

Removal of Total Organic Carbon

A Technical Review - Part 1

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The Composition of Total Organic Carbon

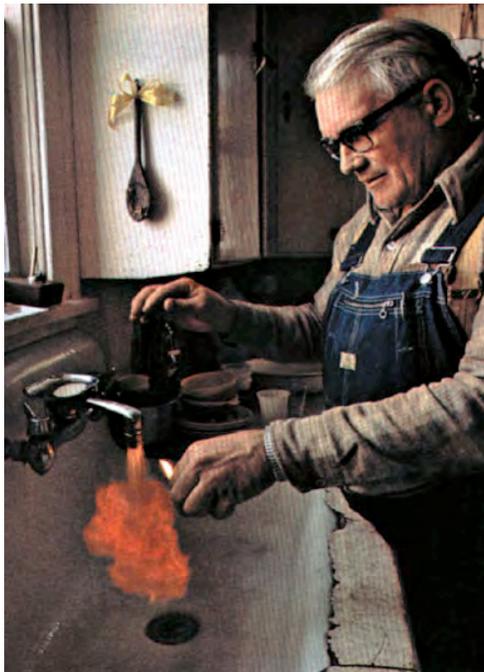
Total Organic Carbon

While measured at concentrations of milligrams of carbon per liter (mg C/l) in most natural waters, total organic carbon (TOC) encompasses a very broad and diverse assortment of compounds and materials, encompassing gases, dissolved solutes and particles. Apart from serving as a gross measurement of a water's cumulative carbon content, this parameter cannot be scientifically defined.

Purgeable Organic Carbon

Particularly in ground waters, methane may be one of the most abundant forms of total organic carbon. Dissolved methane effervesces when well water is brought to the surface and exposed to atmospheric pressure. Used extensively for home heating and cooking during settling of the Great Plains, methane is an explosive gas that has been found in well water at concentrations up to 80 mg/l.

Similarly, in lake waters, decomposition of organic-rich bottom sediments may yield methane and other volatile organic constituents which can be subsequently removed by aeration. Those compounds that can be removed by exposure to the atmosphere or aeration are commonly referred to as 'purgeable'.



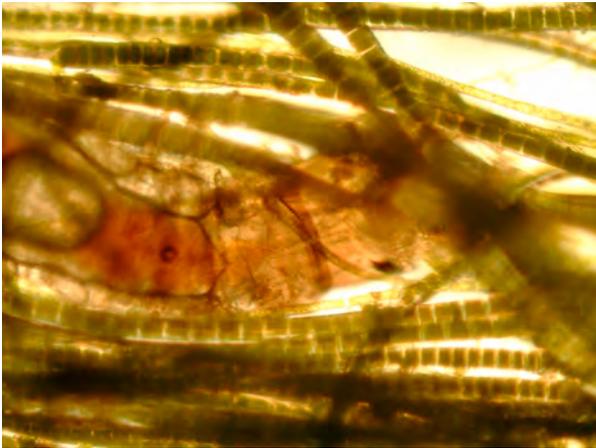
Farmer 'flaming' methane at his tap

Particulate Organic Carbon

Suspended matter in surface waters, while consisting primarily of inorganic silts and clays, also contains a wide variety of organic carbon particles. Particularly in summer, zooplankton, algal cells, filamentous organisms and bacterial cells may comprise a large fraction of the total organic carbon. In addition to microorganisms, a range of amorphous fibrous matter from decaying vegetation and leaves add to the particulate fraction.

Microscopic examination reveals the enormous range of organic debris that may contribute particulate organic carbon to drinking water sources. For example, entrained oil droplets, grease and fatty materials, either of natural or anthropogenic origin, contribute to the particulate organic fraction.

Where the particulate organic carbon fraction is abundant, conventional physical drinking water treatment removal processes, such as coagulation and sedimentation, are highly effective in reducing total organic carbon concentrations along with other suspended matter.



