SECTION 8

LABORATORY PROCEDURES II — SAMPLE ANALYSES

Sample analyses may be conducted by one or more state or private contract laboratories. Because of the toxicity of dioxins/furans and the difficulty and cost of these analyses, relatively few laboratories currently have the capability of performing them. Table 8-1 lists contract laboratories experienced in dioxin/furan analyses.   This list is provided for information purposes only and is not an endorsement of specific laboratories.

8.1   RECOMMENDED ANALYTES

8.1.1   Target Analytes

All recommended target analytes listed in Table 4-1 should be included in screening studies unless reliable historic tissue, sediment, or pollutant source data indicate that an analyte is not present at a level of concern for human health. Additional target analytes should be included in screening studies if states have site-specific information (e.g., historic tissue or sediment data, discharge monitoring reports from municipal and industrial sources) that these contaminants may be present at levels of concern for human health.

Intensive studies should include only those target analytes found to exceed screening values in screening studies (see Section 5.2).

8.1.2   Lipid

A lipid analysis should also be performed and reported (as percent lipid by wet weight) for each composite tissue sample in both screening and intensive studies. This measurement is necessary to ensure that gel permeation chromatography columns are not overloaded when used to clean up tissue extracts prior to analysis of organic target analytes. In addition, because bioconcentration of nonpolar organic compounds is dependent upon lipid content (i.e., the higher the lipid content of the individual organism, the higher the residue in the organism), lipid analysis is often considered essential by users of fish and shellfish monitoring data. Consequently, it is important that lipid data are obtained for eventual inclusion in a national database of fish and shellfish contaminant data.

Table 8-1. Contract Laboratories Conducting Dioxin/Furan Analyses In Fish and Shellfish Tissues[a]

Alta Analytical Laboratory[b]
5070 Robert J. Matthews Parkway, Suite 2
Eldorado Hills, CA 95762
916/933-1640
FAX: 916/933-0940
Bill Luksemburg

Battelle-Columbus Laboratories[b]
505 King Avenue
Columbus, OH 43201
614/424-7379
Karen Riggs

Midwest Research Institute[b]
425 Volker Boulevard
Kansas City, MO 64110
816/753-7600, ext. 1160/1557
FAX: 816/753-8240
John Stanley/Tom Sack
e-mail: JStanley@mriresearch.org
          tsack@mriresearch.org

New York State Department of Health[b]
Wadsworth Center
Empire State Plaza
P.O. Box 509
Albany, NY 12201-0509
518/473-3378
FAX: 518/473-2895
Patrick O'Keefe

Pacific Analytical, Inc.[b]
6349 Paseo Del Argo
Carlsbad, CA 92009
760/438-3100
FAX: 760/931-9479
Bruce Colby

Axys Analytical Services[b]
P.O. Box 2219
2045 Mills Road
Sidney, BC V8L 3
Canada
250/656-0881; Toll Free 1-888-373-0881
Coreen Hamilton/Dale Hover/Laurie Phillips

Pace Analytical Services[b]
7726 Moller Road
Indianapolis, IN 46268
317/875-5894
FAX: 317/872-6189
Mick Mayse

Triangle Laboratories[b]
Alston Technical Park
801 Capitola Drive
Durham, NC 27713
919/544-5729
FAX: 919/544-5491
Phil Albro

Wellington Environmental Consultants[b]
398 Laird Road
Guelph, Ontario N1G 3X7
Canada
519/822-2436
Judy Sparling/Brock Chittin/Colleen Tashiro

Wright State University[b]
175 Brehm Laboratory
3640 Colonel Glen Highway
Dayton, OH 45435
937/775-2202
FAX: 937/775-3122
Thomas Tiernan/Garrett Van Ness

Quanterra Environmental Services
Knoxville Laboratory
5815 Middlebrook Pike
Knoxville, TN 37921
423/588-6401
FAX: 423/584-4315
David Thal/Tom Yoder

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[a] This list should not be construed as an endorsement by EPA of these laboratories, but is provided for information purposes only.
[b] Laboratory participating in Method 1613 interlaboratory (round-robin) dioxin study (May 1991).

