Disinfection by-product analysis in drinking water

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Chloroform and other brominated trihalomethanes (THMs) were first identified as disinfection by-products (DBPs) in chlorinated water in the 1970s. Because of their potential health effects, the U.S. EPA (Washington, DC) promulgated the THM regulation in 1979. The regulation covers water systems serving 10,000 or more people. Since then, many other DBPs have been identified in chlorinated and ozonated drinking waters. These DBPs include haloacetic acids (HAA), haloacetonitriles, haloacetaldehydes, cyanogen halides, aldehydes, ketoacids, chlorite, bromate, and other organic and inorganic compounds. Due to their wide occurrence and potential health risks, the U.S. EPA promulgated the Stage I Disinfectants and Disinfection Byproducts (D-DBP) Rule in 1998. In 1998, the U.S. EPA also promulgated the Information Collection Rule (ICR) to collect the background information on DBPs and pathogens for the Stage II D-DBP rule. The D-DBP rule covers almost all public water systems.

To assist water utilities monitoring DBPs in their finished water, the U.S. EPA published a list of approved analytical methods under the D-DBP rule. These methods are listed in Table 1. The object of the present article is to review analytical methods for common DBPs in drinking water. Several nonregulated DBPs are also included since they may be regulated in future regulations or used for treatment process control. Common analytical problems are also discussed as well.

### Trihalomethanes

Trihalomethanes, including trichloromethane (chloroform), bromodichloromethane, chlorodibromomethanes, and tribromomethane (bromoform), are one of two major groups of organic disinfection by-products identified in chlorinated water. They are formed by the reactions between chlorine and natural organic matter including humic and fulvic substances. Because of their carcinogenic risks, trihalomethanes were first regulated by the U.S. EPA under the THM regulation in 1979 with a maximum contaminant level (MCL) at 100 µg/L for total THMs (TTHMs). Based on new information about their carcinogenic risks, the MCL for TTHMs was lowered to 80 µg/L in the new stage I D-DBP rule.

As shown in Table 1, currently there are three approved methods for THM analysis. Both U.S. EPA Methods 502.2 and 524.2 are purge-and-trap GC methods. U.S. EPA Method 502.2 uses photoionization and electrolytic conductivity detection in series for sample detection. U.S. EPA Method 524.2 uses MS for sample detection. Both methods can be used for many other regulated and unregulated volatile organic chemicals.

In addition to THMs, U.S. EPA Method 551.1 could also be used for monitoring haloacetonitriles, chloral hydrate, chloropirin, and chloropropanones. U.S. EPA Method 551.1 uses micro liquid-liquid extraction (with methyl t-butyl ether [MTBE]), GC separation, and electron capture detection (ECD). In addition to DBPs, U.S. EPA Method 551.1 could also be used to analyze eight chlorinated solvents and 16 halogenated pesticides/herbicides.

In comparison with U.S. EPA Method 551, there are several significant revisions in U.S. EPA Method 551.1. One of the revisions involves extraction salt. Sodium chloride was used in U.S. EPA Method 551. However, because of its high bromide impurity, which reacts with residual chlorine and natural organic matter, sodium chloride causes higher brominated DBP levels (or artifacts) and noisier GC backgrounds. U.S. EPA Method 551.1 suggests the use of sodium sulfate. U.S. EPA Method 551.1 also added pentane as a solvent choice if chloral hydrate is not analyzed.

For THM analysis, the author suggests that U.S. EPA Methods 502.2 and 524.2 be used if samples need to be analyzed for other regulated and unregulated volatile organic chemicals. However, if a sample is analyzed for DBP formation and control, U.S.

### Table 1

<table>
<thead>
<tr>
<th>DBPs</th>
<th>Approved methods for DBP analysis (MCL)</th>
<th>U.S. EPA approved methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>THMs</td>
<td>80 µg/L</td>
<td>U.S. EPA Methods 502.2, 524.2, and 551.1</td>
</tr>
<tr>
<td>HAA</td>
<td>60 µg/L</td>
<td>U.S. EPA Methods 552.2, 552.3, and 6251</td>
</tr>
<tr>
<td>Chlorite</td>
<td>1 mg/L</td>
<td>U.S. EPA Methods 300.0 and 300.1</td>
</tr>
<tr>
<td>Bromate</td>
<td>10 µg/L</td>
<td>U.S. EPA Method 3001</td>
</tr>
</tbody>
</table>
EPA 551.1 should be used since that method provides information on other DBPs in addition to THMs.

