of Mean (5 Samples)		
	CHCl_3 (49.5 $\mu\text{g/L}$)—%	Br-THMs (30.0 $\mu\text{g/L}$)—%	TTHMs (79.5 $\mu\text{g/L}$)—%
Laboratory 1	+5.2	-6.7	+0.7
Laboratory 2	-1.7	-2.1	-1.8
Laboratory 3	-2.1	-19.3	-8.6
Laboratory 4	-0.3	-10.7	-4.3
Laboratory 5	+9.2	+11.7	+10.2
Laboratory averages	+2.1	-5.4	-0.8
On-line monitor 1*	-4.0	+2.0	-1.7
On-line monitor 2*	+0.1	+3.7	+1.5
On-line monitor 3*	-5.2	+4.9	-1.4
On-line monitor averages	-3.0	+3.5	-0.5

Br-THMs—brominated THMs, CHCl_3 —chloroform, THM—trihalomethane, TTHMs—total THMs

*THM-100, Aqua Metrology Systems, Sunnyvale, Calif.

TABLE 2 On-line THM monitor* versus USEPA TTHM methods (5 samples)

Parameter	USEPA Method 524.2 (4 Laboratories)			USEPA Method 551.1 (1 Laboratory)			On-line THM monitor		
	CHCl ₃	Br-THMs	TTHM	CHCl ₃	Br-THMs	TTHM	CHCl ₃	Br-THMs	TTHM
Average— $\mu\text{g/L}$	50.1	28.5	78.6	52.0	28.0	80.0	47.9	31.1	79.0
Accuracy†—%	+1.3	-5.1	-1.1	+5.2	-6.7	+0.7	-3.0	-3.5	-0.5
RSD—%	5.4	5.9	5.2	6.4	6.6	6.4	0.9	2.3	1.0

Br-THMs—brominated THMs, CHCl₃—chloroform, RSD—relative standard deviation, THM—trihalomethane, TTHMs—total THMs, USEPA—US Environmental Protection Agency

*THM-100, Aqua Metrology Systems, Sunnyvale, Calif.

†Data based on spiked THM levels of CHCl₃ (49.5 $\mu\text{g/L}$) and Br-THMs (30.0 $\mu\text{g/L}$; TTHM = 79.5 $\mu\text{g/L}$)

80–120% with relative percent difference (RPD) of 20%. All of the laboratory results met these specifications, but there was greater variability among individual laboratories, with total THM results ranging from 69.7 to 91.2 $\mu\text{g/L}$. CHCl₃ results showed less bias than those of the Br-THMs. Only one lab had results that were as accurate as the on-line

THM monitor results for CHCl₃, the Br-THMs, and the TTHMs.

PRECISION OF THE METHOD

The reproducibility of the spiked water sample for each analytical laboratory was calculated on the basis of five measurements performed during five days. On each of the three on-line THM monitor instru-

ments, the same water source was automatically measured 20 times at the fastest throughput, completing the measurements in 26 hours. This experimental method was designed to mitigate the effect of the THM loss from the bulk water sample by its evaporation into the accumulating head-space as the water level dropped in the bottles. On each instrument the

TABLE 3 On-line THM monitor* versus onsite and offsite laboratories

Parameters	On-Line Monitor	Onsite Lab	Offsite Lab	Comment
Real-time THM monitoring	Yes	Yes	No	Continuous on-line monitoring of THMs
No human intervention	Yes	No	No	Fully automated for unattended operation
Accuracy	Yes	Yes	Yes	Demonstrated as accurate as a certified lab
Repeatability	Yes	No	No	More reproducible than laboratory techniques
Bias	Yes	No	No	Slightly better accuracy than laboratory techniques
Turnaround time	Yes	Yes	No	Same-day turnaround time
Detection limit	No	Yes	Yes	More sensitive laboratory methods
Speciation of individual THMs	No	Yes	Yes	On-line monitor has limited speciation capabilities.
Operating cost savings	Yes	No	No	Laboratory techniques require trained chemist.
Sampling cost reduction	Yes	No	No	On-line monitor does not require manual sampling.
Treatment cost savings	Yes	Yes	No	Rapid changes in THM levels can be identified and remediation processes can be modified.
Use for regulatory reporting	No	Yes	Yes	On-line monitor is not currently a USEPA-approved method.
Usefulness for pilot studies	Yes	Yes	No	Fast turnaround time allows modification of treatments.
Usefulness for Stage 2 D/DBPR compliance	Yes	Yes	Yes	On-line monitor can ensure levels will support satisfactory compliance results.
Use for contract compliance at consecutive systems handover points	Yes	No	No	Ability to measure at high frequency and report via telemetry

D/DBPR—Disinfectants/Disinfection Byproducts Rule, THM—trihalomethane, USEPA—US Environmental Protection Agency

*THM-100, Aqua Metrology Systems, Sunnyvale, Calif.

first five analyses were used for this comparison, although any random set of five analyses would have generated statistical data not significantly different. A comparison of the percentage of accuracy in measuring Br-THMs and CHCl₃ among the on-line monitors and the commercial laboratories is shown in Figure 2.