Note: Because the concentrations of contaminants, particularly nonpolar organics, are often correlated with the percentage of lipid in a tissue sample, contaminant data are often normalized to the lipid concentration before statistical analyses are performed. This procedure can, in some instances, improve the power of the statistical tests. States wishing to examine the relationship between contaminant concentrations and percentage of lipid should refer to Hebert and Keenleyside (1995) for a discussion of the possible statistical approaches.

8.2 ANALYTICAL METHODS

This section provides guidance on selecting methods for analysis of recommended target analytes. Analytical methods should include appropriate procedures for sample preparation (i.e., for digestion of samples to be analyzed for metals and for extraction and extract cleanup of samples to be analyzed for organics).

8.2.1 Lipid Method

It is recommended that a gravimetic method be used for lipid analysis. This method is easy to perform and is commonly used by numerous laboratories, employing various solvent systems such as chloroform/methanol (Bligh and Dyer, 1959), petroleum ether (California Department of Fish and Game, 1990; U.S. FDA, 1990), and dichloromethane (NOAA, 1993a; Schmidt et al., 1985). The results of lipid analyses may vary significantly (i.e., by factors of 2 or 3), however, depending on the solvent system used for lipid extraction (Randall et al., 1991; D. Swackhamer, University of Minesota, personal communication, 1993; D. Murphy, Maryland Department of the Environment, Water Quality Toxics Division, personal communication, 1993). Therefore, to ensure consistency of reported results among fish contaminant monitoring programs, it is recommended that dichloromethane be used as the extraction solvent in all lipid analyses.

In addition to the effect of solvent systems on lipid analysis, other factors can also increase the inter- and intralaboratory variation of results if not adequately controlled (Randall et al., 1991). For example, high temperatures have been found to result in decomposition of lipid material and, therefore, should be avoided during extraction. Underestimation of total lipids can also result from denaturing of lipids by solvent contaminants, lipid decomposition from exposure to oxygen or light, and lipid degradation from changes in pH during cleanup. Overestimation of total lipids may occur if a solvent such as alcohol is used, which results in substantial coextraction of nonlipid material. It is essential that these potential sources of error be considered when conducting and evaluating results of lipid analyses.

8.2.2 Target Analyte Methods

EPA has published interim procedures for sampling and analysis of priority pollutants in fish tissue (U.S. EPA, 1981); however, official EPA-approved methods are available only for the analysis of low parts-per-billion concentrations of some metals in fish and shellfish tissues (U.S. EPA, 1991g). Because of the lack of official EPA-approved methods for all recommended target analytes, and to allow states and Regions flexibility in developing their analytical programs, specific analytical methods for recommended target analytes in fish and shellfish monitoring programs are not included in this guidance document.

Note: A performance-based analytical program is recommended for the analysis of target analytes. This recommendation is based on the assumption that the analytical results produced by different laboratories and/or different methods will be comparable if appropriate QC procedures are implemented within each laboratory and if comparable analytical performance on round-robin comparative analyses of standard reference materials or split sample analyses of field samples can be demonstrated. This approach is intended to allow states to use cost-effective procedures and to encourage the use of new or improved analytical methods without compromising data quality. Performance-based analytical programs currently are used in several fish and shellfish monitoring programs, including the NOAA Status and Trends Program (Battelle, 1989b; Cantillo, 1991; NOAA, 1987), the EPA Environmental Monitoring and Assessment Program (EMAP) (U.S. EPA, 1991e), and the Puget Sound Estuary Program (1990d, 1990e).

Analytical methods used in fish and shellfish contaminant monitoring programs should be selected using the following criteria:

- Technical merit—Methods should be technically sound; they should be specific for the target analytes of concern and based on current, validated analytical techniques that are widely accepted by the scientific community.

- Sensitivity—Method detection and quantitation limits should be sufficiently low to allow reliable quantitation of the target analytes of concern at or below selected screening values. Ideally, the method detection limit (in tissue) should be at least five times lower than the selected SV for a given target analyte (Puget Sound Estuary Program, 1990e).

