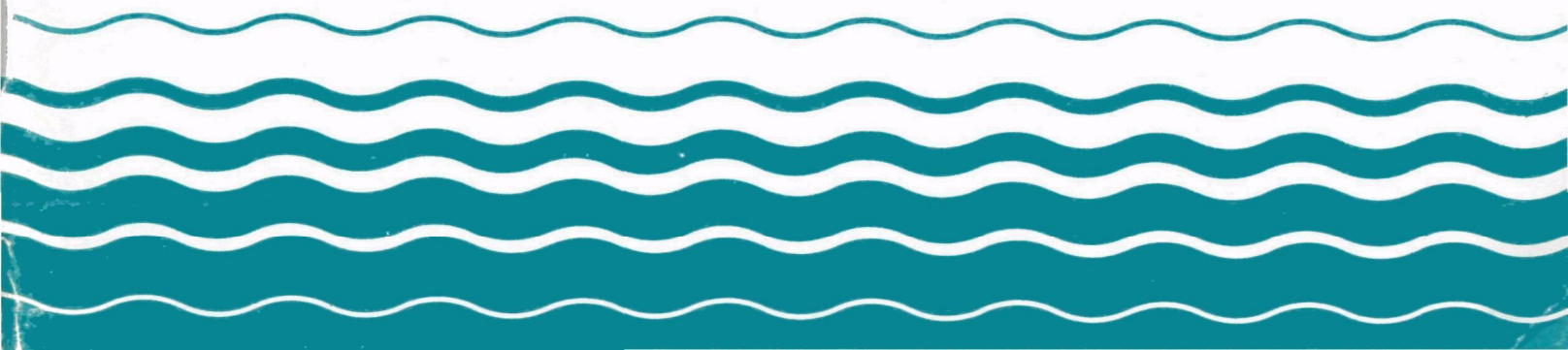




Water

# **Trihalomethanes in Drinking Water**

## **Sampling, Analysis, Monitoring and Compliance**



TRIHALOMETHANES IN DRINKING WATER  
Sampling, Analysis, Monitoring and Compliance

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## INTRODUCTION

On November 29, 1979, the Environmental Protection Agency (EPA) promulgated an amendment to the National Interim Primary Drinking Water Regulations (NIPDWR) to control trihalomethanes (THMs) in drinking water (see 44 F.R. 68624). The amendment established a maximum contaminant level (MCL) of 0.10 mg/l and associated monitoring and reporting requirements for total trihalomethanes (TTHMs). Community water systems which use a disinfectant and serve more than 75,000 persons were to begin monitoring and be in compliance with the MCL, 1 and 2 years, respectively, following promulgation. Community systems which use a disinfectant and serve 10,000 to 75,000 persons are to begin monitoring and be in compliance with the MCL 3 and 4 years, respectively, following promulgation.

On February 28, 1983, EPA published an amendment to the TTHM implementation regulations (see 48 F.R. 8406). This amendment defines both those treatment techniques which the Administrator has determined are generally available (taking costs into consideration) for TTHM control and criteria by which individual states or other primacy agencies\* may issue variances to the TTHM rule. The available treatment methods are discussed in a later section of this guidance.

The underlying objective of the regulation is to provide public drinking water with fewer potential chemical health hazards while ensuring continued protection against pathogenic microorganisms. The purposes of this document are to provide guidance to assist EPA Regional offices, individual states and affected systems in their implementation of the TTHM regulation, and to help ensure that actions taken toward implementation will be consistent. This document is purely advisory in nature and is meant to supplement the regulation. Any discussion of definitive requirements, i.e., actions which "must" be taken, should be evaluated in light of the applicable promulgated regulations.

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Hereinafter, the term "primacy agency" will be used to describe the entity possessing primary enforcement authority under the Safe Drinking Water Act, either individual state regulatory agencies or (in those states which have not accepted primacy) EPA.

## EFFECTIVE DATES OF THE MCL, MONITORING, REPORTING REQUIREMENTS

To facilitate coordination with other program requirements of the NIPDWR, the first quarter of required THM monitoring for systems serving over 75,000 ended on March 31, 1981, and the effective MCL date for the first annual running average ended on December 31, 1981. Similarly, for systems serving between 10,000 and 75,000, the first quarter of required THM monitoring will end on March 31, 1983 and the effective date for the MCL will be December 31, 1983. In the promulgated regulations the effective MCL dates were November 29, 1981, and November 29, 1983, for the respective system sizes. This would require the running annual average to be calculated from quarters ending February 28, May 31, August 31 and November 29. For purposes of convenience to state programs, for consistency with all previous regulations and for workability with the Model State Information System (MSIS), and the Federal Reporting Data System (FRDS) to be discussed later in this guidance, the quarters will now end on March 31, June 30, September 30 and December 31.

In the promulgated regulation the quarterly averages were required to be reported to the state within 30 days of the system's receipt of such results. For consistency with reporting requirements listed in Section 141.31 as amended on August 27, 1980 in 45 F.R. 57343, TTHM quarterly averages will be reported to the state within (a) the first 10 days of the month following the month in which the system received its results or (b) if the required monitoring period is stipulated otherwise by the primacy agency, within the first ten days following the end of that period during which the system received its results.

## MONITORING FOR TTHMS

### Trihalomethanes Analysis (see 40 CFR 141.30(e))

Measurements must be made in accordance with EPA Method 501.1, "The Analysis of Trihalomethanes in Finished Waters by the Purge and Trap Method", with Method 501.2, "The Analysis of Trihalomethanes in Drinking Water by Liquid-Liquid Extraction", with Method 501.3, "Measurement of Trihalomethanes in Drinking Water with Gas Chromatography/Mass Spectrometry and Selected Ion Monitoring" or with EPA Method 510.1, "The Determination of the Maximum Total Trihalomethane Potential". (Methods 501.1, 501.2, 501.3, and 510.1 are available from the Environmental Monitoring and Support Laboratory (EMSL) in Cincinnati, Ohio). The Office of Drinking Water, Technical Support Division in conjunction with the American Water Works Association has prepared a four part audio-visual program detailing THM sampling and analysis consistent with these methods. This program is available for loan on 3/4 inch U-Matic and 1/2 inch VHS video tape, as well as 16 mm film. For further information contact: Mr. Steven Merritt, Audio-Visual Library, U.S. Environmental Protection Agency, 26 W. St. Clair Street, Cincinnati, Ohio 45268.

### MTP (Maximum Total Trihalomethane Potential)

The MTP determination attempts to maximize the formation of THMs such that the test results might be indicative of how high the TTHM concentration in the distribution system might become under conditions favoring TTHM formation. It may be used by systems employing ground water sources to demonstrate the appropriateness of the reduced monitoring requirements (discussed below) allowed under the TTHM regulations.

The MTP determination has two parts: (1) a 7-day terminal THM measurement under conditions of simple storage of a distribution sample at 25°C in the presence of a disinfectant residual, and, (2) if the requirement for a disinfectant residual is not met at the end of the storage period, EPA Method 510.1 is performed on a fresh sample.

Method 510.1 is designed to be a reasonable (but high) estimate of a terminal THM value for ground water systems. Because Method 510.1 is applied only when a disinfectant residual is not present after performing the first part of the MTP determination (simple sample storage and analysis), its purpose is to measure precursors in those systems exhibiting a disinfectant demand higher than the disinfectant dose added at the treatment plant. Such systems have THM potentials that may often be higher than demonstrated by instantaneous THM monitoring in the distribution system, and thus are those most likely to exceed the MCL with changes in disinfection practice.

The water sample used for this determination should be taken from a point in the distribution system that reflects maximum residence time. Procedures for sample collection and handling are given in Methods 501.1 and 501.2. No reducing agent is added at the time of sample collection to stop the chemical reaction that produces THMs. The intent is to promote higher THM formation than ever reasonably would be expected in the distribution system. Four experimental parameters affecting maximum THM production are: pH, temperature, reaction time and the presence of a disinfectant residual. These parameters are dealt with as follows:

Measure the concentration of the disinfectant residual at the selected sampling point. Proceed only if the disinfectant residual concentration is greater than 0.2 mg/l. Collect triplicate 40 ml water samples at the pH prevailing at the time of sampling, and prepare a method blank\* according to Methods 501.1 and 501.2. Seal and store these samples together for 7 days at 25°C or above. After this time period, open one of the sample containers and check for disinfectant residual. "Absence" of a disinfectant residual invalidates the sample for further analysis. Residual concentrations less than 0.2 mg/l should be considered "absent" to account for possible analytical error. Once a disinfectant residual has been demonstrated, open another of the sealed samples and determine total THM concentrations using either of the analytical methods.

In the case of sample invalidation because of disinfectant residual depletion, additional samples should be taken and the analysis should proceed according to method 510.1. In this method chlorine is added to provide an initial concentration of 5 mg/l and the solution is buffered at a pH of 9.0 to 9.5 prior to incubation at 25°C or above for 7 days. The high pH and temperature, and long incubation time will produce a higher THM formation than is to be expected in the distribution system, which is the main objective of the test. Systems which can demonstrate an MTP value of less than 0.10 mg/l under experimental conditions favoring TTHM formation are prime candidates for reduced monitoring.

