

WHITEPAPER

Analytical and Measuring Instruments

Drinking Water
Analysis Guide



Public Water Systems (PWS) provide drinking water to 90% of Americans. PWS's are regulated by the United States Environmental Protection Agency (USEPA). Water systems and laboratories testing drinking water for Safe Drinking Water Act (SDWA) compliance must be certified and must use USEPA approved methods. Approved methods are listed in the Code of Federal Regulations (CFR). Approved methods are developed by the USEPA, other government agencies, universities, consensus method organizations, water laboratories, and instrument manufacturers.

Laboratories analyze PWS water samples and provide the PWS with information on the quality of the water. Water samples analyzed include:

1. Source water to check for contamination and water quality characteristics
2. Process water to provide information on the treatment process
3. Finished water to verify that the water meets USEPA maximum contaminant levels (MCL)

An analytical method is a procedure that determines the concentration of a contaminant in a water sample. Analytical methods describe:

1. How to collect, preserve, and store the sample
2. How to extract, digest, separate, and quantify contaminants in the sample
3. Quality control criteria that must be met for compliance
4. How to report results

In general, an analytical method:

1. Is applicable to routine analysis of samples
2. Is suitable to measure the contaminant in the concentration of interest
3. Provides necessary accuracy and precision to demonstrate compliance
4. Includes instructions from sampling to analysis
5. Incorporates all required quality control and quality assurance (QA/QC)

■ National Primary Drinking Water Regulations

National Primary Drinking Water Regulations (NPDWR) are legally enforceable standards that apply to all public water systems. These standards intend to protect public health by establishing maximum concentrations of contaminants allowed in finished drinking water. For enforcement, these rules require that laboratories are certified and use only approved methods for analysis. Unless specifically stated in the method, laboratories are not allowed to modify sampling, preservation, or any other conditions required in the method.

■ Lists of Chemical Contaminants, their MCL, and potential sources of contamination

Table 1: Disinfection by Products and Disinfectants

Contaminant	MCL (mg/L)	Source of contamination
Bromate	0.010	Byproduct of disinfection
Chlorite	1.0	Byproduct of disinfection
Haloacetic Acids (HAA5)	0.080	Byproduct of disinfection
Trihalomethanes	0.080	Byproduct of disinfection
Chloramines (as Cl ₂)	4	Disinfectant
Chlorine (as Cl ₂)	4	Disinfectant
Chlorine Dioxide (as ClO ₂)	0.8	Disinfectant

Table 2: Inorganic Chemicals

Contaminant	MCL (mg/L)	Source of Contamination
Antimony	0.006	Petroleum refining, fire retardants, ceramics, electronics
Arsenic	0.010	Naturally occurring, herbicide, glass and electronics production
Barium	2	Drilling mud, metal refineries, naturally occurring
Beryllium	0.004	Metal refineries. Coal burning power plants and factories, electrical, aerospace, and defense industries
Cadmium	0.005	Corrosion of galvanized pipes, naturally occurring, metal refineries, battery waste
Chromium (total)	0.1	Steel mills, paper and pulp mills
Copper	1.3	Corrosion of household plumbing, naturally occurring
Cyanide (free)	0.2	Steel and metal factories, plastic and fertilizer factories, gold and silver processing
Fluoride	4.0	Additive, naturally occurring, fertilizer and aluminum factories
Lead	0.015	Corrosion of lead solder in household plumbing, naturally occurring
Mercury (inorganic)	0.002	Naturally occurring, refineries and factories, leaking landfills
Nitrate Nitrogen	10	Fertilizer runoff, leaking septic tanks, sewage, naturally occurring
Nitrite Nitrogen	1	Fertilizer runoff, leaking septic tanks, sewage, naturally occurring
Selenium	0.05	Petroleum refineries, mine runoff, naturally occurring
Thallium	0.002	Leaching from ore-processing, electronics, glass and drug factories