Algal Filaments & Zooplankton: Bloomington, IL



Coagulation with Ferric Sulfate: Little Rock, AR

Distinguishing Particulate from Dissolved Organic Carbon

In distinguishing between particulate and dissolved organic carbon, there can be a 'gray zone', depending upon the means used to separate particles from solutes. Whereas algal cells are commonly recovered on 3 μm membranes, the millions of bacteria per milliliter generally present in lake and river waters are separated on membranes with 0.2 μm pores. With the development of *neutron track-etched polycarbonate membrane filters* with ever finer pore sizes, the still more abundant virus particles can now be retained on 0.01 μm membranes. Such fine pores may also separate some of the larger humic acid molecules further blurring the distinction between particulate and dissolved. Increased (enhanced) coagulant dosages may flocculate and entrain those very small particles (0.01-1 μm) that contribute little to treated water turbidity but might make a measurable contribution to total organic carbon.

Partitioning of Organic Carbon Fractions

A basic partitioning or fractionation of total organic carbon is illustrated in the figure below. Membrane filtration divides total organic carbon into dissolved and particulate fractions. By aeration, the dissolved fraction is further separated into purgeable and non-purgeable organic carbon. Particulate organic carbon may be further subdivided into cell mass (microorganisms) and other organic detritus.

Often, when organic carbon concentrations are reported in engineering reports or literature, only non-purgeable dissolved organic carbon (NPOC) has actually been measured. This is because the field samples collected have been allowed to remain open to the atmosphere allowing volatile gases to escape while particles have either been allowed to settle out or have been removed by membrane filtration.

A careful analyst will indicate that NPOC has actually been measured. In many instances, there is little or no data available on purgeable or particulate organic carbon, making it impossible to determine how much of the total organic carbon would have been removed by conventional physical treatment methods.

DISSOLVED		PARTICULATE	
<p><i>Purgeable</i></p> <ul style="list-style-type: none"> • methane • volatile organic matter 	<p><i>Non-Purgeable</i></p> <ul style="list-style-type: none"> • humic materials • fulvic and humic acids 	<p><i>Cell Mass</i></p> <ul style="list-style-type: none"> • algae • bacteria 	<p><i>Organic Detritus</i></p> <ul style="list-style-type: none"> • woody fibers • pollen

Dissolved organic carbon (DOC) has been further fractionated for purposes of estimating removals by adsorbents, such as the conventional metal coagulants. In attempting to model DOC removal by coagulation, Kastl et al. (J. AWWA, Feb. 2004) assumed that DOC was comprised of three fractions:

humic acid	removal dependent upon pH	pH adjusted coagulation
nonpolar	removal independent of pH	conventional coagulation
nonsorbable	not removed by sorption	not removed by coagulation

Based on their individual responses to the conventional metal coagulants (iron, aluminum), this proposed fractionation of organic matter would further define the treatability of TOC in drinking water sources. For example, if a lake water contained DOC which was largely *nonsorbable*, any form of coagulation would fail to offer significant DOC reduction. If the DOC was primarily *nonpolar*, pH adjustment would not be required for effective removal.

Owing to the wide variation in the composition of organic matter in drinking water sources, it is impossible to predict the potential for TOC reduction without first conducting a series of physical separations or coagulation studies on a specific water.

Measurement of Total Organic Carbon

TOC is comparatively difficult and costly for water utilities to measure. Contract laboratories presently charge \$15 to \$20 per sample. While nominal, this cost discourages many long-term, large-scale water utility monitoring programs. Alternately, laboratory TOC analyzers may cost \$30,000 and require constant operator attention in order to perform reliably. As a result, TOC data is primarily generated by regulatory agencies, research centers and well-equipped water utilities, particularly if they are combatting tastes and odors.

The Hach Chemical Company currently markets a simplified method for measuring TOC and DOC that can be performed in water treatment plant laboratories. This simplified method promises to make these measurements more widely accessible for treatment process evaluation and control.