Haloacetic acids

HAAs are another major group of organic disinfection by-products in chlorinated water. Similar to THMs, HAAs are formed by the reactions between chlorine and natural organic matter. There are nine common HAAs: monochloroacetic acids (MCAA), monobromoacetic acids (MBAA), dichloroacetic acids (DCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), trichloroacetic acid (TCAA), bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA), and tribromoacetic acid (TBAA). DCAA is a probable human carcinogen and TCAA also poses both developmental and carcinogenic risks. An MCL of five HAAs, including MCAA, MBAA, DCAA, DBAA, and TCAA, was set at 60 µg/L under the Stage I D-DBP regulation.²

Currently, there are three approved methods for HAA analysis: U.S. EPA Methods 552.1 and 552.2 and Standard Method 6251.² All three approved methods include sample extraction, methylation, and GC-ECD detection. U.S. EPA Method 552.2 and Standard Method 6251 use micro liquid-liquid extraction with MTBE. Both sodium sulfate and sulfuric acid are added to samples to increase the extraction efficiency. U.S. EPA Method 552.1 uses solid-phase extraction with ion exchange resins. Standard Method 6251 uses a common methylating reagent, diazomethane, for HAA methylation. Due to its hazardous nature, diazomethane is replaced with acidic methanol in U.S. EPA Methods 552.1 and 552.2. A capillary GC-ECD is used in all three methods. Comparison studies on these methods were reported by Barth and Fair.¹¹ and Xie et al.¹² The author (of this article) suggests that U.S. EPA Method 552.2 or Standard Method 6251 be used due to the poor HAA extraction efficiency using U.S. EPA Method 552.1, especially in water containing high levels of sulfate or chloride.

Diazomethane and acidic methanol are two of the choices for HAA methylation. Diazomethane should be freshly prepared. The concentration of the diazomethane could be estimated by checking the color of the solution. For both diazomethane and acidic methanol, incomplete methylation of HAAs, especially trihaloacetic acids, has been reported in several laboratories. The author suggests that calibration curves be prepared with each batch of the HAA samples to compensate the effect of the incomplete methylation of HAAs.

Bromate and chlorite

Bromate is a primary inorganic ozonation by-product in water containing bromide. Reacting with ozone, bromide is first oxidized to hypobromous acid leading to the formation of bromate. Since bromate is a probable human carcinogen, an MCL of 10 µg/L was promulgated under the Stage I D-DBP regulation.³ This MCL was developed largely due to the fact that 10 µg/L was the current practical quantification limit for bromate in drinking water.

Chlorite is a degradation by-product of chlorine dioxide, which is commonly used as an oxidant or disinfectant. The concentrations of chlorite in treated water vary between 30 and 70% of the chlorine dioxide dose. Due to its neurodevelopmental effects, chlorite is regulated at an MCL of 1 mg/L under the Stage I D-DBP regulation.

U.S. EPA Methods 300.0 and 300.1 are ion chromatographic (IC) methods. Both methods use IC separation, subsequent suppression, and conductivity detection. For chlorite analysis, both U.S. EPA Method 300.0 and 300.1 can be used. However, the former is not sensitive enough to determine mg/L levels of bromate, especially in the presence of mg/L levels of chlorite. For bromate analysis, only U.S. EPA Method 300.1 can be used. This method, which specifies a high-capacity IC column, improves chromatographic resolution and minimizes chromatographic interferences from common anions including chloride. For bromate analysis, aged guard and analytical columns can cause irregular baselines, poor resolution, and poor sensitivity.³ Therefore, the resolution must be closely monitored and the column replaced immediately when resolution starts to deteriorate. For chlorite analysis, an amperometric titration method, Standard Method 4500-CLO₂ E, could be used for routine daily monitoring in treatment plants. However, chlorite compliance analyses should be conducted using an IC.

Other unregulated disinfection by-products

Haloacetonitriles, chloro hydrate (trichloroacetaldehyde hydrate), chloropirin, and chloropropanones are other major DBPs in chlorinated drinking water. These DBPs were monitored under the ICR and could be regulated under the Stage II D-DBP rule.³ For ICR monitoring, U.S. EPA Method 551.1 is the approved method. For chloro hydrate analysis, MTBE should be used as the extraction solvent. Pentane can only be used as the extraction solvent when chloro hydrate is not analyzed.