Table 3: Organic Chemicals

Contaminant	MCL (mg/L)	Source of Contamination
Acrylamide	0	Added during wastewater treatment
Alachlor	0.002	Herbicide runoff
Atrazine	0.003	Herbicide runoff
Benzene	0.005	Leaking underground storage tanks, industrial discharge
Benzo(a)pyrene	0.0002	Leaking storage tanks
Carbofuran	0.04	Agricultural runoff
Carbon Tetrachloride	0.005	Chemical and industrial plants
Chlordane	0.002	Leaching of contaminated sites
Chlorobenzene	0.1	Chemical or agricultural discharge
2,4-D	0.07	Herbicide runoff
Dalapon	0.2	Herbicide runoff
1,2-Dibromo-3-chloropropane (DBCP)	0.0002	Agricultural runoff
o-Dichlorobenzene	0.6	Industrial discharge
p-Dichlorobenzene	0.075	Industrial discharge
1,2-Dichloroethane	0.005	Industrial discharge
1,1-Dichloroethylene	0.007	Industrial discharge
Cis-1,2-Dichloroethylene	0.07	Industrial discharge
Trans-1,2-Dichloroethylene	0.1	Industrial discharge
Dichloromethane	0.005	Discharge from drug and chemical factories
1,2-Dichloropropane	0.005	Industrial discharge
Di(2-ethylhexyl)adipate	0.4	Discharge from chemical factories
Di(2-ethylhexyl)phthalate	0.006	Discharge from rubber and chemical factories
Dinoseb	0.007	Herbicide runoff
Dioxin (2,3,7,8-TCDD)	0.00000003	Emissions from waste incineration
Diquat	0.02	Herbicide runoff

Endothall	0.1	Herbicide runoff
Endrin	0.002	Leaching of contaminated sites
Epichlorohydrin	0	Impurity of water treatment chemicals
Ethyl benzene	0.7	Leaking underground storage tanks
Ethylene Dibromide	0.00005	Discharge from petroleum refineries
Glyphosate	0.7	Herbicide runoff
Heptachlor	0.0004	Leaching of contaminated sites
Heptachlor epoxide	0.0002	Breakdown of heptachlor
Hexachlorobenzene	0.001	Discharge from metal refineries or agricultural chemical factories
Hexachlorocyclopentadiene	0.05	Discharge from chemical factories
Lindane	0.0002	Agricultural runoff
Methoxychlor	0.04	Agricultural runoff
Oxamyl	0.2	Agricultural runoff
Polychlorinated Biphenyls (PCBs)	0.0005	Leaking landfills and leaching of contaminated sites
Pentachlorophenol	0.001	Discharge from wood preservation processes
Pichloram	0.5	Herbicide runoff
Simazine	0.004	Herbicide runoff
Styrene	0.1	Discharge from rubber and plastic factories, leaching of landfills
Tetrachloroethylene	0.005	Discharge from dry cleaning and factories
Toluene	1	Leaking underground storage tanks, discharge from petroleum refineries
Toxaphene	0.003	Agricultural runoff
2,4,5-TP (Silvex)	0.05	Leaching of contaminated sites
1,2,4-Trichlorobenzene	0.07	Discharge from textile factories
1,1,1-Trichloroethane	0.2	Discharge from degreasing processes
1,1,2-Trichloroethane	0.005	Discharge from chemical factories
Trichloroethylene	0.005	Discharge from metal degreasing processes
Vinyl Chloride	0.002	Leaching of PVC
Xylenes (total)	10	Leaking underground storage tanks

■ National Secondary Drinking Water Contaminants

National Secondary Drinking Water Contaminants (NSDWRs) are non-enforceable guidelines regulating contaminants that may cause cosmetic effects or aesthetic effects in drinking water. EPA recommends these MCLs be met, but systems are not required to comply. Many states choose to enforce these limits.

Table 4: Secondary Drinking Water contaminants and noticeable effects

Contaminant	MCL (mg/L unless otherwise noted)	Noticeable effects above the MCL
Aluminum	0.05 – 0.2	Colored water
Chloride	250	Salty taste
Color	15 (C.U.)	Visible color
Copper	1.0	Metallic taste
Corrosivity	Not corrosive	Corrodes pipes
Fluoride	2.0	Discolored teeth
Foaming Agents (surfactants or MBAS)	0.5	Frothing and foaming, cloudy, bitter taste
Iron	0.3	Yellow or orange stain
Manganese	0.05	Brown or black stain, metallic taste
Odor	3 (TON)	Rotten egg smell, musty smell
pH	6.5 – 8.5 (S.U.)	Corrosion, metallic taste or deposits
Silver	0.10	Skin and eye discoloration
Sulfate	250	Salty taste
Total Dissolved Solids	500	Salty taste, deposits
Zinc	5	Metallic taste

■ More Information about Disinfection Byproducts

Water suppliers often add a disinfectant to protect drinking water from water borne pathogens. Disinfectants may be chlorine, chlorine dioxide, chloramine, ozone, or treatment with ultraviolet light. Disinfection procedures can be complicated because the disinfectant can react with constituents in the sample, such as organic matter or bromide, and form byproducts that may pose health risks.

A major challenge in water disinfection is adding enough disinfection chemical to kill all pathogens and maintain the byproduct concentration below the MCL. Table 1 listed the disinfectants and disinfection byproducts that are regulated by the USEPA.