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For greater discussion of a method blank, see Section 6.4.9 of Method 501.1 or Section 6.4.10 of Method 501.2

## Reduced Monitoring Requirements (see 40 CFR 141.30(b)-(c))

### (1) Surface Water Systems

Systems with any portion of their source being surface waters are required to monitor a minimum of four samples per quarter per plant. After one year of compliance-data monitoring, a system may request that the primacy agency allow a reduced monitoring frequency of no less than one TTHM sample per quarter, taken at a point in the distribution system that reflects the maximum residence time of the water served.\*

If the system has only one source water, but more than one treatment plant, the composite system may be allowed to reduce its monitoring after one year to a minimum of one sample per quarter per plant at the point reflecting maximum residence time. If treatment plants within a system receive their water from different surface sources the system should not reduce its monitoring to less than one TTHM analysis per plant per quarter at the point reflecting maximum residence time. If one of the sources to the system is ground water, the primacy agency may find it appropriate to reduce the required samples for the treatment plant receiving the ground water (not the entire system) to one MTP sample per year. In multiple source systems it may not be possible to determine maximum residence time sampling points for the different source waters. In such cases it is appropriate to measure one quarterly terminal TTHM value for the finished water from each treatment plant receiving a different source water to fulfill the minimum monitoring requirements. Terminal TTHM is defined according to the conditions of the system, i.e., the TTHM determined after incubation for a period and temperature equivalent to those at the maximum residence time of the distribution system. (8)

The decision to reduce monitoring frequency must be made by the primacy agency on a case-by-case basis and should take into account monitoring data, quality and stability of the source water, and the type of treatment. The following are recommended guidelines for reducing monitoring requirements for surface water systems:

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If the state is conducting the TTHM analysis as a service to the system there is no need for such a request. The state that is doing the TTHM analysis can make the decision on when reduced monitoring can be applied to the specific system.



- (a) The instantaneous THM determination in the distribution system should never be greater than 0.10 mg/l. The system should demonstrate that the instantaneous THM concentration is less than 0.10 mg/l when maximum THM formation is likely to occur (i.e., during periods of highest TOC, pH and temperature).
- (b) As a worst-case example, systems can make MTP determinations during periods of highest expected THM formation. Systems with less than 0.10 mg/l MTP under such conditions are prime candidates for reduced monitoring frequency while those with greater than 0.10 mg/l MTP are not necessarily excluded from reduced monitoring.
- (c) The source water should be relatively stable in regard to TOC, pH, turbidity and temperature. If these parameters fluctuate greatly, the system should demonstrate, at least with quarterly monitoring, that this does not significantly affect the variability of the THM levels at different times of the year. The significance of THM variability depends on the annual THM running average; i.e., as the value of the annual running average decreases, the percent scatter of THMs becomes less important since the MCL will not be approached.
- (d) The treatment process should remain relatively constant throughout the year. If not, the system should demonstrate, at least through quarterly monitoring, that THM levels in the distribution system will not vary significantly as the treatment process changes, e.g., THMs must be monitored in the distribution system before and after such changes are made.
- (e) Systems using chloramines for residual disinfection will have minimized further formation of THMs and will have less THM variation in their distribution systems; therefore, they should be considered prime candidates for reduced monitoring.
- (f) The systems should demonstrate that reduced monitoring will take place during periods and at locations reflecting maximum THMs in the distribution system.

The primacy agency should specify the reduced monitoring permitted to the system. Should the system experience an important change in either its source of water or its treatment program, it must immediately reinstitute the four samples per quarter monitoring initially required. The system must continue on that program for at least one year and the sampling frequency should not be reduced until the data baseline is re-established and the primacy agency concurs with any reduction. Treatment changes that could potentially increase THM formation in the distribution system should be considered important. Examples of this include increasing the pH for corrosion control, adopting pre-chlorination, increasing the disinfection dosage, changing the coagulant type and/or decreasing its dosage for purposes other than THM control, or changing from a chloramine or chlorine dioxide residual to one of free chlorine. THM levels obtained under reduced monitoring should reflect maximum rather than average concentrations within the system. These data should be used to demonstrate compliance but are not intended to demonstrate non-compliance. Rather, such data should be used for determining whether the required number of samples (as designated by the primacy agency) have been taken and whether that system may remain under the reduced monitoring program. If any result obtained under a reduced monitoring program ever exceeds 0.10 mg/l, then that result should be used only as a trigger to require that system to return to the standard frequency. The original sampling requirements must be immediately reinstated if any THM result (under a reduced monitoring protocol) exceeds 0.10 mg/l and is confirmed by at least one check sample taken promptly after the results of the first analysis are received. In such a case, the result which triggered the return would not be used in any calculations for compliance determination and would, in essence, be discarded. If the value of the check sample is below 0.10 mg/l, prompt additional sampling and a quality control check by the laboratory performing the analysis should be conducted in order that the primacy agency may determine if reduced monitoring is still appropriate. A synopsis of the decision-making process for reduced monitoring in surface water systems is shown in Figure 1.

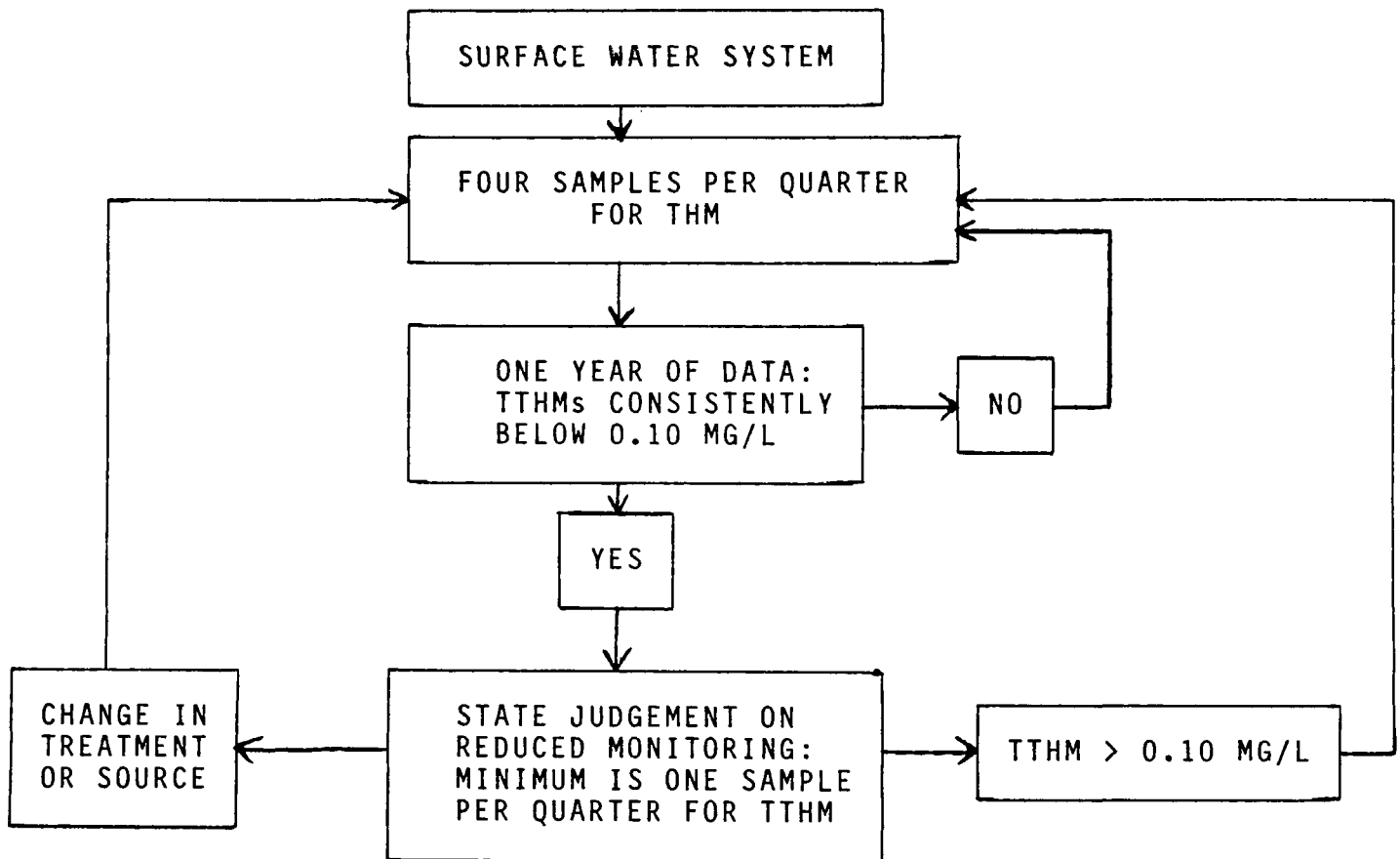
## (2) Ground Water Systems

Ground water systems generally have lower and more consistent precursor content than surface water systems. The regulation thus allows monitoring requirements for systems exclusively using ground water to be reduced to a minimum of one maximum total trihalomethane potential (MTP) test per year, for each aquifer contained in the system, taken at a point in the distribution system reflecting maximum residence time. In multiple aquifer systems it may not be possible to determine the points of maximum residence time. In such cases it may be

FIGURE 1

CONSIDERATIONS FOR REDUCED MONITORING REQUIREMENTS  
SURFACE WATER SYSTEMS

The minimum monitoring requirement is four samples per quarter per plant. Partially reduced monitoring requirements may be appropriate in certain cases. Upon written request from the public water system, primacy agencies may reduce the requirements through consideration of appropriate data as follows:



FACTORS FOR CONSIDERATION:

- o Monitoring Data, MTP, TTHM, TOC
- o Quality and Stability of Source Water
- o Type of Treatment

appropriate to sample for MTP at the finished water of each plant. Systems using multiple wells drawing water from a single aquifer may, with primacy agency approval, be considered as one treatment plant in regard to monitoring requirements. In order to immediately reduce monitoring requirements to the minimum, the system should provide a data base substantiating that the MTP is less than 0.10 mg/l during the period of maximum TTHM formation and/or when TOC concentrations are highest.