TOC analysis (Bloomington, IL) supports taste-and-odor removal by GAC filtration

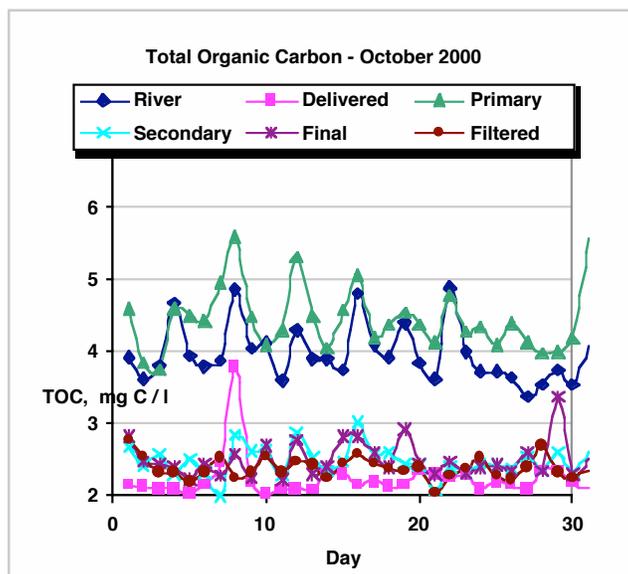
Concentrations of TOC in Missouri Drinking Waters

Some of the earliest field data on TOC in drinking water in the United States was obtained as part of a joint effort between the University of Missouri-Columbia Department of Civil Engineering and the Missouri Department of Natural Resources (MDNR). In 1979, MDNR collected finished water samples from 101 Missouri drinking water distribution systems statewide.

These early analytical results, subsequently confirmed by succeeding studies, indicated that Missouri drinking waters were low in organic content but varied markedly in average concentrations depending upon their source. For these distributed drinking waters, TOC was equal to NPOC.

NPOC in 101 Missouri Distributed Drinking Waters - 1980		
Source Water	Number	Average NPOC, mg C/l
Lakes	23	4.8
Rivers	18	3.6
Wells <100 feet deep	16	1.2
Wells >100 feet deep	42	0.2

Long-term monitoring data from the Kansas City, Missouri water plant shows that Missouri River TOC is reduced from about 4 to 2 mg C/l by treatment, including lime softening. In part, this 50% reduction represents the removal of particulate organic carbon along with Missouri River suspended solids. During treatment, TOC is actually found to increase in the primary settling basins where lime sludge is returned and mixed with river water to recover magnesium as a recycled coagulant.



TOC at various stages of treatment - Kansas City, MO

TOC Concentrations in Illinois Waters

For comparison, Illinois (IEPA) data indicates that Lake Michigan water TOC averages 1.9 mg C/l whereas 352 other Illinois surface waters average 9.4 mg C/l.

Illinois ground waters exhibit TOC concentrations ranging over two orders of magnitude from 0.2 to 24.5, averaging 5.6 mg C/l. These reported concentrations are far greater than those observed in Missouri well waters and may be related to the substantial deposits of organic-rich soil found in many of Illinois' agricultural regions. Whatever the source of organic matter, TOC levels in Illinois ground waters appear to approach and exceed those found in Missouri *surface* waters. Despite this, in the absence of defined surface water contamination, ground waters are exempt from regulations requiring TOC reductions.

TOC (mg C/l) in Illinois Waters	Average	Maximum	Minimum	Number
Lake Michigan IEPA 1999 - 2003	1.9	8	0.8	146
Groundwater (82) ISWS 1971 - 2000	5.6	24.5	0.2	82
Surface Water (352) STORET data 2003	9.4	19	3	352

Mississippi River Basin TOC

USGS measurements of DOC in Mississippi River Basin waters illustrate some interesting trends that may be found in natural waters. Instead of the headwaters exhibiting low DOC and gradually increasing along with human activity and downstream waste discharges, DOC concentrations are found to be highest near the origin of the Mississippi and progressively decrease downstream. The influx of both the Missouri and the Ohio Rivers actually *reduce* DOC concentrations in the Mississippi below each confluence. By the time the Mississippi flow reaches New Orleans, DOC has been reduced by 69%.