Control of disinfection byproduct formation (DBP) is accomplished by minimizing DBP precursors. Chlorine reacts with naturally occurring organic matter to form Trihalomethanes and Haloacetic acids. Organic matter in drinking water sources and finished drinking water is measured as Total Organic Carbon (TOC). Water systems that use traditional filtration methods for removal of organic matter are required to remove certain percentages of TOC depending upon the concentration of TOC and alkalinity in the source water. This rule only applies to systems treating surface water. In essence, a system measures the source water and finished water once monthly for TOC and calculates the % TOC removal. Table 5 shows the percent TOC removal requirements as a function of TOC and alkalinity concentration.

Table 5: TOC Removal requirements

Source Water TOC (mg/L)	Source Water Alkalinity (mg/L as CaCO ₃)		
	0 – 60	60 – 120	Greater than 120
2.0 – 4.0	35.0 %	25.0 %	15.0 %
4.0 – 8.0	45.0 %	35.0 %	25.0 %
Greater than 8.0	50.0 %	40.0 %	30.0 %

■ Sampling and Sample Preservation for Inorganic and Organic Constituents in Drinking Water

Samples are only representative of the water when taken and must be analyzed within a certain time, from beginning with sample collection to the time the analysis begins. This time interval is called the “holding time” and holding times must be met for USEPA compliance reporting. Each method specifies a holding time and preservation requirements. Preservation includes, but is not limited to, sample bottle type, chemical additive, and temperature.

Follow the procedure below to assist in collection of an acceptable sample and to maintain the integrity of the sample after collection.

1. Obtain sample bottles, preservative, and chain of custody (COC) forms from the laboratory that will be doing the testing.
2. The acids and bases used as preservatives are dangerous and should be handled with care. Wear gloves and eye protection when handling preservatives.
3. Collect samples in a dust free area protected from rain or snow.
4. Select a faucet free of aeration devices, hoses, and screens. Remove water filters unless the scope of the sampling is to evaluate the filter.
5. Collect sample from a faucet high enough to prevent touching the bottle to the faucet.
6. Unless you are collecting a “first draw”, turn on the cold water faucet for 2 – 3 minutes. Using your finger, or a thermometer, measure the temperature and collect sample when the temperature has stabilized. Slow the water so that it evenly fills the bottle without risk of overflow or splashing the preservative.
7. Seal the bottle and fill out the COC form.
8. Deliver the sample to the laboratory in a timely manner to ensure that holding times will be met.

Inorganic Non-metals



1 liter HDPE held at 4°C
Alkalinity 14 days
TDS 7 days
Foaming Agents 48 hours
Anions 28 days

Inorganic Nutrients



250 mL HDPE
H₂SO₄ to pH ≤ 2
4° C
Nitrate + Nitrite Nitrogen 28 days
TOC 28 days

Trace Metals



1 liter HDPE
HNO₃ to pH ≤ 2
4° C
Trace metals 6 months
Mercury 28 days

Cyanide



1 liter HDPE
NaOH to pH 12
4° C
14 Days

Haloacetic Acids



1 liter amber glass with Teflon lined cap
Ammonium chloride
4° C
14 days (depending on method)

Volatile Organics



40 milliliter glass vials with Teflon lined caps
Collect in duplicate at minimum
4° C and pH \leq 2 (depending on method)
14 days

Semi-Volatile Organics



1 liter amber glass with Teflon lined cap
4° C
7 days to extraction

■ Instruments for the Analysis of Drinking Water

Analytical Balance



An analytical balance, such as the Shimadzu AUW-320, is used for accurate measurement of reagents for standard preparation, or for determining the mass of total dissolved solids (TDS).

UV-Visible Spectrophotometer



A UV-Visible spectrophotometer, such as the Shimadzu UV-1800, can be used to measure UV-254, disinfectants, or almost any of the conventional pollutants such as MBAS, cyanide, or nitrate and nitrite nitrogen. Smaller laboratories can use visible spectrophotometry methods to determine trace metals, such as iron, manganese, and chromium in drinking water samples.

Atomic Absorption Spectrophotometry



Atomic Absorption Spectrophotometry (AA) is a single element technique used to measure metals in aqueous samples. AA is the instrument of choice for laboratories running fewer than six elements per sample in only a few samples per day because of its great flexibility and lower operating costs. AA can be operated in three atomization modes: flame, furnace, or hydride. Flame AA is used to measure elements in the ppm (mg/L) range while furnace and hydride measure elements in the ppb (ug/L) or low ppb range. Hydride or furnace atomization is especially useful for the determination of arsenic, antimony, and selenium.