If a system under the minimum monitoring requirements changes its source water or treatment program (i.e., a treatment change that could increase THM formation as previously discussed) it must immediately sample to determine whether continued reduced monitoring is appropriate. If the MTP is ever greater than 0.10 mg/l and such results are confirmed by a check sample taken promptly after the results of the original sample are received, the system must immediately begin taking and analyzing four samples per quarter per year for one full year. If the check sample is less than 0.10 mg/l, additional monitoring and laboratory quality control checks should be conducted before the primacy agency determines if reduced monitoring can be continued. As previously discussed, TTHM levels obtained during reduced monitoring will reflect maximum concentrations within the system rather than average conditions and are intended to demonstrate compliance, not demonstrate non-compliance. Figure 2 is a synopsis of the decision process for reduced monitoring in ground water systems.

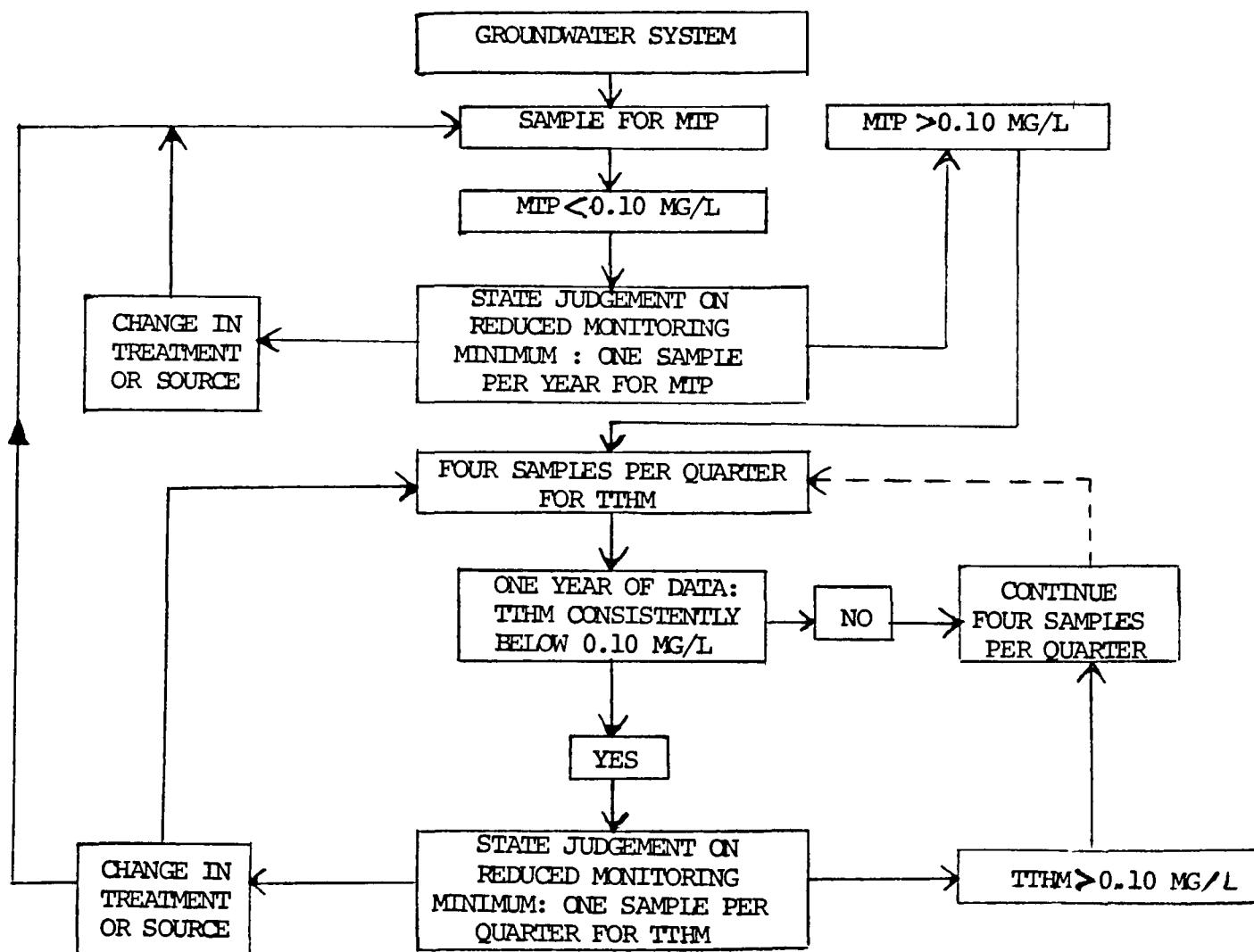
#### When to Monitor

Quarterly monitoring periods will end on March 31, June 30, September 30 and December 31 (see discussion on effective dates of the MCL, monitoring and reporting requirements). Monitoring within each quarter should take place during the same month (i.e., first, second or third) of each quarter to ensure representation of seasonal effects.

FIGURE 2

CONSIDERATIONS FOR REDUCED MONITORING REQUIREMENTS  
GROUNDWATER SYSTEMS

The minimum monitoring requirement is four samples per quarter per plant: systems using multiple wells drawing raw water from a single aquifer may with primacy agency approval be considered as one treatment plant. Reduced monitoring requirements may be appropriate in certain cases; upon written request from the public water system, primacy agencies may reduce the requirements through consideration of appropriate data as follows:



Factors for Consideration :

- o Monitoring Data, MTP, TTHM, TOC
- o Type of Treatment
- o Quality and Stability of Source Water

## Sampling Locations

1. Sampling locations from taps in the distribution system should be approved by the primacy agency.
2. No more than seventy-five percent of the samples must be collected from locations that represent the majority of people served. The sampling sites should be separated equally from each other in the distribution system to the extent possible.
3. At least twenty-five percent of the samples must be collected from a location(s) reflecting maximum residence time. This must be from a remote point(s) in the distribution system through which there is active water passage, i.e., not a dead end.
4. In cases of more than one water source and/or treatment plant in a system, sampling points should be determined so as to be quantitatively and qualitatively representative of each water source.
5. For each treatment plant in a system, there must be at least four sampling locations. Upon primacy agency approval, water from a single aquifer may be considered a single treatment plant for determining the minimum number of samples required.
6. In situations where a system has two separate plants, both drawing water from the same source, via the same intake, the primacy agency may elect to treat the plants as one for the purpose of determining the number of TTHM samples required to be taken, if the two plants:
  - a) have like treatment processes, and
  - b) serve the same distribution system or serve distribution networks with similar maximum residence times.

Primacy agencies should use extreme care in allowing this sampling merger and should do so only after the two plants demonstrate:

- a) similar analytical results, and
  - b) separate compliance with the 0.10 mg/l MCL.
7. The primacy agency should determine whether booster chlorination stations should be considered separate treatment plants within a system. If booster chlorina-

tion stations are not considered a treatment plant, then it is recommended that the number of sampling locations beyond such chlorination points be based on population density throughout the distribution system. The sample(s) reflecting maximum residence time must be taken in the extremity of the distribution system beyond such chlorination points.

8. Sampling for trihalomethanes should be a continuing program. Once sample locations have been established for an individual water system, they should remain the same unless there is a substantial reason for changing (e.g., change in water source and/or in the entry point to the distribution system). In such cases the primacy agency must be notified. Sample collection locations should therefore be selected carefully such that year-round access is assured while inconvenience to the customer is minimized.
9. Fire hydrants must not be used as sampling points. Samples from a hydrant may not provide "representative" water quality.
10. All samples must be representative of the water in the water main and not "dead" water from the building or water service piping. Sampling points at buildings having large service lines and only periodic use (e.g., large churches and department stores) should be avoided.
11. Samples should not be collected at buildings having their own water softener or purifier unless the faucet used for sampling is not connected to the water conditioner.

#### Surveillance for Other Organic Compounds

It is recommended that systems ask the certified laboratories conducting their THM analysis also to be alert for other peaks on their chromatograms. The Office of Drinking Water strongly encourages all systems to examine all of the data available from their THM analysis. In addition to demonstrating compliance with the MCL, a typical THM analysis can indicate the presence of other potentially serious contaminants. Chromatographic peaks which appear with significant amplitude and consistency reflect other volatile organic compounds which should be identified and reported so that the significance of the contaminant(s) can be evaluated.

DETERMINATION OF COMPLIANCE WITH THE MCL (see 40 CFR 141.30(d))

1. Sampling from two types of locations are required:

at least 25 percent from those reflecting maximum residence time (type "A") and no more than 75 percent from those reflecting the quality of water consumed by the majority of customers (type "B").

For purposes of compliance, the system must determine its annual running average from quarterly averages having the above distribution. If more than four samples are taken in a quarter, and they are not a multiple of four and are not in accord with the above distribution, the following formula must be used for determining the quarterly average:

$$\begin{aligned} & (\text{average of type "A" samples}) \times 0.25 \\ & + (\text{average of type "B" samples}) \times 0.75 \\ & = \text{quarterly average.} \end{aligned}$$

2. For systems with more than one treatment plant, the quarterly average, representative of each treatment plant, should be determined separately. The quarterly average for the entire system must be calculated by weighting the averages from each of the treatment plants (total number of treatment plants = n) as follows:

$$\begin{aligned} & (\text{quarterly average for samples representing treatment plant 1}) \\ & \quad \times (\text{fraction of flow* into system from plant 1}) \\ & + (\text{quarterly average for samples representing treatment plant 2}) \\ & \quad \times (\text{fraction of flow* into system from plant 2}) \dots \\ & + \dots (\text{quarterly average for samples representing treatment plant n}) \\ & \quad \times (\text{fraction of flow* into system from plant n}) \\ & = \text{quarterly average for system.} \end{aligned}$$

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For purposes of this determination only, flow is defined as the average daily flow for the subject treatment plant during the subject compliance period.



