

SAMPLING METHODS

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SOURCE: APHA, 2005

a) Manual Sampling

Manual sampling involves minimal equipment but may be unduly costly and time-consuming for routine or large-scale sampling programs. It required trained field technicians.

b) Automatic Sampling

Automatic samplers can eliminate human errors in manual sampling, can reduce labour costs, and may provide the means for more frequent sampling.

c) Sorbent Sampling

These methods offer advantages of rapid, inexpensive sampling if the analytes can be adsorbed and desorbed efficiently and water matrix is free of particulates that plug the sorbent.

7.2.6 Sampling Containers

Containers typically made of plastics or glass. Silica, boron and sodium are leached may be leached from soft glass but not plastic, and trace levels of pesticides and metals may sorb onto walls of glass containers. For samples containing organic compound, do not use plastic containers except those made of fluorinated polymers such as polytetrafluoroethylene (PTFE). Use glass containers for all organics analyses such as volatile organics, semivolatile organics, pesticides, PCBs, and oil and grease. Use amber colored glass containers to minimise photodegradation. Container caps, typically plastic can also be a problem. Do not use caps with paper liners. Use foil or PTFE liners but be aware that metal liners can contaminate samples collected for metals analysis and they may react with the sample if it is acidic or alkaline.

7.2.7 Sample Volumes

Collect 1-L sample for most physical and chemical analyses. Do not use samples from the same container for multiple testing requirements because methods of collecting and handling are different for each type of test. Always collect enough sample volume in appropriate container in order to comply with sample handling, storage and preservation requirements.

7.2.8 Sample Storage and Preservation Before Analysis

a) Certain cations are subjected to loss by adsorption on, or ion exchange with, the walls of glass container. These include Al, Cd, Cr, Cu, Fe, Mn, Pb, and Zn which are best collected in a separate clean bottle and acidified with nitric acid to a pH below 2.0 to minimise precipitation and adsorption on containers wall.

b) Zero head space is important in preservation of samples with volatile organic compounds and radon. Carefully filling the bottle so that the top of meniscus is above the top of the bottle rim. After capping or sealing bottle, check for air bubbles by inverting and gently tapping it. Discard the sample and repeat refilling bottle with new sample until no air bubbles are observed.

c) Keep samples as cool as possible (4°C) without freezing to minimise the potential volatilization or biodegradation between sampling and analysing. Avoid using dry ice

because it will freeze samples and may cause glass to break. Preferably pack samples in crushed or cubed ice.

d) Analyse the samples as quickly as possible on arrival at the laboratory, if not possible, preferably store at 4°C.

e) Add preservatives to the sample bottle initially so that all sample portions are preserved as soon as collected.

Table 7.1. Containers, Preservation Techniques and Holding Times (APHA, 2005)