Mississippi River and Tributaries	Dissolved Organic Carbon DOC, mg C/l	Discharge m ³ /s
Minneapolis, MN	12	410
LaCrosse, WI	10	1600
Dubuque, IA	9.9	2300
Davenport, IA	8.5	2600
Quincy, IL	6.4	3900
Missouri River	3.7	1800
St. Louis, MO	5.0	7300
Cairo, IL	5.2	7800
Ohio River	2.4	4000
Memphis, TN	4.4	13400
Greenville, MS	4.1	15600
Natchez, MS	3.8	17600
Baton Rouge, LA	3.8	16000
New Orleans, LA	3.7	4340

USEPA Regulation of TOC

Whereas most of the organic constituents that contribute to TOC in natural waters are of natural origin, some are anthropogenic (man-made). Among these are agricultural and industrial chemicals, as well as those inadvertently created by the disinfection of drinking water sources. Disinfection by-products (DBPs) from the chlorination of drinking water include the trihalomethanes and haloacetic acids.

The USEPA's 2004 Edition of the *Drinking Water Standards and Health Advisories* lists 170 organic chemicals known to be or suspected of being harmful to human health. Maximum Contaminant Levels (MCLs) or the highest level of the contaminant allowed in drinking water have been set to regulate 59 of these, whereas two are regulated by a treatment technique.

The USEPA provides the following argument for elaborating a still more specific rule governing disinfectant and disinfection by-products:

"Stage 1 Disinfectants and Disinfection Byproducts Rule (USEPA, December 1998)

In the past 25 years, the Safe Drinking Water Act (SDWA) has been highly effective in protecting public health and has also evolved to respond to new and emerging threats to safe drinking water. Disinfection of drinking water is one of the major public health advances in the 20th century. One hundred years ago, typhoid and cholera epidemics were common through American cities; disinfection was a major factor in reducing these epidemics.

However, the disinfectants themselves can react with naturally-occurring materials in the water to form unintended byproducts which may pose health risks. In addition, in the past ten years, we have learned that there are specific microbial pathogens, such as *Cryptosporidium*, which can cause illness and is resistant to traditional disinfection practices.

Amendments to the SDWA in 1996 require EPA to develop rules to balance the risks between microbial pathogens and disinfection byproducts (DBPs). It is important to strengthen protection against microbial contaminants, especially *Cryptosporidium*, and at the same time, reduce potential health risks of DBPs. The Stage 1 Disinfectants and Disinfection Byproducts Rule and Interim Enhanced Surface Water Treatment Rule, announced in December 1998, are the first of a set of rules under the 1996 SDWA Amendments.

"PUBLIC HEALTH CONCERNS While disinfectants are effective in controlling many microorganisms, they react with natural organic and inorganic matter in source water and distribution systems to form DBPs. Results from toxicology studies have shown several DBPs (e.g., bromodichloromethane, bromoform, chloroform, dichloroacetic acid, and bromate) to be carcinogenic in laboratory animals. Other DBPs (e.g., chlorite, bromodichloromethane, and certain haloacetic acids) have also been shown to cause adverse reproductive or developmental effects in laboratory animals. Several epidemiology studies have suggested a weak association between certain cancers (e.g., bladder) or reproductive and developmental effects, and exposure to chlorinated surface water. More than 200 million people consume water that has been disinfected. Because of the large population exposed, health risks associated with DBPs, even if small, need to be taken seriously.

"WHO MUST COMPLY WITH THE RULE? The Stage 1 Disinfectants and Disinfection Byproducts Rule applies to all community and nontransient noncommunity water systems that treat their water with a chemical disinfectant for either primary or residual treatment.

"WHAT DOES THE RULE REQUIRE? The Stage 1 Disinfectant and Disinfection Byproduct Rule updates and supersedes the 1979 regulations for total trihalomethanes. In addition, it will reduce exposure to three disinfectants and many disinfection byproducts.

The rule establishes maximum residual disinfectant level goals (MRDLGs) and maximum residual disinfectant levels (MRDLs) for three chemical disinfectants - chlorine, chloramine and chlorine dioxide. It also establishes maximum contaminant level goals (MCLGs) and maximum contaminant levels (MCLs) for total trihalomethanes, haloacetic acids, chlorite and bromate.

Water systems that use surface water or ground water under the direct influence of surface water and use conventional filtration treatment are required to remove specified percentages of organic materials, measured as total organic carbon (TOC), that may react with disinfectants to form DBPs. Removal will be achieved through a treatment technique (enhanced coagulation or enhanced softening) unless a system meets alternative criteria.