Although not required by the regulation, the annual running average representative of each treatment plant within the system should also be reported to the primacy agency. Systems are encouraged to ensure that each treatment plant within the system distributes water within the limits of the MCL. Because of mixing, obtaining samples from a common distribution system that uniquely represents each of the different treatment plants feeding into the system may not be possible. In such cases terminal THM determinations from the finished water of each treatment plant may be useful for making judgements as to how best to achieve compliance with the TTHM MCL (as discussed in the section on evaluating treatment options). Terminal THM is the measured trihalomethane concentration after the reaction between precursors and free chlorine has been allowed to continue in a sealed container at the temperature and for the maximum residence time of that water in the distribution system (8).

3. For calculating the annual running average, each quarterly average must be given equal weight regardless of the number of samples taken per quarter.
4. The annual running average must be computed to two significant figures. If this is greater than 0.10 mg/l (i.e., 0.11 or above), the system is out of compliance and must follow the public notification procedures, a summary of which is contained in the Appendix. Rounding-off numbers shall be in accordance with Water Supply Guidance No. 72 (see Appendix).

## CONSECUTIVE SYSTEMS

A system purchasing water in whole or in part from another system is considered a "consecutive system". Such systems having populations greater than 10,000 are required to meet the MCL; however, it may not be reasonable to consider each consecutive system as a separate system in regard to monitoring requirements. If TTHM levels at the most remote points of the combined systems are well below the MCL, the primacy agency may determine it appropriate to permit reduced monitoring in the preceeding systems having shorter residence times.

If the preceeding system exceeds the MCL, the consecutive system is also likely to do so and it is then in the mutual best interest for the two or more systems to work together so that all will be in compliance with the MCL. Without such mutual co-operation, it would be possible for a treatment change in the main system to reduce the parent's average TTHM levels below 0.10 mg/l while the consecutive system remained out of compliance. The parent system should, at least, make the appropriate modifications to reduce the THM concentration below 0.10 mg/l at the point where the consecutive system receives the water. In cases where the preceding system has average TTHMs just below 0.10 mg/l within its distribution system and is reluctant to make treatment changes in concern for the system receiving its water, several treatment options for the consecutive system exist to stop further THM formation. These include the addition of ammonia to combine with any remaining free chlorine and provide a chloramine residual, or, in lieu of additional chlorination (if that residual has been exhausted), the addition of chlorine dioxide or other alternate disinfectants. The use of chloramines should be considered only after a careful analysis of all aspects of the chloramination technology, including the potential health risks associated with its use. Extensive discussions of these issues are contained both later in this document and in several references (4, 7, 16, 22-24).

A combination of parent and consecutive systems wherein the total population served is above 10,000 while the individual system populations are each below 10,000 is an anomalous situation but one not to be easily dismissed. Although the regulation does not require compliance by any of such affected systems, the primacy agency may (after suitable study) determine that compliance by one or more of those systems is desirable. Such an extension should be pursued only after the overriding concern for continual maintenance of suitable microbiological quality at all points in the combined systems has been satisfied.

## THE ROLE OF MSIS

The Model State Information System (MSIS) will implement automatic determination of compliance with trihalomethane (THM) sampling requirements for the compliance quarter ending March, 1981. Each calendar quarter, violations will be determined for failure to sample by public water systems that serve at least 75,000 people and employ a disinfection agent, or for which trihalomethane monitoring is required under federal or state regulation. Within constraints set forth in the regulation, the state may specify through MSIS, the total number of THM samples required from a specified system, annual reduced monitoring frequency for a specified system, or the total number of treatment plants from which a minimum of four samples per plant per quarter will be required. Each sample must be identified as representative either of the distribution system or of the maximum residence time of water in the system. MSIS will identify failure to adhere to the sampling ratio of 25 percent to 75 percent of the number of required samples representing, respectively, the maximum and average residence times of water in the distribution system. For example, a system would not be in violation if it conducts more than the minimum number of sample analyses as long as it adheres to the criterion of 25% of samples representing maximum residence time.

In determination of trihalomethane contamination, MSIS will appropriately apply factors of 0.25 and 0.75, respectively, to single sample analysis results in calculating the sum of 4 equally weighted quarterly averages that will be used to determine compliance with the MCL. Quarterly averages calculated by MSIS do not necessarily reflect the percentage of total flow from individual treatment plants. For each Public Water Supply, MSIS will accept a previously calculated, weighted average of all analysis results per quarter, for use in annual contamination determination.

## MICROBIOLOGICAL CONCERNS AND SAFEGUARDS (see 40 CFR 141.30(f))

Systems should take specific precautionary measures to ensure that the microbiological integrity of their water is not compromised as a result of treatment modifications to reduce THM levels. The THM regulations require that before a water system makes a significant modification to its existing treatment process, for the purposes of achieving compliance with the THM MCL, the system must submit to and receive approval from the primacy agency a plan describing its projected course of action. This plan must indicate both the proposed treatment modifications and the safeguards intended to be taken to protect the microbiological quality of the drinking water. Figure 3 illustrates a recommended course of action for providing adequate safeguards while meeting the THM MCL.

Modifications that might be considered significant are those whose effects on microbiological quality cannot be predicted. For example:

- o a change in the type, dosage, point of application or contact time of the disinfectant;
- o a change in or blending of the source water;
- o the installation of an open finished water reservoir; or,
- o the addition of an adsorbent (e.g., activated carbon) in the treatment chain.

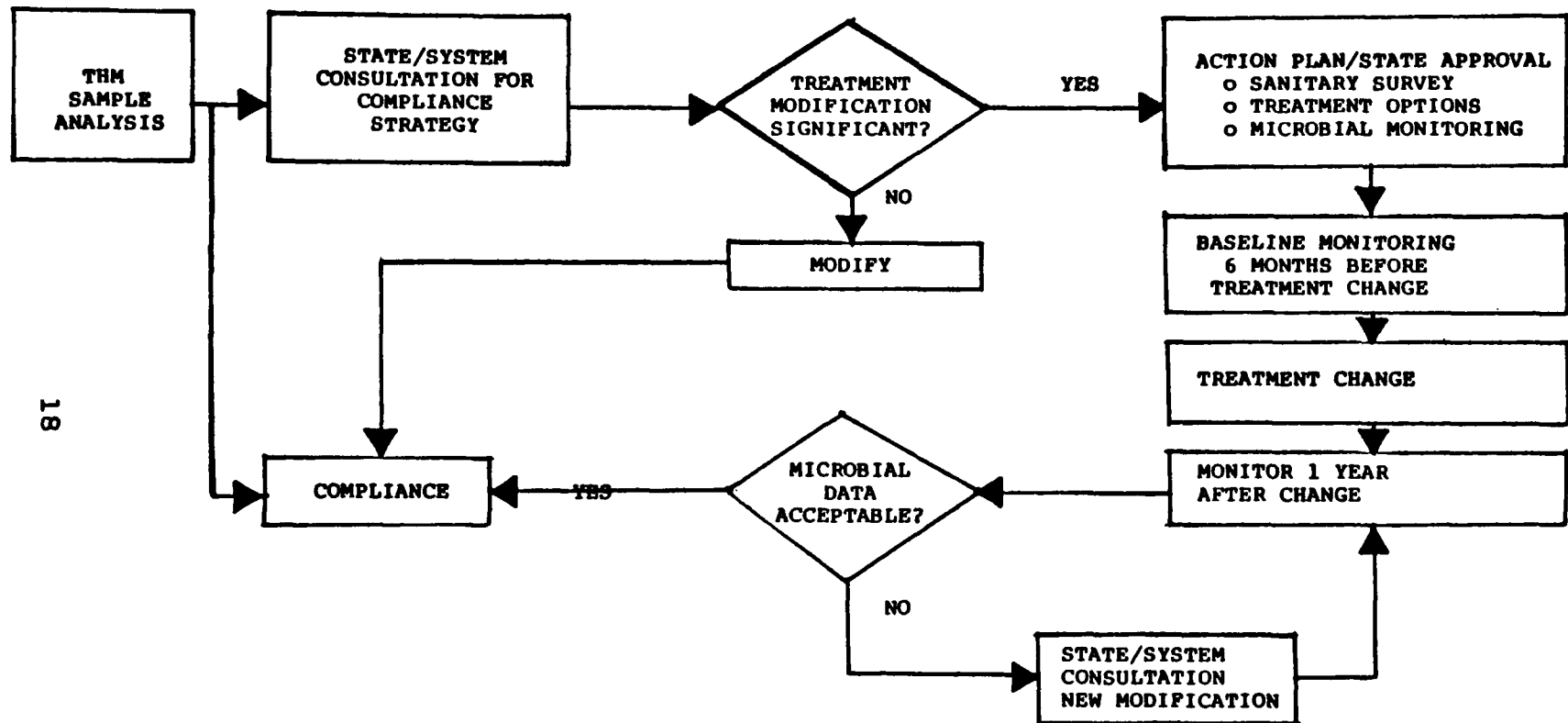
If after consultation with the system, the primacy agency determines that the proposed modifications are significant (i.e., may pose an increased potential human health risk), then the system must submit an action plan which contains at least the specific provisions detailed below:

### Evaluation of System for Sanitary Defects

The system's action plan should include provision for a thorough sanitary survey of the entire system (source, treatment train and distribution system) before any treatment changes for THM control are formally proposed. The purpose of the survey is to collect information to determine the capability of a system to continuously provide water that both meets the NIPDWR and is adequately protective of public health. Any sanitary defect or unsound treatment practice must be identified and corrected before THM control practices are initiated.