TABLE 1060:I. SUMMARY OF SPECIAL SAMPLING AND HANDLING REQUIREMENTS*						
Determination	Container†	Minimum Sample Size mL	Sample Type‡	Preservation§	Maximum Storage	
					Recommended	Regulatory
Acidity	P, G(B)	100	g	Refrigerate	24 h	14 d
Alkalinity	P, G	200	g	Refrigerate	24 h	14 d
BOD	P, G	1000	g, c	Refrigerate	6 h	48 h
Boron	P (PTFE) or quartz	1000	g, c	HNO ₃ to pH <2	28 d	6 months
Bromide	P, G	100	g, c	None required	28 d	28 d
Carbon, organic, total	G (B)	100	g, c	Analyze immediately; or refrigerate and add HCl, H ₃ PO ₄ , or H ₂ SO ₄ to pH <2	7 d	28 d
Carbon dioxide	P, G	100	g	Analyze immediately	0.25 h	N.S.
COD	P, G	100	g, c	Analyze as soon as possible, or add H ₂ SO ₄ to pH <2; refrigerate	7 d	28 d
Chloride	P, G	50	g, c	None required	N.S.	28 d
Chlorine, total, residual	P, G	500	g	Analyze immediately	0.25 h	0.25 h
Chlorine dioxide	P, G	500	g	Analyze immediately	0.25 h	N.S.
Chlorophyll	P, G	500	g	Unfiltered, dark, 4°C Filtered, dark, -20°C (Do not store in frost-free freezer)	24-48 h 28 d	
Color	P, G	500	g, c	Refrigerate	48 h	48 h
Specific conductance	P, G	500	g, c	Refrigerate	28 d	28 d
Cyanide						
Total	P, G	1000	g, c	Add NaOH to pH >12, refrigerate in dark#	24 h	14 d; 24 h if sulfide present
Amenable to chlorination	P, G	1000	g, c	Add 0.6 g ascorbic acid if chlorine is present and refrigerate	stat	14 d; 24 h if sulfide present
Fluoride	P	100	g, c	None required	28 d	28 d
Hardness	P, G	100	g, c	Add HNO ₃ or H ₂ SO ₄ to pH <2	6 months	6 months
Iodine	P, G	500	g	Analyze immediately	0.25 h	N.S.
Metals, general	P(A), G(A)	1000	g, c	For dissolved metals filter immediately, add HNO ₃ to pH <2	6 months	6 months
Chromium VI	P(A), G(A)	1000	g	Refrigerate	24 h	24 h
Copper by colorimetry*			g, c			
Mercury	P(A), G(A)	1000	g, c	Add HNO ₃ to pH <2, 4°C, refrigerate	28 d	28 d
Nitrogen						
Ammonia	P, G	500	g, c	Analyze as soon as possible or add H ₂ SO ₄ to pH <2, refrigerate	7 d	28 d
Nitrate	P, G	100	g, c	Analyze as soon as possible; refrigerate	48 h	48 h (28 d for chlorinated samples)
Nitrate + nitrite	P, G	200	g, c	Add H ₂ SO ₄ to pH <2, refrigerate	1-2 d	28 d
Nitrite	P, G	100	g, c	Analyze as soon as possible; refrigerate	none	48 h
Organic, Kjeldahl*	P, G	500	g, c	Refrigerate, add H ₂ SO ₄ to pH <2	7 d	28 d
Odor	G	500	g	Analyze as soon as possible; refrigerate	6 h	N.S.
Oil and grease	G, wide-mouth calibrated	1000	g	Add HCl or H ₂ SO ₄ to pH <2, refrigerate	28 d	28 d
Organic compounds						
MBAs	P, G	250	g, c	Refrigerate	48 h	N.S.
Pesticides*	G(S), PTFE-lined cap	1000	g, c	Refrigerate, add 1000 mg ascorbic acid/L if residual chlorine present	7 d	7 d until extraction; 40 d after extraction
Phenols	P, G, PTFE-lined cap	500	g, c	Refrigerate, add H ₂ SO ₄ to pH <2	*	28 d until extraction
Purgeables** by purge and trap	G, PTFE-lined cap	2 × 40	g	Refrigerate; add HCl to pH <2; add 1000 mg ascorbic acid/L if residual chlorine present	7 d	14 d

TABLE 1060:I. CONT.

Determination	Container†	Minimum Sample Size mL	Sample Type‡	Preservation§	Maximum Storage	
					Recommended	Regulatory
Base/neutral & acids	G(S) amber	1000	g, c	Refrigerate	7 d	7 d until extraction; 40 d after extraction
Oxygen, dissolved	G, BOD bottle	300	g	Analyze immediately	0.25 h	0.25 h
Electrode				Titration may be delayed after acidification	8 h	8 h
Winkler						
Ozone	G	1000	g	Analyze immediately	0.25 h	N.S.
pH	P, G	50	g	Analyze immediately	0.25 h	0.25 h
Phosphate	G(A)	100	g	For dissolved phosphate filter immediately; refrigerate	48 h	N.S.
Phosphorus, total	P, G	100	g, c	Add H ₂ SO ₄ to pH <2 and refrigerate	28 d	
Salinity	G, wax seal	240	g	Analyze immediately or use wax seal	6 months	N.S.
Silica	P (PTFE) or quartz	200	g, c	Refrigerate, do not freeze	28 d	28 d
Sludge digester gas	G, gas bottle	—	g	—	N.S.	
Solids ⁹	P, G	200	g, c	Refrigerate	7 d	2-7 d; see cited reference
Sulfate	P, G	100	g, c	Refrigerate	28 d	28 d
Sulfide	P, G	100	g, c	Refrigerate; add 4 drops 2N zinc acetate/100 mL; add NaOH to pH >9	28 d	7 d
Temperature	P, G	—	g	Analyze immediately	0.25 h	0.25 h
Turbidity	P, G	100	g, c	Analyze same day; store in dark up to 24 h, refrigerate	24 h	48 h

* For determinations not listed, use glass or plastic containers; preferably refrigerate during storage and analyze as soon as possible.

† P = plastic (polyethylene or equivalent); G = glass; G(A) or P(A) = rinsed with 1 + 1 HNO₃; G(B) = glass, borosilicate; G(S) = glass, rinsed with organic solvents or baked.

‡ g = grab; c = composite.

§ Refrigerate = storage at 4°C ± 2°C; in the dark; analyze immediately = analyze usually within 15 min of sample collection.

|| See citation¹⁰ for possible differences regarding container and preservation requirements. N.S. = not stated in cited reference; stat = no storage allowed; analyze immediately.

If sample is chlorinated, see text for pretreatment.