Percent TOC Removal Required			
Source Water TOC mg C/l	Alkalinity 0 -60 mg CaCO ₃ eq./l	Alkalinity 60 -120 mg CaCO ₃ eq./l	Alkalinity > 120 mg CaCO ₃ eq./l
> 2 - 4	35	25	15
> 4 - 8	40	35	25
> 8	50	40	30

Systems meeting at least one of the alternative compliance criteria in the rule are not required to meet the removals in this table. Systems practicing softening must meet the TOC removal requirements in the last column to the right.

“WHAT ARE THE COMPLIANCE DEADLINES? Large surface water systems are required to comply with the Stage 1 Disinfectants and Disinfection Byproducts Rule and Interim Enhanced Surface Water Treatment Rule by January 2002. Ground water systems and small surface water systems must comply with the Stage 1 Disinfectants and Disinfection Byproducts Rule by January 2004.

“WHAT ARE THE COSTS AND BENEFITS OF THE RULE? EPA estimates that implementation of the Stage 1 Disinfectants and Disinfection Byproducts Rule will result in:

“The total annual cost of the rule is about \$700 million. EPA believes that the benefits exceed the costs of the Stage 1 Disinfectants and Disinfection Byproducts Rule. An estimated 116 million households are affected by the Stage 1 Disinfectants and Disinfection Byproducts Rule. EPA estimates that 95 percent of the households will incur additional costs of less than \$1 per month on their water bills. An additional four percent will pay between \$1 and \$10 per month more, and one percent are expected to incur increased water bills of \$10 to \$33 per month, if they choose to install treatment. However, many of these systems may chose less costly non-treatment options, such as consolidation. The majority of households incurring the highest costs are small systems serving less than 10,000 people that have never been regulated for DBPs.”

Evaluation of TOC Removal Requirement

The intent of USEPA's TOC removal requirements, seemingly to provide an additional measure of protection of public health against as yet undiscovered but potentially harmful disinfection by-products resulting from the reaction of disinfectants with dissolved organic compounds and as measured by the surrogate, TOC, appears laudable. Extending this rationale, it would be difficult to argue against the distillation of water for the virtually complete removal of the full spectrum of *potential* contaminants: organic, inorganic, microbiological, radionuclide and, possibly, unknown. However, in USEPA's rulemaking process, both TOC removal requirements and the mandated means by which it must be achieved, progressively became ever more convoluted and seriously inconsistent in terms of the amount of protection provided various consumers.

Limitation of TOC Removal Requirement to Surface Waters

Perhaps the most significant inconsistency was the assignment of the TOC requirement only to utilities deriving their water from surface water sources along with groundwaters under the influence of surface water. This concession avoided regulation of the numerous, small groundwater systems using well waters; even those containing as much as or more TOC than many larger systems affected by the requirement. As a result, a northern Missouri water utility with 3 mg C/l in their surface water source would have to reduce its finished water TOC to 2 mg C/l whereas a central Illinois groundwater supply with 24 mg C/l would have no TOC reduction requirement.

TOC Removal as a Function of Initial TOC

Another seemingly significant concession appears to have been made to utilities having high source water TOC concentrations. Irrespective of the source and nature of the TOC, some utilities with TOC > 8 mg C/l must achieve a 30% reduction whereas others with 2.1 mg C/l might have to achieve 35% removal. This would result in finished water TOC concentrations of 5.6 and 1.4 mg C/l, respectively. If TOC concentration is a credible index of the potential formation of *unidentified* DBP contaminants, this inconsistency does not lead to equal health protection.

Utilities having less than 2 mg C/l TOC are exempt from the removal requirement. This, despite evidence that some low TOC surface water sources exhibit high yields of disinfection by-products (e.g., trihalomethanes) owing to the nature (reactivity) of the organic material present (USGS, Thurman).

Another example of inconsistency may be drawn from the Mississippi River drainage basin data. The 12 mg C/l TOC in the Minneapolis region, possibly resulting from timber operations, including debarking, might be compared with the 3.8 mg C/l observed at Baton Rouge. In the lower region, the Mississippi River receives drainage from numerous petrochemical operations. Failure to recognize and identify the regional sources and nature of the TOC further undermines the rationale for the public health benefits made in establishing a nationwide TOC removal requirement.