Cyanogen chloride is a disinfection by-product commonly detected in chloraminated drinking waters. Cyanogen bromide, a bromide analogue of cyanogen chloride, is also formed in chloraminated or ozonated waters that are high in bromide. Due to its instability in chlorinated waters, cyanogen chloride generally is not present in water containing a free chlorine residual. Because of its potential health effects, cyanogen chloride was monitored under ICR, and could be regulated in the Stage II D-DBP rule.³ There are three methods for analyzing cyanogen chloride in drinking water:¹⁴ purge-and-trap GC-MS,¹⁵ headspace GC-ECD,¹⁶ and micro liquid-liquid extraction GC-ECD.¹⁷ The purge-and-trap GC-MS method for cyanogen chloride...
was used under the ICR monitoring. However, this method requires the use of a specialized instrument, a purge-and-trap GC-MS system. A heated purge is also required if the analysis of cyanogen bromide is needed. The headspace GC-ECD method is a relatively simple and rapid analytical method. The micro liquid–liquid extraction GC-ECD method was originally developed for cyanogen bromide analysis. This method was further developed for both cyanogen chloride and cyanogen bromide analysis. The sample injection could be easily automated with a common GC autosampler.

Aldehydes are a group of ozonation by-products that are formed by the reaction of ozone and humic substances in water. There are seven major aldehydes, including formaldehyde, acetaldehyde, propanal, butanal, pentanal, glyoxal, and methyl glyoxal, in ozonated drinking water. The typical levels of aldehydes in ozonated water range from 5 to 20 μg/L. Due to their potential health risks, aldehydes were monitored under ICR by U.S. EPA laboratories, and may be regulated under the Stage II D-DBP rule. The concentration of aldehydes could also be used as a chemical surrogate for assimilable organic carbon (AOC) or biodegradable dissolved organic carbon (BDOC), which measures the biological stability of treated drinking water in distribution systems and the biological treatability of the ozonated water. For aldehyde analysis, two common methods are U.S. EPA Method 556 and Standard Method 6252. Both methods use O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) to derivatize aldehydes to their pentafluorobenzyl oximes in aqueous phase. Their oxime derivatives are then extracted with hexane and analyzed using GC-ECD. For aldehyde analysis, one of the challenges is obtaining aldehyde-free reagent water to prepare aqueous standards. Formaldehyde and acetaldehyde are commonly present in indoor air or ion exchange resins for generating reagent water. Low background levels of formaldehyde and acetaldehyde in reagent water could be removed by UV radiation, or simply by boiling the water.

Ketoacids are another group of ozonation by-products, including glyoxylic acid, pyruvic acid, and ketomalonic acid. The concentrations of ketoacids are approx. 5–10 times higher than that of aldehydes in ozonated waters. Although there is little concern about the group’s health effects, the concentration of ketoacids could be used as a potential chemical surrogate for AOC or BDOC in ozonated waters. For ketoacid analysis, there are two established analytical methods that use double derivatization and GC-ECD detection. Both methods use PFBHA derivatization to convert ketoacids to their oximes in aqueous phase. Following MTBE extraction, one method uses diazomethane for ketoacid methylation, and another uses acetic anhydride. Both methods use GC-ECD for separation and detection. Very few laboratories have conducted ketoacid analyses. Both dirty injectors and extracts containing PFBHA could cause chromatographic interferences and poor sensitivity. A calibration curve should be prepared for each batch of samples. Since ketoacids are easily biodegradable, these samples should be analyzed within 24 hr or properly preserved.

Summary

Four groups of disinfection by-products are regulated under the U.S. EPA Phase I Disinfectants and Disinfection Byproduct Rule. These disinfection by-products are trihalomethanes, haloacetic acids, bromate, and chlorite.

There are three approved methods for monitoring trihalomethanes. U.S. EPA Method 551.1 is suggested since it also analyzes other disinfection by-products including haloacetonitriles, chloral hydrate, chloropicrin, and chloropropanones. The author suggests that U.S. EPA Method 300.1 is suggested. Aged IC columns could significantly affect the separation and detection for bromate. For other unregulated disinfection by-products, including cyanogen chloride, aldehydes, and ketoacids, a list of methods is given in Table 2.

| Table 2 | Suggested analytical methods for disinfection by-products |
| DBPs | Analytical Methods |
| Haloacetonitriles | U.S. EPA Method 511.1 |
| Chloral hydrate | U.S. EPA Method 511.1 |
| Chloropicrin | U.S. EPA Method 511.1 |
| Chloropropionones | U.S. EPA Method 511.1 |
| Cyanogen chloride | U.S. EPA Method 524.2, 13 and method by Xie and Reckhow |
| Aldehydes | U.S. EPA Method 556 and Standard Method 6252 |
| Ketoacids | Methods by Xie and Reckhow and Xie et al. |

For chlorite and bromate analysis, U.S. EPA Method 300.1 is suggested. Aged IC columns could signiﬁcantly affect the separation and detection for bromate.

For other unregulated disinfection by-products, including cyanogen chloride, aldehydes, and ketoacids, a list of methods is given in Table 2.

References

BY-PRODUCT ANALYSIS continued


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