

Extract from manual:

U. S. Environmental Protection Agency. 1983.

Sample preservation. pp.xv-xx. In **Methods for Chemical Analysis of Water and Wastes**, EPA-600/4-79-020. U.S.E.P.A., Cincinnati, Ohio, USA.

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## TABLE 1:

### RECOMMENDATION FOR SAMPLING AND PRESERVATION OF SAMPLES, ARRANGED ACCORDING TO MEASUREMENT

(see note 1, below)

Complete and unequivocal preservation of samples, either domestic sewage, industrial wastes, or natural waters, is a practical impossibility. Regardless of the nature of the sample, complete stability for every constituent can never be achieved. At best, preservation techniques can only retard the chemical and biological changes that inevitably continue after the sample is removed from the parent source. The changes that take place in a sample are either chemical or biological. In the former case, certain changes occur in the chemical structure of the constituents that are a function of physical conditions. Metal cations may precipitate as hydroxides or form complexes with other constituents; cations or anions may change valence states under certain reducing or oxidizing conditions; other constituents may dissolve or volatilize with the passage of time. Metal cations may also adsorb onto surfaces (glass, plastic, quartz, etc.), such as, iron and lead. Biological changes taking place in a sample may change the valence of an element or a radical to a different valence. Soluble constituents may be converted to organically bound materials in cell structures, or cell lysis may result in release of cellular material into solution. The well known nitrogen and phosphorus cycles are examples of biological influence on sample composition. Therefore, as a general rule, it is best to analyze the samples as soon as possible after collection. This is especially true when the analyze concentration is expected to be in the low ug/l range.

Methods of preservation are relatively limited and are intended generally to (1) retard biological action, (2) retard hydrolysis of chemical compounds and complexes, (3) reduce volatility of constituents, and (4) reduce absorption effects. Preservation methods are generally limited to pH control, chemical addition, refrigeration, and freezing.

The recommended preservative for various constituents is given in **Table 1**. These choices are based on the accompanying references and on information supplied by various E.P.A. Quality Assurance Coordinators. As more data become available, these recommended holding times will be adjusted to reflect new information. Other information provided in the table is an estimation of the volume of sample required for the analysis, the suggested type of container, and the maximum recommended holding times for samples properly preserved.

**TABLE 1**

Measurement -----	Vol. Req. (ml) -----	Container (note 2) -----	Preservative (notes 3,4) -----	Holding Time (note 5) -----
<b>100. Physical</b>				
Color	50	P,G	Cool, 4 deg. C	48 Hrs.
Conductance	100	P,G	Cool, 4 deg. C	28 Days
Hardness	100	P,G	HNO <sub>3</sub> - pH below 2	6 Mos.
Odor	200	G only	Cool, 4 deg. C	24 Hrs.
pH	25	P,G	None Req.	Analyze Immediately
Residue				
Filterable	100	P,G	Cool, 4 deg. C	7 Days
Non-filterable	100	P,G	Cool, 4 deg. C	7 Days
Total	100	P,G	Cool, 4 deg. C	7 Days
Volatile	100	P,G	Cool, 4 deg. C	7 Days
Settleable Matter	1000	P,G	Cool, 4 deg. C	48 Hrs.
Temperature	1000	P,G	None Req.	Analyze Immediately
Turbidity	100	P,G	Cool, 4 deg. C	48 Hrs.
<b>200. Metals</b>				
Dissolved	200	P,G	Filter on site, HNO <sub>3</sub> - pH below 2	6 Mos.
Suspended	200		Filter on site	6 Mos. (8)
Total	100	P,G	HNO <sub>3</sub> - pH below 2	6 Mos.
Chromium (6)	200	P,G	Cool, 4 deg. C	24 Hrs.
Mercury				
Dissolved	100	P,G	Filter, HNO <sub>3</sub> - pH below 2	28 Days
Total	100	P,G	HNO <sub>3</sub> - pH below 2	28 Days
<b>300. Inorganics, Non-Metallics</b>				
Acidity	100	P,G	Cool, 4 deg. C	14 Days
Alkalinity	100	P,G	Cool, 4 deg. C	14 Days
Bromide	100	P,G	None Req.	28 Days
Chloride	50	P,G	None Req.	28 Days
Chlorine	200	P,G	None Req.	Analyze Immediately