TOC Removal as a Function of Alkalinity

TOC removal requirements also vary with alkalinity. This was included in the rule because high alkalinity represented an operational obstacle to *enhanced coagulation*, USEPA's designated treatment. Enhanced coagulation requires higher (more acidic) coagulant dosages or the supplemental addition of acid for the reduction of pH and the source water's natural alkalinity. Lowered pH facilitates the removal of only that portion of the TOC (humic acids) that can be sorbed on the precipitated coagulant at reduced pH. Because larger additions of acid are required for more alkaline waters, the TOC removal requirement is progressively relaxed with increasing alkalinity as a concession to cost and practicality.

The operational difficulty of restoring the alkalinity of water following coagulation at reduced pH does not seem to have been fully recognized. Failure to properly and consistently restore and readjust the alkalinity, pH and buffer capacity of the finished water is likely to result in increased corrosion of distribution mains and household plumbing, leading to potential violations with regard to lead and copper.

Failure to meet TOC Removal Requirements

In addition to removal of a portion of TOC by the entrainment of particulate organic matter within coagulant floc, Kastl et al., 2004 postulated that a portion of dissolved organic compounds (e.g., humic substances: humic and fulvic acids) are removed on hydrous metal oxide coagulants by sorption. This being so, there is no *optimum* dosage of coagulant, but a continuing incremental increase in DOC removal accompanying increased coagulant dosages.

Operationally, it is probable that waters whose TOC contains little particulate organic carbon and whose DOC consists primarily of *nonsorbable* organic compounds (relatively small, comparatively biodegradable, non-humic, hydrophilic acid molecules) will not exhibit significant TOC reductions from either the increased addition of coagulant or by coagulation at low pH. However, these nonsorbable organic compounds are reported to contribute less to the formation of the DBPs than the humic substances (Croue et al., 1998).

The observation that sorbable and nonsorbable organic compounds differ in yields of DBPs further undermines the rationale for mandating a specific TOC removal requirement without some prior knowledge of the nature of the organic matter present. In other words, does the specific organic matter present react with the applied disinfecting agents to produce DBPs?

Alternative Compliance Criteria

Because USEPA is aware of the numerous deficiencies in the TOC removal requirements, the Agency has provided a complex and, for many utilities, costly methodology to allow an unrealistic TOC removal requirement to be modified or waived. The following *Alternative Compliance Criteria* have been abstracted from USEPA's *Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual (1999)*.

Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual (USEPA, 1999)

"Certain waters are less amenable to effective removal of TOC by coagulation or precipitative softening. For this reason, alternative compliance criteria have been developed to allow plants flexibility for establishing compliance with the treatment technique requirements.

These criteria recognize the low potential of certain waters to produce DBPs, and also account for those waters not amenable to good TOC removal that may not meet the Step 1 TOC removal requirement.

A plant can establish compliance with the enhanced coagulation or enhanced softening TOC removal requirement if any one of the following six alternative compliance criteria is met:

1. *Source water TOC <2.0 mg/l*: If the source water contains less than 2.0 mg/L of TOC, calculated quarterly as a running annual average, the utility is in compliance with the treatment technique.

2. *Treated water TOC <2.0 mg/l*: If a treated water contains less than 2.0 mg/l TOC, calculated quarterly as a running annual average, the utility is in compliance with the treatment technique.

3. *Raw water SUVA 2.0 l/mg-m*: If the raw water specific ultraviolet absorption (SUVA) is less than or equal to 2.0 l/mg-m, calculated quarterly as a running annual average, the utility is in compliance with the treatment technique requirements.

4. *Treated Water SUVA 2.0 l/mg-m*: If the treated water SUVA is less than or equal to 2.0 l/mg-m, calculated quarterly as a running annual average, the utility is in compliance with the treatment technique requirements.