Figure 3

RECOMMENDED PROCEDURE FOR ENSURING  
MICROBIOLOGICAL SAFETY OF DRINKING WATER



There are many excellent sanitary survey protocols available from e.g., the Conference of State Sanitary Engineers or the American Water Works Association (AWWA). The survey protocol should, as a minimum, include the following elements:

- (a) an examination of the source water and the potential for its pollution. For surface water sources, attention should be directed to the location of wastewater treatment plants, storm water drains and sewer outfalls, and characteristics of the watershed drainage area. For ground water sources inspection should include the drainage area and habitation, local geology, nature of soil and rock strata, slope of the water table and potential sources of pollution.
- (b) an examination of the complete treatment and distribution system including the adequacy of each unit process, the sanitary safety of the storage and distribution facilities (including all pump stations) and the potential for cross-connection contamination.
- (c) an evaluation of the previous 12 months of microbiological records and chemical analyses on water from the source, the treatment plant and the distribution system.
- (d) an evaluation of operating plans and records for present capacity, demand and production.
- (e) a review of the training, experience and capabilities of the personnel.
- (f) a review of the laboratory equipment and procedures, including the qualifications of the laboratory personnel.
- (g) an examination of system compliance for federal, state and local regulations and plumbing codes.
- (h) a summary and analysis of all facts pertinent to potential or existent health hazards within the system from the source to the consumer's tap.

The person making the survey should have education in basic sanitary sciences and have experience in the concerns mentioned above. A survey report, summarizing the above findings, including maps and sketches where appropriate, should be submitted with the system's action plan for THM control.

#### Evaluation of Treatment Options

Following the sanitary survey and correction of any sanitary defects, the system should develop a plan for optimizing existing unit processes for THM control; this should be submitted to the primacy agency as part of the action plan. The plan should provide a comprehensive evaluation of any existing unit processes for such parameters as precursor removal, disinfection efficiency and formation of THMs. Appropriate THM control options can be assessed only with a fundamental and thorough knowledge of the prevailing efficiency of the entire treatment process. A THM profile through the treatment plant and distribution system should be developed to show where control can be exercised (2, 8).

Selection of the most appropriate treatment options will be influenced by their apparent effectiveness for lowering THM concentration, the microbiological quality of the raw water, raw and finished water quality and costs. Several treatment options may need to be considered before the optimum can be selected.

#### Baseline Water Quality Survey

The system's action plan should also include a detailed description of its baseline monitoring survey. The purpose of this survey is to detect changes in the quality of the water within the system, resulting from treatment modifications, that may lead to increased public health risk.

Total coliforms are the most commonly used indicators for the microbiological quality of drinking water and are essential to this baseline survey. This use, however, needs to be supplemented with the use of other microbiological and chemical parameters to ensure that subtle deteriorations in water quality and attendant increased risk to public health do not remain undetected. For example, the lack of coliform recovery by itself does not guarantee an absence of pathogens (9-11). Coliforms are less resistant to environmental stress and disinfection than some pathogenic viruses and bacteria. More of the pathogenic organisms either may survive the altered treatment process, thereby directly increasing the public health risk, or may multiply in finished waters leading to slime deposits, tubercule formation and interference with coliform determination (11).

The water quality should be monitored before and after the THM treatment modifications are implemented. Over long periods of time changes in water quality can be masked by normal seasonal variations. Therefore, the survey should begin a minimum of 6 months before the treatment modification (including at least the warmest water month) and continue for 1 year after the treatment modification. Changes in water quality due to normal seasonal variations, volume of water storage or stream flow, and unusual weather conditions can be important to the interpretation of data. The influence of these effects should be evaluated before decisions are reached concerning potentially detrimental changes in the quality of the water.

#### (1) Water Quality Parameters

Parameters which may aid in evaluating both the impact of THM controls upon and the continued optimum microbiological quality of finished drinking water include:

- ° total coliforms,
- ° standard plate count incubated for two (2) days at both 35° C and 20° C,
- ° heterotrophic plate count incubated for at least five (5) days at environmental temperature (e.g., 20° C), or at 28° C using R-2A media with 7-day incubation (see Appendix for media preparation),
- ° disinfectant residual,
- ° enteric viruses in systems with grossly polluted source waters,
- ° turbidity ,
- ° total fecal coliforms,
- ° fecal streptococci,
- ° orthophosphate,
- ° ammonia nitrogen,
- ° total organic carbon,
- ° pH, and
- ° temperature.



A primacy agency should decide which of the above (or additional) parameters are appropriate for inclusion in the system's baseline survey, given the local conditions at specific supplies (see 40 CFR 141.30 (f)). The approved plan should require the maintenance of an active disinfectant residual throughout the distribution system at all times both during and after any proposed treatment modifications. Required monitoring should be sufficient to demonstrate the presence of this active residual.

Analytical procedures appropriate to the microbiological parameters listed above can be found in the 15th edition of Standard Methods for the Examination of Water and Wastewater (12), or Microbiological Methods for Monitoring the Environment (13). Analytical procedures appropriate to the physical and chemical parameters listed above can be found in Standard Methods for the Examination of Water and Wastewater (12), Methods for Chemical Analysis of Water and Wastes (14), and the Annual Book of ASTM Standards, Part 31 Water (15). Those methods which are recommended are shown in Table 1. A discussion of certain water quality parameters follow:

#### o Bacteriological Quality

The presence of total coliforms in finished water indicates potential penetration of the treatment barrier by pathogenic bacteria. These organisms should not be present at any time in the treatment plant effluent or in the distribution system. If any such organisms are present, then this potential problem should be identified and corrected.

The standard plate count at 35°C is an indicator for the potential presence of opportunistic pathogens, such as certain strains of Pseudomonas and Flavobacterium, and organisms which can interfere in the total coliform test (23). The standard plate count at the lower temperature accommodates slower growing bacteria that are adapted to the aquatic environment; this is particularly suited for indicating bacterial growth within the distribution system. To obtain maximum sensitivity, optimum temperatures and incubation times should be determined. Standard plate counts taken before and after alterations in the disinfection process can be useful in detecting changes in bacteriocidal effectiveness.

Table 1 -- Recommended Chemical and Physical Methods

<u>Parameter</u>	<u>Methodology</u>	<u>EPA(14)</u>	<u>SM(12)</u>	<u>ASTM(15)</u>
Turbidity	Nephelometric	180.1	214A	--
pH	Potentiometric	150.1	423	D1293-78 A or B
Temperature	Thermometer	--	212	--
TOC	Combustion or Oxidation Low Level TOC	415.1  (See appendix)	505*	D2579-78(A)*
Ammonia Nitrogen	For drinking water, need not distill if using nesslerization, the electrode or automated phenate. However, must concen- trate by distilling if using titration. **	-- 350.3 350.1 -- 350.2	417B -- 417E 417F 417D	D1426-79 (A) D1426-79 (D) D1426-79 (C) --
Orthophos- phate	The ascorbic acid method automated or manual or manual two- reagent	365.1 365.2 365.3	424G 424F --	-- D515-78 (A) --

\*

This method's sensitivity is approximately 1.0 mg/l. Therefore, it may not be appropriate for use by all systems in all situations.

\*\*

The titrimetric method is used primarily for measuring relatively high NH<sub>3</sub>-N concentrations (i.e., above 5.0 mg/l) and this may not be appropriate for use by all systems in all situations.

A new medium, R-2A, has been developed by EPA which yields a significantly greater number of bacterial colonies and colony types than SPC agar. Consideration should be given to using R-2A agar in lieu of SPC agar for lower temperature incubation. The investigators suggest 28°C incubation for 7 days. R-2A agar is available as a commercial dehydrated medium product or can be prepared from the formulation that appears in the Appendix.

#### o Disinfectant Residual

A free chlorine residual, if used, should be greater than or equal to 0.2 mg/l at all times and places in the distribution system. A chloramine residual, if used, should be kept above 0.5 mg/l. These residuals should be maintained to prevent microbial growth and to minimize the risk of potential contamination from cross connection and back siphonage. Experience indicates coliform regrowth in the distribution system may occur during warm periods at free chlorine residuals of 0.1 mg/l or less (16).

If chlorine dioxide is used, the total oxidant (i.e., chlorine dioxide, chlorite and chlorate) residual should be kept below 1.0 mg/l; this is because of concern for potential hematological effects (from chlorine dioxide and chlorite). Chlorine dioxide residuals alone should be kept above 0.2 mg/l to provide adequate protection in the distribution system. Further discussion of these issues is contained in Water Supply Guidance # 74, located in the Appendix.

#### o Enteric Viruses

At the present, there are practical limitations with the analytical methods used to determine enteric virus presence in drinking water. Therefore, monitoring for viral breakthrough should be considered optional provided a sanitary inspection of water plant records indicates conventional water treatment processes are functioning properly. Where source waters are grossly polluted (excess of 20,000 total coliform or 2,000 fecal coliforms per 100 ml) virus monitoring of the water treatment processes involved in modifications is recommended as a part of the baseline study.

EPA is currently attempting to develop a low cost effective method, using coliphage, for indicating treatment effectiveness in reducing the number of enteric viruses. Method development and testing is now underway. It is anticipated that this method, when fully developed, will be a more sensitive analytic tool than those presently available. EPA will disseminate this information as soon as it becomes available (31).

#### o Turbidity, Temperature, pH

Increases in turbidity due to a treatment system modification are not acceptable because of potential increases in competition for available oxidant from other oxidizable materials, which could reduce disinfection effectiveness (28). Optimum precursor and turbidity removal should be attempted without increasing the pH before the point of disinfection. If the pH is significantly lowered either to reduce THM formation or improve precursor removal in a clarification process, this might, however, significantly increase the corrosivity of the water. The potential of such trade-offs should be considered before such treatment changes are made.

Temperature and pH affect THM formation, disinfection effectiveness and microbial activity. When the water is warmest, microbial activity is potentially at a maximum. However, disinfection effectiveness is then also at a maximum (at a minimum when water is coldest). Free chlorine and chloramines are significantly more biocidal at lower pH values. Apparent anomalies in the microbial data base might thus be explained by irregularities in temperature and pH changes within the system.

