

Control DBP Formation in Wastewater Effluent With the Use of Online THM Analyzers

Controlling trihalomethanes (THMs) discharged from wastewater treatment plant (WWTP) final effluent has become an important issue in the United States. WWTPs are sources of numerous disinfection by-products (DBPs) and DBP precursors. WWTP effluents also contain inorganic substances such as ammonia, nitrite, bromide and iodide that influence DBP formation in rivers, lakes and groundwater sources supplying water to drinking water treatment plants downstream of WWTPs.



DBPs are a health and regulatory concern given their link to increased risk of certain cancers and adverse reproductive effects. THMs and haloacetic acids (HAAs) are the two most abundant groups of known DBPs. To protect surface water quality, state and local environmental protection agencies have set regulatory limits for THMs in treated wastewater effluents discharged to surface waters. The four regulated THMs are chloroform (CHCl_3), bromodichloromethane (CHCl_2Br), dibromochloromethane (CHClBr_2) and bromoform (CHBr_3).

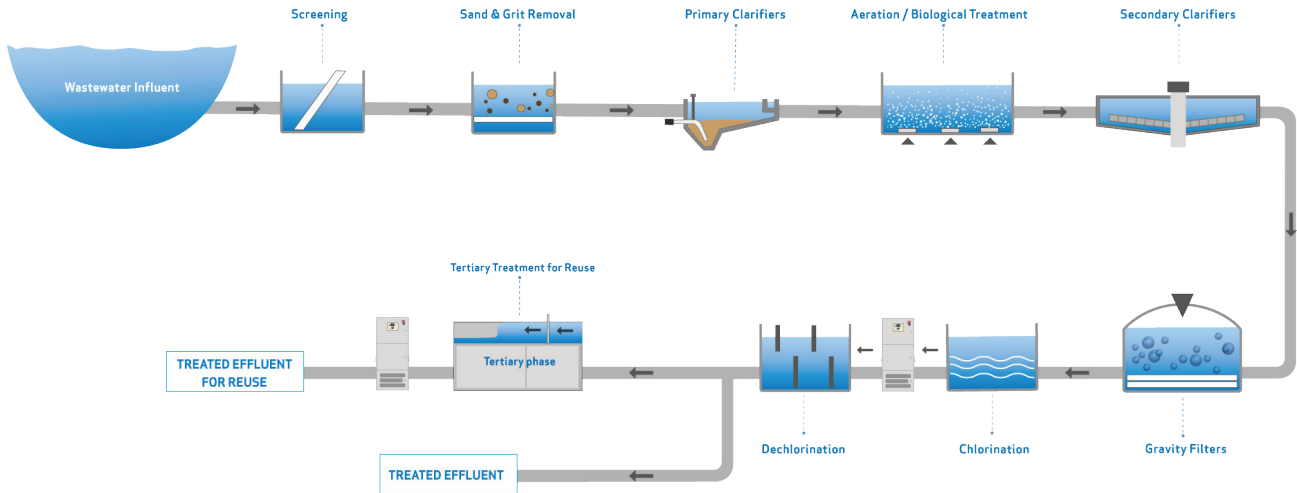
THM Formation in Wastewater Treatment Plants

Wastewater Treatment Plants across the United States are facing stringent effluent permit limits for THMs. Chlorination is the most widely used method for disinfecting treated wastewater. The reaction of free chlorine with certain organic compounds in wastewater leads to DBP formation, including THMs. THM formation can be affected by numerous water quality and treatment factors. Source water characteristics including the type and abundance of organics precursors, as well as bromide and iodide concentrations, influence formation and speciation of THMs in WWTPs. Plant-specific disinfection variables affecting THM formation include contact time, pH, chlorine dose and temperature.

The presence of ammonia in treated wastewater effluents will react with the chlorine disinfectant to form chloramines. In general, chloramines form fewer THMs and HAAs than free chlorine. While the addition of ammonia to form chloramines is a practical method of controlling THM formation, the process may increase total nitrogen effluent concentrations. At present, WWTPs also face stringent federal, state and local effluent discharge requirements on nitrogen and ammonia. As a result, finding a balance between THM mitigation strategies and ammonia-, nitrogen- and nutrient-removal process systems is imperative to ensure complete regulatory compliance.

The Importance of Measuring THM Levels in Wastewater Effluent

In order to reduce the formation of DBPs and increase the potential for chloramine formation, while minimizing nitrogen and ammonia levels, measurement of THM levels in the effluent prior to and following the chlorine injection point is necessary. The automation of sampling, analysis and reporting available through online THM analyzers characterize and monitor THM levels while providing operational staff with immediate, real-time and accurate daily reports on THM levels. The precision of online THM analyzers can be equivalent to or better than those of onsite or offsite laboratories.



Wastewater Treatment Process and Placement of Online THM Analyzers

Fluctuations in THM levels are difficult to characterize through external laboratory analysis. Results from external analysis are typically returned up to 10 business days later, at which point the underlying water quality parameters have changed. Online THM analyzers allow operators to ensure THM levels are in compliance with required target values and also to check for deviations from stable values. The high frequency data provided through online THM analyzers afford operators the ability to effectively monitor treatments systems and mitigate the impact of a potential regulatory breach through timely adjustment of contaminant remediation processes for ammonia, DBPs and nitrogen.