Cyanides	500	P,G	Cool, 4 deg. C, NaOH - pH over 12 0.6g ascorbic acid (6)	14 Days (7)
Fluoride	300	P,G	None Req.	28 Days
Iodide	100	P,G	Cool, 4 deg. C	24 Hrs.
Nitrogen				
Ammonia	400	P,G	Cool, 4 deg. C, H2SO4 - pH below 2	28 Days
Kjeldahl, Total	500	P,G	Cool, 4 deg. C, H2SO4 - pH below 2	28 Days
Nitrate + Nitrite	100	P,G	Cool, 4 deg. C, H2SO4 - pH below 2	28 Days
Nitrate (9)	100	P,G	Cool, 4 deg. C,	48 Hrs.
Nitrite	50	P,G	Cool, 4 deg. C,	48 Hrs.
Dissolved Oxygen				
Probe	300	G bottle + top	None Req.	Analyze Immediately
Winkler	300	G bottle + top	Fix on site and store	8 Hours
Phosphorus				
Ortho-P, dissolved	50	P,G	Filter on site, Cool, 4 deg. C	48 Hrs.
Hydrolyzable	50	P,G	Cool, 4 deg. C, H2SO4 - pH below 2	28 Days
Total	50	P,G	Cool, 4 deg. C, H2SO4 - pH below 2	28 Days
Total, dissolved	50	P,G	Filter on site, Cool, 4 deg. C, H2SO4 - pH below 2	24 Hrs.
Silica	50	P only	Cool, 4 deg. C	28 Days
Sulfate	50	P,G	Cool, 4 deg. C	28 Days
Sulfide	500	P,G	Cool, 4 deg. C, add 2 ml zinc acetate plus NaOH - pH over 9	7 Days
Sulfite	50	P,G	None Req.	Analyze Immediately

#### 400. Organics

BOD	1000	P,G	Cool, 4 deg. C	48 Hrs.
COD	50	P,G	Cool, 4 deg. C, H2SO4 - pH below 2	28 Days
Oil & Grease	1000	G only	Cool, 4 deg. C, H2SO4 - pH below 2	28 Days

Organic carbon	25	P,G	Cool, 4 deg. C, H2SO4 or HCl to pH below 2	28 Days
Phenolics	500	G only	Cool, 4 deg. C, H2SO4 - pH below 2	28 Days
MBAS	250	P,G	Cool, 4 deg. C	48 Hrs.
NTA	50	P,G	Cool, 4 deg. C	24 Hrs.

1. More specific instructions for preservation and sampling are found with each procedure as detailed in this manual. A general discussion on sampling water and industrial wastewater may be found in ASTM, Part 31, p. 72-82 (1976) Method D-3370.
2. Plastic (P) or Glass (G). For metals, polyethylene with a polypropylene cap (no liner) is preferred.
3. Sample preservation should be performed immediately upon sample collection. For composite samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then samples may be preserved by maintaining at 4 deg. C until compositing and sample splitting is completed.
4. When any sample is to be shipped by common carrier or sent through the United States Mails, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table I the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO<sub>3</sub>) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).
5. Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still considered valid. Samples may be held for longer periods only if the permittee, or monitoring laboratory, has data on file to show that the specific types of sample under study are stable for the longer time, and has received a variance from the Regional Administrator. Some samples may not be stable for the maximum time period given in the table. A permittee, or monitoring laboratory, is obligated to hold the sample for a shorter time if knowledge exists to show this is necessary to maintain sample stability.
6. Should only be used in the presence of residual chlorine.
7. Maximum holding time is 24 hours when sulfide is present. Optionally, all samples may be tested with lead acetate paper before the pH adjustment in order to determine if sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.

8. Samples should be filtered immediately on-site before adding preservative for dissolved metals.
  9. For samples from non-chlorinated drinking water supplies conc. H<sub>2</sub>SO<sub>4</sub> should be added to lower sample pH to less than 2. The sample should be analyzed before 14 days.
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