#### o Nutrients

Organic carbon, measured as TOC, ammonia nitrogen and orthophosphate serve as nutrients for microorganisms, including those that cause disease; they also represent the products of microbial activity and cell decomposition. The presence of these nutrients can stimulate as well as indicate microbial activity.

Adequate disinfection would be suggested by the maintenance of low bacterial counts in the distribution system during periods of highest nutrient concentration (e.g., during algal blooms or turnover in lakes and large reservoirs, or from agricultural runoff or upstream discharge). In cases where systems use either, or both, ammonia or phosphate in their treatment processes, monitoring for nutrient concentrations is probably inappropriate.

#### (2) Monitoring Locations and Frequency

The purpose of monitoring for the above water quality parameters is to develop a baseline by which possible changes in treated water quality can be determined subsequent to the installation of THM control practices. This monitoring should be in addition to or in conjunction with that conducted to satisfy minimum sampling requirements specified in the NIPDWR.

Weekly analysis for total coliforms, standard plate counts and disinfectant residuals should be conducted for periods of 6 months before (including the warmest water month) and 12 months after the treatment change. Samples should be collected from the raw water, at a point in the treatment plant just before final disinfection, from the treatment plant effluent and from the ends of the distribution system. During periods of abnormal increases in source water pollution of other raw water quality discontinuities, daily monitoring at the above sampling points may be appropriate.

Long term microbiological effects of treatment modifications will be observed initially in the low-flow or dead-end sections of the distribution network. These locations frequently have accumulated sediments where waterborne organisms can become established. Sampling of dead-end sections should be done on a weekly basis, rotating site locations so as to include all major dead-ends during the warm season.

Disinfectant residuals should be measured at the treatment plant effluent and at all sample points in the distribution system.

### (3) Interpretation of Data

Information gathered during the pre- and post-treatment phases is designed to detect subtle changes in water quality that are related to microbial survival and activity within the system. This information should be used in conjunction with the sanitary survey and the analysis of the existing treatment train to determine whether the public health is at risk due to microbial penetration of some portion of the treatment barrier. In comparing data obtained in the pre- and post-treatment studies, any deterioration of water quality from test sites within the treatment plant and/or distribution system should be carefully evaluated.

## APPROACHES TO CONTROLLING TTHMs

The production of safe drinking water in the United States traditionally has been based on the multi-barrier concept. This concept requires that water be taken from the best source available, treated by appropriate unit processes to meet applicable drinking water quality standards, disinfected and transported to the consumer through water distribution systems free from sanitary defects. The goal of water treatment always has been, and will continue to be, the production of drinking water free from pathogenic contamination. The underlying principle in control of THMs is that as THM control practices are conceived and put into practice, the water supplied to the consumer must continue to be of optimal microbiological quality. Such a principle is consistent with ODW's repeatedly stated concern over the possible human health risks associated with exposure to any disinfecting agent or other chemical additive. ODW's consistent position has been that the generation of excessive amounts of disinfection by-products is to be avoided, ideally through the optimization of existing and/or conventional unit processes such that excessive application of any chemical oxidant is avoided.

The appropriate approach for systems to follow in controlling THMS is described in detail in Technologies and Costs for the Removal of Trihalomethanes from Drinking Water (29) and in the amendment to the TTHM implementation regulations (48 F.R. 8406).

Those documents define three general categories of technologies for controlling THMs:

- ° Group I technologies are the "Best Generally Available Treatment Methods for Reducing TTHMS." These techniques are each widely recognized, relatively low cost and relatively highly effective for controlling TTHMS. These frequently will be the methods of choice for affected systems attempting to comply with the TTHM MCL (see Table 2).
- ° Group II technologies are not generally available (as defined by statute) but may be both available and appropriate for certain systems in meeting the TTHM MCL (see Table 2). The amendment also discusses the criteria by which variances may be granted to non-compliant systems by primacy agencies. Compliance schedules associated with variances from the MCL may include a requirement that affected systems examine the availability, feasibility, cost and effectiveness (for their particular system) of the technologies in this Group.

TABLE 2

Included in the Group I technologies are:

- Use of chloramines as an alternate or supplemental disinfectant or oxidant.
- Use of chlorine dioxide as an alternate or supplemental disinfectant or oxidant.
- Improved existing clarification for THM precursor reduction.
- Moving the point of chlorination to reduce TTHM formation and, where necessary, substituting for the use of chlorine as a pre-oxidant chloramines, chlorine dioxide or potassium permanganate.
- Use of powdered activated carbon for TTHM precursor or TTHM reduction seasonally or intermittently at dosages not to exceed 10 mg/l on an annual average basis.

Included in the Group II technologies are:

- Introduction of off-line water storage for TTHM precursor reduction.
- Aeration for TTHM reduction, where geographically and environmentally appropriate.
- Introduction of clarification where not currently practiced.
- Consideration of alternative sources of raw water.
- Use of ozone as an alternate or supplemental disinfectant or oxidant.

Included in the Group III technologies are:

- Granular Activated Carbon (GAC)
- Biologically Activated Carbon (BAC)

- Group III technologies are not required to be considered as potential solutions to a TTHM compliance problem but may be studied by some systems for reducing TTHMS (see Table 2).

More detailed descriptions of each of these options and discussion of when each might or might not be applicable are contained in Treatment Techniques for Controlling Trihalomethanes in Drinking Water (2). Each technique has advantages and disadvantages; site-specific factors will probably affect the final treatment choice. Some specific microbiological concerns with certain of the technologies which should be considered by the primacy agency are discussed below.

Improved clarification (or introduction of clarification) to remove additional THM precursors, assuming pH is not increased, will improve the disinfection effectiveness of the oxidant. Waters with minimum disinfectant demand and turbidity will promote maximum contact between pathogens and the disinfectant. Thus improved coagulation may also improve disinfection effectiveness. For example, the presence of organic material has been shown to decrease the amount of virus removed by alum or ferric chloride coagulation (17).

Shifting chlorination to a point of minimum precursor concentration will reduce disinfectant contact time and microbial die-off in the early stages of treatment. Thus, greater reliance is placed on pathogen removal by coagulation, settling, filtration and post-disinfection. Also, chlorination (with adequate contact time) is most effective in the post-treatment phase where suspended material and disinfectant demand is at a minimum. Field studies indicate that the microbiological integrity of finished water (i.e., following post-disinfection) can be maintained after shifting the chlorination point to later in the treatment train (16). Problems such as slime growth in settling basins, which are often controlled by pre-chlorination, may be controlled by alternate treatment (e.g., potassium permanganate, or chlorine dioxide).

Chloramines as an alternate disinfectant are generally recognized to be a relatively less efficient disinfectant than free chlorine, ozone and chlorine dioxide when relative lethality coefficients are compared on a one-to-one basis in laboratory studies. However, in actual practice the mechanisms for chloramine



disinfection are markedly different from those for free chlorine disinfection (4,7). These statements are based on comparison of lethality coefficients from laboratory experiments using "clean" water (i.e., containing only seeded microorganisms and the disinfectants in distilled water). How actual field conditions affect the relative biocidal efficiency of different disinfectants is a subject of continuing investigation. Under field conditions free chlorine, chlorine dioxide or ozone are reduced at a greater rate than chloramines. Based upon the product of residual concentration and contact time, the disinfectant with the lower lethality coefficient catches up quickly in performance relative to the disinfectant with a high lethality coefficient at the same initial dosage (19), i.e., under long contact times chloramines can kill the same number of microorganisms as other oxidants. One study found that in tertiary sewage effluents combined chlorine residuals were nearly as effective as ozone or free available chlorine for bacterial and viral destruction (20). The use of chloramines (with long contact times) as the primary disinfectant (in conjunction with adequate physical/chemical treatment) has been shown to both provide adequate disinfection (based on coliform and standard plate counts) and restrain bacterial growth in the distribution system (19, 22-24). If chloramines are used as a primary disinfectant, then it is critical that long contact times be maintained at the optimum chlorine-to-ammonia nitrogen ratio.

Although certain conditions may allow it, chloramines generally have not been recommended as a primary disinfectant, i.e., used without a preceding stronger disinfectant such as free chlorine or chlorine dioxide. The adequacy of viral inactivation by chloramines, even with long contact times, has been questioned. Chloramines are recognized and accepted as a secondary disinfectant to provide protection in the distribution system (4). Post-chloramine application to stop THM formation should generally follow disinfection with free chlorine, chlorine dioxide or an equally effective disinfection period with ozone. High energy mixing in the contact tank may allow shorter free chlorine contact times. Treatment systems should demonstrate that the use of chloramines, either as as primary or secondary disinfectant, does not create a potential reduction in disinfection efficiency.

One recent study has raised questions on the merits of using chloramine residual protection in the distribution system (25). Field conditions simulated in the laboratory suggested that a free chlorine residual was significantly

more effective than a combined chlorine residual in protecting a distribution system from contamination of sewage infiltration. In addition, free chlorine (because of its disappearance) was shown to be a better indicator of possible sewage contamination than chloramines.

Chlorine Dioxide as an Alternative Disinfectant - The use of chlorine dioxide is not as widespread as that of chlorine. As of 1977, chlorine dioxide was being used at 84 and 495 water treatment plants in the U.S. and Europe, respectively (5). It has been used for pretreatment (taste and odor control and removal of iron and manganese) in the U.S. and for final disinfection in Europe. Lack of widespread application in the U.S. was due to higher cost and more complex application equipment and control. However, due to anticipated regulatory action, several treatment plants have adopted chlorine dioxide to reduce THM concentrations in their finished water (3).