The online THM-100™ water quality instruments from Aqua Metrology Systems provide real-time, accurate and reliable data on THM levels. This data helps users make informed decisions at all phases of their THM mitigation strategy; treatment design, commissioning, operations and optimization.

Online THM-100™ Analyzer-Principles of Operation

THM analyzers employ two essential steps to determine THM values. First, extraction and concentration of THMs from a water sample using a head-space, purge and trap (P/T) or membrane permeation approach. Second, separation and detection of THMs using a gas chromatography (GC)/electron capture detector, e-nose sensors, colorimetric or fluorescence meter.

The THM-100 combines the P/T and colorimetric techniques into one THM instrument while eliminating the pitfalls commonly associated with each approach.

The online THM-100 analyzer is based on the 100-year old Fujiwara reaction specific for THM detection. However, the methodology has been modified to allow for robust and reproducible analysis, inclusive of THM speciation via an instrument that does not require operation by a skilled technician.

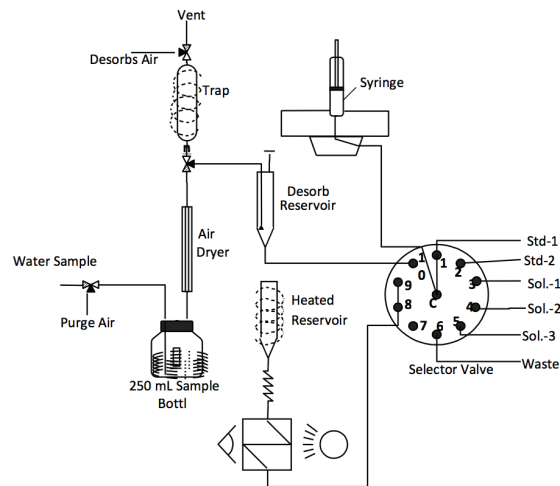


Aqua Metrology Systems THM-100™

P/T-GC techniques often require the use of gas (helium or argon), external manual calibration, and operation by skilled technicians. In colorimetric methods, concentrated THMs react with alkaline pyridine or its derivative to form a red colour or a fluorescent product for measurement via a colorimetric or fluorescence detector. Pyridine produces a hazardous and smelly waste; and usually THM speciation is not possible through a traditional colorimetric approach using the Fujiwara chemical reaction.

The online THM-100 analyzer is based on the 100-year old Fujiwara reaction specific for THM detection. However, the methodology has been modified to allow for robust and reproducible analysis, inclusive of THM speciation via an instrument that does not require operation by a skilled technician.

Following a “purge-and-trap” sampling method, desorption into a chemical mixture is used to generate a coloured product and time-resolved spectrophotometric analysis for detection and determination of speciated THM levels. The THM-100 analyzer uses the following analytical methodology:



Analytical Method for Online THM-100™ Analyzer

- (1) A 250-mL sample is abstracted from the on-line water supply and used to fill the purge vessel (container).
- (2) The water in the container is purged with air and the volatile compounds are retained on the trap containing an adsorbent material, thus extracting the THMs from the water sample via purge-and-trap.
- (3) Once the purging time is completed, the trapped analytes (THMs) are thermally desorbed and dissolved into a proprietary chemical reagent mixture.
- (4) The solution is heated and generates a red color, whose intensity is measured spectrophotometrically. The reagent mixture produces a reaction with the THMs that is based on the Fujiwara reaction, which has been modified to minimize possible interferences from other compounds present in the sample. A derivative of pyridine and an aqueous base is employed, thus converting the four THMs into the same colored product. Note- 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 or three different times and a proprietary algorithm calculates the speciation concentration of the individual THMs.

The THM-100 reports values for the THM dominating species of chloroform or bromoform, depending upon the makeup of sampling water, as well as Total THM and has an accuracy specification of $\pm 10\%$. It has also demonstrated a relative standard deviation of 3% or less on CHCl_3 and approximately 1% or less on the total THM. Results are delivered through communication options including 4-20 mA current loop, USB download from the monitor, and cloud-based data service.

The THM-100 is programmed with a default standard sampling schedule of every 4 hours; average sampling time of 90 – 110 minutes. A more or less frequent sampling schedule can be programmed to meet application specific needs. The online analyser uses three reagents and two on-board calibration standards.

The system runs a daily validation and can be configured to run a full calibration more frequently than once a week if required. Onboard reagents and THM calibration standards compensate for variations in the colorimetric reaction, ambient temperature fluctuations and aging of the trap. Automated calibrations coupled with quarterly maintenance and servicing, result in minimal instrument drift over extended periods. Software continually monitors the performance of internal run-time parameters of the THM-100 and alerts the user to the need for more frequent calibration if needed.

Aqua Metrology Systems also monitors the health of the THM-100 remotely, 24/7, and works with their clients to ensure the instrument remains online and working under optimal conditions.

Online THM Analyzers and the Benefit of High Frequency THM Data

The online THM-100 water quality instruments from Aqua Metrology Systems provide real-time, accurate and reliable data on THM levels. This data helps users make informed decisions at all phases of their THM mitigation strategy; treatment design, commissioning, operations and optimization.

Online THM analyzers offer WWTPs the opportunity to optimize disinfection and process controls while reducing DBP formation in wastewater effluent to meet strict THM effluent permit regulations.