5. *Raw Water TOC <4.0 mg/l; Raw Water Alkalinity >60 mg/l (as CaCO₃); TTHM <40 µg/l; HAA5 <30 µg/l*: It is more difficult to remove appreciable amounts of TOC from waters with higher alkalinity and lower TOC levels. Therefore, utilities that meet the above criteria can establish compliance with the treatment technique requirements. All of the parameters (e.g., TOC, alkalinity, TTHM, HAA5) are based on running annual averages, computed quarterly. TTHM and HAA5 compliance samples are used to qualify for this alternative performance criterion. Additionally, utilities that have made a clear and irrevocable financial commitment (prior to the utility's effective compliance date for the DBPR) to technologies that will limit TTHM and HAA5 to 40 µg/l and 30 µg/l respectively, do not have to practice enhanced coagulation if the TOC and alkalinity levels of this criterion also are met.

6. *TTHM <40 µg/l and HAA5 <30 µg/l with only chlorine for disinfection*: Plants that use only free chlorine as their primary disinfectant and for maintenance of a residual in the distribution system, and achieve the stated TTHM and HAA5 levels, are in compliance with the treatment technique. The TTHM and HAA5 levels are based on running annual averages, computed quarterly. TTHM and HAA5 compliance samples are used to qualify for this alternative performance criterion.

Softening plants may demonstrate compliance if they meet any of the six alternative compliance criteria listed above or one of the two alternative compliance criteria listed below:

1. Softening that results in lowering the treated water alkalinity to less than 60 mg/l (as CaCO₃).

2. Softening that results in removing at least 10 mg/l of magnesium hardness (as CaCO₃). Softening plants that currently practice lime softening are not required to change to lime-soda ash softening by the enhanced softening treatment technique.

"Finished Water SUVA Jar Testing

Specific ultraviolet absorption (SUVA) is an indicator of the humic content of water. It is a calculated parameter equal to the ultraviolet (UV) absorption at a wavelength of 254 nm divided by the dissolved organic carbon (DOC) content of the water (in mg/l). The principle behind this measurement is that UV-absorbing constituents will absorb UV light in proportion to their concentration. Waters with low SUVA values contain primarily non-humic organic matter and are not amenable to enhanced coagulation. On the other hand, waters with high SUVA values generally are amenable to enhanced coagulation. A treated water SUVA criterion may allow some utilities to determine compliance with the treatment technique if the SUVA value is less than 2.0 l/mg-m. The determination of SUVA should be made on finished water that has not been exposed to any oxidant during treatment. If there is no oxidant (such as chlorine) added prior to the finished water TOC and UV-254 monitoring, full-scale samples can be used to calculate SUVA to allow comparison with this criterion. However, if oxidants are added prior to the finished water TOC and UV-254 monitoring, the utilities are required to establish treated water SUVA by conducting a jar test in which no disinfectants are added. The jar test can be performed by adding an equivalent amount of coagulant (metal coagulant plus any polymer that is used in full-scale) in a jar test apparatus and performing bench-scale coagulation tests. After completion of the jar test, the settled water should be characterized for its DOC and UV-254 parameters to calculate SUVA. (Filtration with a pre-washed 0.45 µm membrane is required for DOC and UV-254 determination). Due to interference from iron in the UV-254 measurement, utilities using ferric salts for coagulation are required to conduct the jar test described above using equivalent amounts of alum.

"TREATMENT TECHNIQUE WAIVER

Plants that consistently fail to achieve the PODR (i.e., the slope of the TOC vs. coagulant dose curve is never greater than 0.3 mg/l TOC removed per 10 mg/l alum or equivalent dose of ferric salt added) at all coagulant dosages during the Step 2 jar test procedure, are considered to have a water unamenable to enhanced coagulation, and may apply to the State for a waiver from the enhanced coagulation requirements. The plant should provide supporting documentation to the State to demonstrate that it was unable to achieve the PODR. States may require plants to continue quarterly Step 2 testing to demonstrate that the water is unamenable to enhanced coagulation."

Alternative Compliance Criteria 5 and 6 appear to acknowledge the probability that low yields of TTHM and HAA5 are an indication that unknown DBPs are not being formed in excessive amounts. Why this reasoning was not extended to the use of combined residuals or disinfection in general is not clear.