Under some conditions, chlorine dioxide is a more effective biocide than chlorine (7), and offers potentially better protection than chloramines against pathogen penetration of the treatment barrier. Its usage, however, must be carefully controlled. Chlorine dioxide breaks down in water to chlorite, chlorate and ultimately chloride ions. Individuals having certain enzyme deficiencies might be sensitive to these agents; however, preliminary tests have not demonstrated this effect. To provide a margin of safety from the possible effect of ingested chlorine dioxide and chlorite, the concentration of the total residual oxidants should be monitored and kept below 1.0 mg/l in the distribution system. The previously recommended level of 0.5 mg/l has been re-examined and raised slightly as the result of studies reported in 1981 (30).

Daily samples for such analyses should be collected from the effluent of the clearwell and the results should be submitted to the primacy agency along with THM data. The method for determining total residual oxidants (including chlorate, which may also have a related health risk) is still being developed. Until this is available, Methods 330.6 or 330.7 (available from the Environmental Monitoring and Support Laboratory (EMSL) in Cincinnati, Ohio) or 411C (Standard Methods, 15th edition) may be used for determining chlorine dioxide and chlorite residuals; the sum of the residuals should be less than 1.0 mg/l.

Although chlorine dioxide may not be reduced as much as free chlorine because it does not react with ammonia, its use as a residual disinfectant is likely to be limited because of the recommended maximum residual level of total oxidants.

However, optimizing the removal of reducing substances, before the addition of chlorine dioxide as well as using chlorine dioxide that is relatively free from traces of chlorite and chlorate may permit its use. Also, this will minimize the potential formation of other disinfection by-products having unknown health risks.

Where pre-disinfection cannot be eliminated, chlorine dioxide, applied in low doses, may provide both adequate initial disinfection and good THM control (3). Subsequent addition of chemicals to reduce residual chlorite (e.g.,  $\text{Fe}^{++}$ , sulfur dioxide) may also be considered if chlorine dioxide is being used for disinfection early in the treatment processes. Free chlorine or chloramines, depending on the remaining THM precursors, could then be used to provide the necessary residual protection.

Ozone as an Alternate Disinfectant - As of 1977, there were over 1,000 water treatment plants in the world using ozonation as a unit process (5). Most of these plants are in Europe where people tend to be extremely critical of the taste and odor often created by chlorination. Ozone is the most powerful oxidant that is commonly used but its residual is short lived (7). Residual protection in the distribution system by another disinfectant is thus essential. Because of potential formation of undesirable by-products, application of ozone, like the other disinfectants, should be delayed until the maximum amount of THM precursors are removed by other unit processes. Application of ozone in the early stages of the treatment process could be practiced when such application creates significant improvements in the efficiency of THM precursor removal by other unit processes such as coagulation, sedimentation, filtration or adsorption. Pilot testing is essential for predicting performance and should precede full-scale application. A summary on the application of ozone for enhancing THM precursor removal, and an explanation of the controversy over existing data is given by Rice (27). An additional consideration is that ozonation of waters having high TOC levels has been known, in the absence of adequate residuals, to result in biological growth that causes problems in distribution systems (6). In such cases, chloramines may not be a suitable residual disinfectant. Monitoring in the distribution system as previously discussed is essential to determine the presence of this effect.

Granular Activated Carbon (GAC) can serve as a valuable adjunct to existing processes for THM precursor removal but its performance is limited depending upon its application. Fresh GAC can remove a high percentage of THM precursors. However, a typical mode of operation for a GAC installation (i.e., replacement of the sand in an existing sand filter) may not provide adequate contact time to effect adequate removal of THM precursors. Further, relatively frequent regeneration or replacement of the carbon may be necessary to sustain a high removal rate. Long-term steady state precursor removal (15-30%), attributed to microbial activity, is possible in bed depths of three feet (2), and this, in conjunction with other preceeding unit processes, might lead to its adoption by a system seeking protection from a broad spectrum of organic contaminants. Free chlorine residuals in water entering a GAC bed are likely to impair microbial degradation of THM precursors and reduce GAC effectiveness. If pre-filter disinfection cannot be eliminated, alternate oxidants such as potassium permanganate should be considered. The effectiveness of GAC largely depends on the quality of the water; thus, pilot testing is essential for predicting its performance. Standard bacterial plate counts have been shown to increase several orders of magnitude in water passing through GAC. This increase has been attributed to the greater availability of organic compounds and nutrients which collect on the carbon. Greater reliance must be placed on post-disinfection as a continuously effective, final treatment barrier to GAC effluent bacterial populations prior to finished water release into the distribution system (16).

It should be emphasized that as THM control practices are implemented, an effective treatment barrier that provides a safe water must be maintained. Requiring that levels of THMs be controlled does not imply that EPA wishes the use of free chlorine as a disinfectant be abandoned. For example, available technologies such as changing the point of chlorination and/or maximizing the efficiency of THM precursor removal in an existing coagulation process, can significantly reduce TTHM levels while maintaining the use of free chlorine. Whatever process or processes are chosen to comply with the TTHM MCL does not detract from the fact that the integrity of the biological quality of the drinking water must not be compromised.

## LABORATORY CERTIFICATION CRITERIA FOR TRIHALOMETHANES

EPA Regional offices should use the following criteria for certifying laboratories for total trihalomethane (TTHM) analysis until the revised laboratory certification manual becomes available. Most of the items below constitute minimum recommended requirements. Laboratories should be encouraged to exceed these minimum criteria.

### I. PERSONNEL

No minimum recommended requirements.

Some optional requirements are specified in, "Manual for the Interim Certification of Laboratories Involved in Analyzing Public Drinking Water Supplies". In addition, if the laboratory performs gas chromatography-mass spectrometry (GC-MS) analyses, the following are recommended minimum qualifications for the GC/MS operator.

1. Training: Satisfactory completion of a minimum one week course in GC/MS offered by equipment manufacturer, professional organization, university or other qualified operator.
2. Experience: Minimum of one year experience in the operation of a GC/MS instrument.

### II. LABORATORY FACILITIES

Minimum Recommended Requirements:

1. The laboratory must maintain a proper source of reagent water which contains less than 0.4 ug/l of each trihalomethane compound.

It is recommended that the laboratory facilities be clean, air conditioned and with adequate lighting at the bench top. It is also recommended that 150 to 200 square feet/person be available. The laboratory should contain at least 15 linear feet of usable bench space per analyst. The laboratory should have provisions for the disposal of chemical wastes.

### III. LABORATORY EQUIPMENT

Minimum Recommended Requirements:

1. Analytical balance: This should provide sensitivity of at least 0.1 mg.

2. Gas chromatograph: A commercial or custom-designed gas chromatograph (GC) with a column oven capable of operating to temperatures up to 200°C. Additional recommended requirements are listed below by methodology.
  - 2.1 TTHM purge and trap: The instrument must be temperature programmable from 45° to 220° at about 8° C/min and equipped with either a microcoulometric titration or electrolytic conductivity detector.
  - 2.2 TTHM by liquid/liquid extraction: The instrument must be equipped with a linearized (frequency modulated) electron capture detector.
  - 2.3 TTHM by gas chromatography/mass spectrometry: The gas chromatograph, which must be temperature programmable, should be interfaced to the mass spectrometer with an all-glass enrichment device and an all-glass transfer line. Mass spectral data are to be obtained with electron-impact ionization at a nominal electron energy of 70 eV. The mass spectrometer must produce a spectrum that meets all criteria in Table 3 when 50 mg. or less of p-bromofluorobenzene is introduced into the gas chromatograph. An interfaced data system is required to acquire, store, reduce and output mass spectral data. The data system must be equipped with software to acquire and manipulate data for only a few ions that were selected as characteristic of trihalomethanes and the internal standard (or surrogate compound).
3. Purge and trap system: A commercial or custom-designed system containing three separate elements.
  - 3.1 Purging device: Must be designed for a 5 ml. sample volume. Gas inlet must disperse finely divided gas bubbles through the sample.
  - 3.2 Trapping device: Must be capable of retaining purged trihalomethanes at room temperatures.
  - 3.3 Desorber assembly: Must be capable of heating the trapping device to 180°C in one minute with less than 40°C overshoot.
4. Drying oven: Temperature set at 105°C for drying of cleaned sample bottles.

TABLE 3. p-BROMOFLUOROBENZENE KEY IONS AND ION ABUNDANCE CRITERIA

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<u>Mass</u>	<u>Ion Abundance Criteria</u>
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	96 to 100% of mass 174
177	5 to 9% of mass 176

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5. Chlorine analysis: If a laboratory measures total trihalomethane potential (MTP), it must have test kits, apparatus or instruments capable of detecting free residual chlorine.

#### IV. GENERAL LABORATORY PRACTICES

No minimum recommended requirements.

Some optional requirements are specified in "Manual for the Interim Certification of Laboratories Involved in Analyzing Public Drinking Water Supplies".

#### V. METHODOLOGY

Minimum Recommended Requirements:

The laboratory must use one of the methods specified below.

Purge and Trap GC - "The Analysis of Trihalomethanes in Finished Waters by the Purge and Trap Method," Method 501.1, EMSL, EPA, Cincinnati, Ohio 45268.

Solvent Extraction, GC - "The Analysis of Trihalomethanes in Drinking Water by Liquid/Liquid Extraction," Method 501.2, EMSL, EPA, Cincinnati, Ohio 45268.

GC/MS - "Measurement of Trihalomethanes in Drinking Water by Gas Chromatography/Mass Spectrometry and Selected Ion Monitoring," Method 501.3, EMSL, EPA, Cincinnati, Ohio 45268.

All other methods are considered alternative analytical techniques and procedures described under Section 141.27 of the NIPDWR are to be followed if a laboratory wishes approval for their use.

#### VI. SAMPLE COLLECTING, HANDLING AND PRESERVATION

When the laboratory has been delegated responsibility for sample collecting, handling and preservation, there must be strict adherence to correct sampling procedures, complete identification of the sample and prompt transfer of the sample to the laboratory.