The reproducibility of the determinants (CHCl₃ and Br-THMs) among the five laboratories ranges from 2 to 9.3% relative standard deviation (RSD), whereas the average percent RSD for their TTHM is < 7% for all labs, all of which are within the USEPA's specification of ±20%. Each on-line, automated instrument demonstrated RSDs of 3% or less on CHCl₃ and Br-THMs, and ~ 1% or less on the TTHM value.

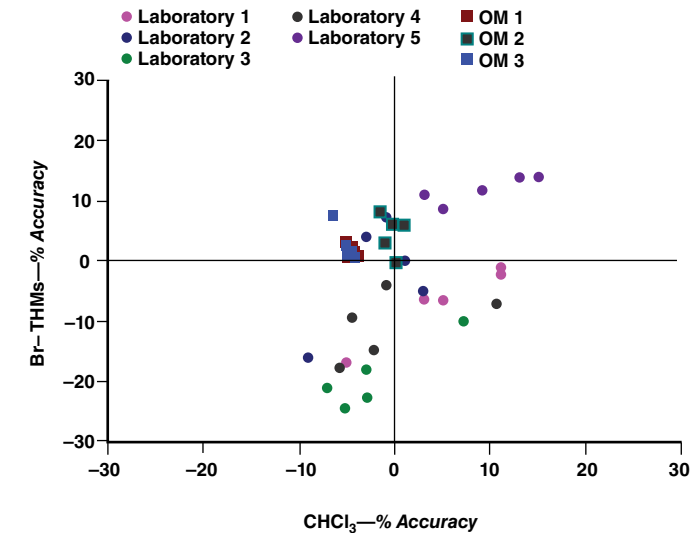
ANALYSIS TURNAROUND TIME

Spiked water samples were collected, preserved, and shipped per the instructions provided by the accredited commercial laboratories without any turnaround time (TAT) specified. The mean TAT was 12 days from the five commercial laboratories, far too slow for proactive management of any active THM mitigation strategy (e.g., enhanced coagulation, secondary filtration, air-stripping). In contrast, the automated, on-line monitor reported TTHM analysis in about 80 minutes, responsive enough to optimize chemical and energy use during remediation. Several local laboratories offer same-day or second-day TAT for THM analysis but at a significantly higher price. Additionally, using these laboratories would still require significant manual intervention to optimize remediation costs.

AUTOMATED, ON-LINE MONITOR VERSUS USEPA TTHM METHODS

As described previously, the on-line instrument uses purge-and-trap, followed by desorption into a chemical mixture that generates a colored product and time-resolved spectrophotometric analysis for detection and determination of the THMs. Four

FIGURE 2 Precision and reliability of on-line monitor* versus offsite laboratories



Br-THMs—brominated THMs, CHCl₃—chloroform, OM—on-line monitor,* THM—trihalomethane

*THM-100, Aqua Metrology Systems, Sunnyvale, Calif.

All results with the exception of most of the Br-THMs from laboratory 3 are within the allowable range of the approved methods.

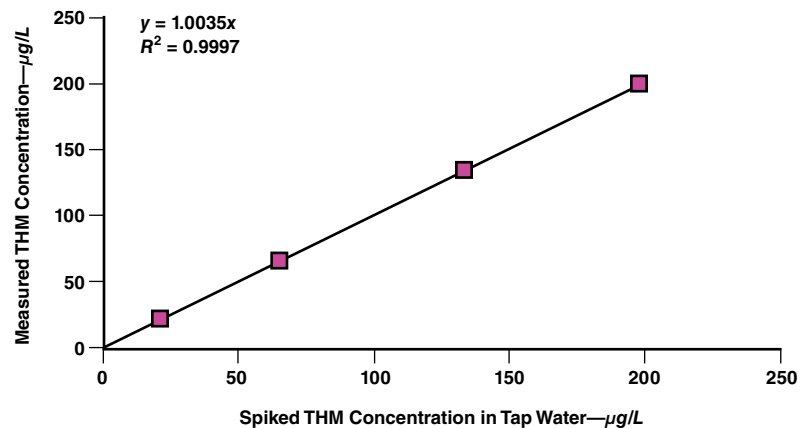
laboratories used USEPA method 524.2, a purge-and-trap gas chromatography (GC)/mass spectrophotometry method, and one laboratory used USEPA method 551.1, a liquid-liquid extraction GC/electron-capture detection method. As shown in Table 2, the precision and bias of the on-line instru-

ments was better than the precision and bias of the laboratory methods.