Inductively Coupled Plasma Atomic Emission Spectroscopy

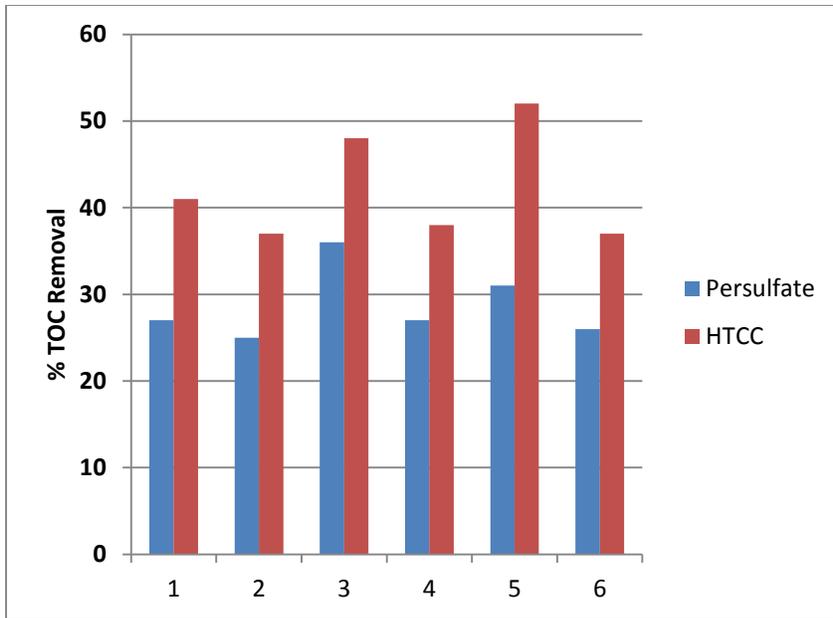


Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) is a multiple element technique used to measure metals and semi-metals in aqueous samples. ICP-AES is capable of analyzing up to 71 elements in 1 – 2 minutes; however, realistically, most laboratories limit the number of metals to 20 or fewer. ICP-AES detection limits are mostly between Flame AA and Furnace AA. Attachments, such as ultrasonic nebulization can lower ICP detection limits significantly. ICP-AES is the instrument of choice for high-throughput laboratories routinely analyzing multiple elements on a large number of samples. ICP-AES should not be used for the determination of arsenic, antimony, or selenium. Use ultrasonic nebulization or furnace AA for the determination of lead.

Total Organic Carbon



Total Organic Carbon (TOC) analyzers are used to measure the organic matter disinfection byproduct precursors in source water and finished drinking water. There are two oxidation modes: wet chemical or high-temperature catalytic combustion. Oxidation converts all carbon in the organic matter to carbon dioxide (CO₂) that is measured by Infrared absorbance. The preferred technique for source water is high-temperature catalytic combustion (HTCC) because it completely oxidizes large organic molecules, such as humic acids, that are not always completely oxidized using wet chemical methods. A higher TOC value measured in the source water results in a higher calculated % TOC removal.



Comparison of TOC Removal between persulfate and HTCC oxidation

Gas Chromatography



A gas chromatograph (GC) is used to separate organic components in a mixture and quantitate them based on response to a detector. GCs, such as the Shimadzu GC-2010 Plus, can be used to measure volatile organics, pesticides, herbicides, or Haloacetic acids. The detectors on the GC respond to a chemical or physical property of the analyte, however, identity of the analyte is estimated only by the time it takes to travel through a column (retention time). Confirmatory analysis on another column is necessary for positive identification of all analytes detected.

Gas Chromatography Mass Spectrometry



Gas Chromatography Mass Spectrometry (GCMS) combines the separation of GC with a mass selective detector that produces a fragmentation pattern specific to each analyte. This provides GC analysis with a means to obtain both qualitative and quantitative information eliminating the need for a second column confirmation. GCMS is used for the analysis of volatiles, semi-volatiles, pesticides, herbicides, and other organic contaminants in drinking water.

Liquid Chromatography Tandem Mass Spectrometry



Liquid Chromatography Tandem Mass Spectrometry (LCMSMS) is a powerful new technique capable of analyzing polar and large molecule organic compounds in drinking water. New methods for emerging contaminants, such as pharmaceutical and personal care products (PPCP), and new methods for polar pesticides and herbicides, such as atrazine and 2,4-D that are difficult to analyze by GC or GCMS methods are being developed. LCMSMS has an advantage of very rapid analysis times (2 – 10 minutes) for large numbers of components with very minimal sample preparation.

■ Conclusion

A safe water supply is essential to the health and well-being of everyone. Ensuring this safe water supply requires skilled technicians with an understanding of current and evolving regulations, as well as the latest instrumentation needed to ensure testing standards are being met. This paper provides an introduction to drinking water sampling, sample preservation, and instruments used to measure contaminants in drinking water. For more information, please contact Shimadzu Scientific Instruments at www.ssi.shimadzu.com.



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