Minimum Recommended Requirements:

1. The collector must be trained in sampling procedures.
2. Sampling locations: As specified in 40 CFR 141.30(b) (1).
3. Sampling procedures: Follow procedures described in Sections 6.4.5 and 6.4.6 of Appendix C, Part I, 40 CFR 141.
4. Sample bottles: Narrow mouth, 25 ml. or greater capacity, screw cap, glass bottles are to be used. Bottle caps should utilize TFE fluorocarbon face silicon septa cap liners.
5. Sample stabilization: For the sample collection of total trihalomethanes, sodium thiosulfate or sodium sulfite must be added to each empty sample bottle just prior to shipping to the sample site.
6. Maximum holding time: All samples must be analyzed within 28 days after collection.

While laboratories should exercise discretion in all aspects of sample collection and handling, where a laboratory has no control over these factors, appropriate documentation should be required from collector(s) to ascertain if minimum requirements are being met. For example, the laboratory can visually check the samples to determine the use of appropriate containers, the presence of air bubbles and proper labeling. If the minimum criteria are not met, then the laboratory director should reject the samples and so notify the authority requesting the analysis.

VII. QUALITY CONTROL

Minimum Recommended Requirements:

1. All quality control data must be available for inspection.
2. A copy of the analytical method used must be available to the analyst(s).
3. A laboratory must demonstrate acceptable performance on USEPA Performance Evaluation samples at least once per year.
4. A laboratory should analyze known reference samples (USEPA Quality Control Sample or equivalent) once per quarter. If errors greater than 20% occur, appropriate corrective action must be taken and documented.

5. For each day on which analyses are initiated, a laboratory method blank must be analyzed with the same procedures used to analyze samples.
6. The laboratory must analyze a known TTHM laboratory control standard each day. If errors exceed 20 percent of the true value, then all trihalomethane results since the previous successful test are to be considered suspect.
7. A minimum of three calibration standards must be analyzed each day to calibrate the gas chromatographic system. If the laboratory can thereby demonstrate that the instrument response is linear through the origin, this requirement can be reduced to one standard within the linear range of the instrument; providing the response of the standard is within + 15 percent of previous calibrations.
8. It is essential that the laboratory analyze a field blank for trihalomethanes with each sample set. If reportable levels for trihalomethanes are demonstrated to have contaminated the field blank, then resampling is essential.
9. The laboratory must analyze 10 percent of all samples for TTHM in duplicate. A continuing record of all calibration checks (accuracy) and duplicates (precision) must be maintained.
10. Each time that the TTHM analytical system undergoes a major modification or prolonged period of inactivity, the precision of the system must be demonstrated by the analysis of replicate laboratory standards.
11. It is critical that laboratories which analyze for TTHMs by liquid-liquid extraction demonstrate that source waters being analyzed do not contain interferences under the chromatographic conditions selected.
12. If a mass spectrometer detector is used for TTHM analysis, the mass spectrometer performance tests described under equipment specifications using BFB must be conducted once during each 8-hour work shift, and records of satisfactory performance and corrective action must be maintained.

#### VIII. DATA HANDLING

##### Minimum Recommended Requirements:

1. If a laboratory is responsible for sample collection, it must document the information required by 40 CFR 141.33 (1) and (2) and return this information to a water supply with the results for each trihalomethane sample. Information required by 40 CFR 141.33(3), (4), and (5) must be transmitted with analytical results along with the detection limits determined for the appropriate set of trihalomethane analyses.
2. Records of chemical analyses must be kept by the laboratory for not less than 3 years. This includes all raw data, calculations and quality control data.

#### IX. MAXIMUM TOTAL TRIHALOMETHANE POTENTIAL

Laboratories that are engaged in the determination of maximum total trihalomethane potential (MTP) must meet the following requirements for that test.

1. Method: Gas chromatography. "Method for the Determination of Maximum Total Trihalomethane Potential - Method 510.1." EMSL, EPA, Cincinnati, Ohio 45268.
2. Sample container: TTHM sample bottle.
3. Supplemental equipment: Constant temperature storage container, water bath or incubator, 25°C or above.
4. The laboratory must be certified for TTHM analysis.

## APPENDIX

## R-2A Media Preparation

<u>Ingredient</u>	<u>Concentration g/l</u>
Yeast Extract	0.5
Proteose Peptone No. 3	0.5
Casamino Acids	0.5
Glucose	0.5
Soluble Starch	0.5
Sodium Pyruvate	0.3
K <sub>2</sub> HPO <sub>4</sub>	0.3
MgSO <sub>4</sub> ·7H <sub>2</sub> O	0.05
Agar	15.0

Dissolve all ingredients except for agar. Adjust pH to 7.2 with K<sub>2</sub>HPO<sub>4</sub> or KH<sub>2</sub>PO<sub>4</sub> before adding agar. Add agar. Heat medium to boiling to dissolve agar and autoclave for 15 minutes at 121°C, 15 psi.

Note: For further information, see "Abstracts of the Annual Meeting of the American Society for Microbiology" (1979); Reasoner, Donald J., Entry N-7, Page 180.

## Water Supply Guidance # 72

All Maximum Contaminant Levels (MCLs) contained in the National Interim Primary Drinking Water Regulations are expressed in the number of significant digits permitted by the precision and accuracy of the specified analytical procedure(s). Data reported to the State or EPA should be in a form containing the same number of significant digits as the MCL. In calculating data for compliance purposes it is necessary to round-off by dropping the digits that are not significant. The last significant digit should be increased by one unit if the digit dropped is 5,6,7, 8 or 9. If the digit is 0, 1, 2, 3 or 4, do not alter the preceding number.

For example, if the monthly mean for coliform bacteria is 1.4999, the reported result should be 1 (one). A result of 3.50 should be rounded to 4 (four).

Chemical and radiological data may be treated in like manner. Analytical results for mercury of 0.0016 would round-off to 0.002 while 5.4 pCi/l of combined radium-226 and radium-228 would round down to 5 pCi/l.

### Public Notification Requirements

If a community water system fails to comply with an applicable maximum contaminant level, fails to comply with an applicable testing procedure or fails to perform any monitoring requirement, then the supplier of water shall report to the state within 48 hours and notify persons served by the system of the failure within three months. Within ten (10) days of completion of each required public notification, the supplier shall submit to the state a representative copy of each type of notice distributed, published or posted.

Determination of MCL compliance with THM is based on the running annual average of quarterly samples collected by the system. If the average of samples covering any twelve (12) month period exceeds the MCL, then the supplier shall report to the state within 48 hours and notify the public within three months. For example: Assume that System A has the following analytical results for the latest four (4) quarters - 0.123 mg/l; 0.095 mg/l; 0.122 mg/l; and 0.098 mg/l respectively. The running annual average =  $(0.123 + 0.095 + 0.122 + 0.098)/4 = 0.11$  mg/l. System A is required to issue a public notice because the annual average of the four quarters exceeds the MCL, even though the fourth quarter's result is less than 0.10 mg/l. This computation of the running annual average is performed quarterly as the new quarterly average is available.

Background

For years, many public water systems have added chloramines (chlorine plus ammonia) to drinking water as a primary or secondary disinfectant. Also, when breakpoint chlorination is not practiced, both inorganic and organic chloramines may be present in finished drinking water. Because of concern regarding the formation of trihalomethanes (THMs) from chlorine and organic matter, and in some cases because of requirements for compliance with drinking water regulations limiting THM concentrations (40 CFR 141.30), a number of water supply systems have switched, or are contemplating switching, from chlorine to chloramine or chlorine dioxide as their primary disinfectant. Any water supply which plans to change disinfectants should be made aware of the potential problems created by such a change and should notify consumers, particularly those most likely to be affected, in advance of the change. Care should also be taken to avoid unnecessarily high levels of combined residuals.

A potentially serious problem arises when tap water containing chloramines is used in hemodialysis (artificial kidney machines). Chloramines pass through the dialysis membrane and their toxicity to patients under dialysis conditions is undisputed (Eaton, et al. 1973). Chlorine dioxide and its by-products may have similar effects. Operators of dialysis centers know that tap water must be treated before use in dialysis, but again there have been a number of cases of illness reported due to chloramine or some other chemical in tap water. The Association for the Advancement of Medical Instrumentation has proposed a limit of 0.1 mg/l for chloramine in hemodialysis water. It is imperative that dialysis centers and users of home dialysis systems be informed that chloramines or chlorine dioxide are to be used in the public water system and that treatment to remove them is essential. Other substances in tap water besides chloramines are also known to interfere with dialysis. These include copper, fluoride, sulfate, nitrate, zinc and aluminum. The types of controls available to users include carbon filtration and reverse osmosis or chemical reduction.



The toxicity of chloramine to fish is well-known. Most breeders and owners of tropical or other aquarium fish know that tap water should not be used in aquaria without proper treatment and aging. Yet, a number of cases of aquarium fish being killed by chloramine in tap water have been reported, particularly when conversion between disinfection methods has occurred at the treatment plant. Since chloramine is more persistent than free chlorine (which is also toxic to fish), treatment and aging of water to be used in aquaria is more critical when chloramine is present. Suggested action for fish fanciers, breeders or pet shop owners includes the use of activated carbon filters. Care needs to be taken to replace filter cartridges before breakthrough can occur.

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### Guidance

Section 141.30(f) directs systems which make any significant modifications to existing treatment processes for the purposes of achieving compliance with Section 141.12(c) to submit and obtain state approval of a detailed plan setting forth proposed modifications. The Office of Drinking Water recommends that utilities changing disinfectants notify the public of the change and that this notification, the text and announcement schedule be included in the plan. In particular the notification should include hospitals, kidney dialysis facilities and fish breeders.

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# **TECHNICAL REPORT DATA**

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