LINEARITY OF ON-LINE INSTRUMENTS

To evaluate the linearity of one on-line instrument, a series of spiked water samples was prepared by adding dif-

FIGURE 3 On-line monitor* linearity of spiked recovery



THM—trihalomethane

*THM-100, Aqua Metrology Systems, Sunnyvale, Calif.

ferent volumes of a THM standard mixture to THM-free water. At each concentration three measurements were made (Figure 3). Analysis of THM-measured versus THM-spiked shows a coefficient of linear regression of 0.999, with a slope of 1.0 and a y-axis intercept at ~ 0 µg/L. This experiment affirms a high degree of linearity in the monitoring of THMs in water samples over this experimental range of 0 to 200 µg/L, well beyond the USEPA regulatory limit of 80 µg/L. The instrument's nominal specification of dynamic range is 5–200 µg/L.

DISCUSSION

The purpose of the study was to benchmark the accuracy of the on-line monitor and its repeatability against

certified laboratories. A secondary benefit was to determine TATs from the certified laboratories to compare against the on-line monitor results.

The precision and bias of the on-line monitor are equivalent to or better than those of the laboratories. Because the monitor is on line TAT is much faster, which enables use of this monitor for pilot studies during modification of treatment. In order to maintain long-term stability of the instrument, there are built-in automatic self-calibrations with onboard reagents and THM calibration standards to compensate for such variations as those in the colorimetric reaction, ambient temperature, and aging of the trap. The automated calibrations are sufficiently frequent and the changes suf-

ficiently small so that together with quarterly maintenance and servicing, the THM measurements have minimal instrument drift over periods of days, weeks, and months.

A summary of the on-line monitor's parameters compared with onsite and offsite laboratories is shown in Table 3.

CONCLUSION

The automated on-line monitor was evaluated in comparison with conventional laboratory methods (USEPA 524.2 and 551.1) for multiple analyses of a single-concentration tap water. The automated on-line equipment showed better precision and lower bias than the laboratory methods. Additionally it had much

On-Line THM Monitor—Accuracy, Reliability, and Repeatability

The R.E. Badger Filtration Plant (REBFP) treats water for the Southern California cities of Rancho Santa Fe, Encinitas, Solana Beach, and Fairbanks Ranch. To reduce the treatment costs and produce higher quality water, the plant has to purchase expensive imported water from the San Diego County Water Authority. It is estimated that changing

the amount of local water used from 30 to 50% saved \$1 million per year.

REBFP has a goal of increasing local water use while remaining in compliance with the Stage 2 Disinfectants/Disinfection Byproducts Rule (D/DBPR). Without the means to continuously monitor trihalomethane (THM) production, the plant selects blends of local and imported waters that would

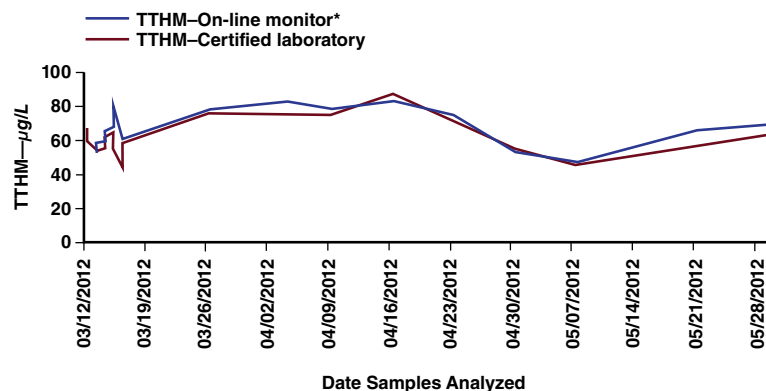
most likely produce lower levels of THMs in order to remain in compliance with the regulations. Typical disinfection by-product (DBP) analysis turnaround time with a contract laboratory can be as long as two weeks—too long to be a practical method for monitoring current production values.

A need was established to have a faster THM analysis turnaround time to optimize the treatment process with regard to THM control. By establishing action levels of THMs at the end of the process, more precise manipulation of flow blends can be achieved without the potential for violations of the D/DBPR.

REBFP evaluated an automated, on-line THM monitor versus grab samples sent to a local certified laboratory for analysis via the US Environmental Protection Agency method 551.1. A 12-week comparison of the on-line monitor versus the laboratory method showed that the on-line monitor meets a repeatability specification of < 5% relative standard deviation with an average percent difference between the two methods of 4.07%.

Figure S1 shows the overall comparability as well as the reliability and

FIGURE S1 TTHM analysis of grab sample by on-line monitor* versus certified laboratory



THM—trihalomethane, TTHM—total THM

*THM-100, Aqua Metrology Systems, Sunnyvale, Calif.

better TAT than the offsite laboratory analyses. Although not accepted as a compliance technique, the instrument can be useful for optimizing treatment to minimize TTHM concentrations at the entry point to the distribution system, particularly during times of rapid water quality fluctuation.

FOOTNOTES

- ¹THM-100, Aqua Metrology Systems, Sunnyvale, Calif.
²Alpha Analytical Laboratories Inc., Ukiah, Calif.
³Babcock Laboratories, Riverside, Calif.
⁴Eaton Analytical Laboratories, Monrovia, Calif.
⁵TestAmerica Laboratories Irvine, Irvine, Calif.
⁶Weck Laboratories Inc., City of Industry, Calif.

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In the past 12 years he has developed and patented nine high-throughput on-line analytical techniques for the detection of trace inorganic and organic compounds. He received his PhD in forensic science from the Department of Chemistry at Punjabi University in Patiala, India. Michael West and Qin Wang are both scientists, Jim Garvey is a director, and Rudy Mui is the chief operating officer, all at AMS.

REFERENCE

CBO (Congressional Budget Office), 1995. The Safe Drinking Water Act: A Case Study of an Unfunded Federal Mandate. CBO, Washington.

<http://dx.doi.org/10.5942/jawwa.2013.105.0160>

ADDITIONAL RESOURCES

A Simple and Inexpensive Kit for Measuring Total Trihalomethanes and Total Haloacetic Acids in Drinking Water (PDF). Emmert, G.L.; Choo, Y.Y.; Larsen, M.L.; Henson, C.M.; Brown, A.W.; & Simone, P.S. Jr., 2011. AWWA Water Quality Technology Conference. Catalog No. WQTC_0075572.

Visit the AWWA store at www.awwa.org/store for more.

accuracy of the online THM monitor. REBFP is developing action levels and standard operating procedures based on THM production. This will allow the operators to maximize the amount of local water without violating the THM standard resulting in substantial savings.

FIELD APPLICATION OF THE ON-LINE MONITOR

The on-line THM monitor has been installed around the world by water treatment facilities for various applications (Table S1). Among them, five important applications are

- compliance monitoring of THM levels in drinking water;
- optimization of processes such as coagulation, filtration, and disinfectant dosing, resulting in operational cost savings;
- optimization of THM remediation in storage and distribution systems, resulting in lower power usage;
- calculating the optimum source blending and treatment processes needed before distribution; and
- contractual compliance with agreed-upon specifications in a consecutive system.

TABLE S1 On-line THM monitor* installation locations and applications

On-Line Monitor Field Locations	Application
Arizona	Process optimization to reduce energy costs for THM remediation in storage and distribution
Eastern New Jersey	THM compliance monitoring in a consecutive system by an end user
San Francisco Bay area, California	Process optimization to maintain THM compliance
Northern California	Process optimization to reduce THM production
Central California	THM compliance monitoring in a consecutive system by a producer
Southern California	Process optimization to reduce cost of purchased water
Ireland	THM compliance monitoring
Portugal	Process optimization to reduce cost of source blending
Northern Scotland	THM compliance monitoring
Southern Scotland	Process optimization to maintain THM compliance
Central Scotland	THM compliance monitoring
Barcelona 1, Spain	THM monitoring for compliance to contractual delivery limits
Barcelona 2, Spain	THM monitoring for compliance to contractual delivery limits
Barcelona 3, Spain	THM monitoring for compliance to contractual delivery limits
Barcelona 4, Spain	Process optimization to reduce cost of source blending with RO-produced water

RO—reverse osmosis, THM—trihalomethane

*THM-100, Aqua Metrology Systems, Sunnyvale, Calif.