- Data quality—The accuracy and precision should be adequate to ensure that analytical data are of acceptable quality for program objectives.

- Cost-efficiency—Resource requirements should not be unreasonably high.

A review of current EPA guidance for chemical contaminant monitoring programs and of analytical methods currently used or recommended in several of these programs (as shown in Table 8-2) indicates that a limited number of analytical

Table 8-2. Current References for Analytical Methods for Contaminants in Fish and Shellfish Tissues

- Analytical Chemistry of PCBs (Erickson, 1991)
- Analytical Methods for Pesticides and Plant Growth Regulators, Vol. 11 (Zweig and Sherma, 1980)
- Analytical Procedures and Quality Assurance Plan for the Determination of Mercury in Fish (U.S. EPA, 1989a)
- Analytical Procedures and Quality Assurance Plan for the Determination of Xenobiotic Chemical Contaminants in Fish (U.S. EPA, 1989c)
- Analytical Procedures and Quality Assurance Plan for the Determination of PCDD/PCDF in Fish (U.S. EPA, 1989b)
- Arsenic Speciation by Coupling High-Performance Liquid Chromatography with Inductively Coupled Plasma Mass Spectrometry (Demesmay et al., 1994)
- Assessment and Control of Bioconcentratable Contaminants in Surface Water (U.S. EPA, 1991a).
- Bioaccumulation Monitoring Guidance: 4. Analytical Methods for U.S. EPA Priority Pollutants and 301(h) Pesticides in Tissues from Marine and Estuarine Organisms (U.S. EPA, 1986a)
- Determination of Arsenic Species by High-Performance Liquid Chromatography - Inductively Coupled Plasma Mass Spectrometry (Beauchemin et al., 1989)
- Determination of Arsenic Species in Fish by Directly Coupled High-Performance Liquid Chromatography-Inductively Coupled Plasma Mass Spectrometry (Branch et al., 1994)
- The quantitation of butyltin and cyclohexyltin compounds in the marine environment of British Columbia. *Appl. Organometal. Chem.* 4:581-590 (Cullen et al., 1990)
- Determination of Butyltin, Methyltin and Tetraalkyltin in Marine Food Products with Gas Chromatography-Atomic Absorption Spectrometry (Forsyth and Cleroux, 1991)
- Determination of Tributyltin Contamination in Tissues by Capillary Column Gas Chromatography-Flame Photometric Detection with Confirmation by Gas Chromatography-Mass Spectroscopy (Wade et al., 1988)
- Determination of Tributyltin in Tissues and Sediments by Graphite Furnace Atomic Absorption Spectrometry (Stephenson and Smith, 1988)
- Environmental Monitoring and Assessment Program Near Coastal Virginian Province Quality Assurance Project Plan (Draft) (U.S. EPA, 1991e)
- Guidelines for Studies of Contaminants in Biological Tissues for the National Water-Quality Assessment Program (Crawford and Luoma, 1993)
- Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue (U.S. EPA, 1981)
- Laboratory Quality Assurance Program Plan (California Department of Fish and Game, 1990)
- Methods for Organic Analysis of Municipal and Industrial Wastewater (40 CFR 136, Appendix A).
- Methods for the Chemical Analysis of Water and Wastes (U.S. EPA, 1979b)
- Methods for the Determination of Metals in Environmental Samples (U.S. EPA, 1991g)
- Official Methods of Analysis of the Association of Official Analytical Chemists (Williams, 1984)
- Pesticide Analytical Manual (PAM Vols. I and II) (U.S. FDA, 1990)
- Puget Sound Estuary Program Plan (1990d, 1990e)
- Quality Assurance/Quality Control (QA/QC) for 301(h) Monitoring Programs: Guidance on Field and Laboratory Methods (U.S. EPA, 1987e)

Table 8-2 (continued)

- Sampling and Analytical Methods of the National Status and Trends Program National Benthic Surveillance and Mussel Watch Projects 1984-92. Volume II. Comprehensive Descriptions of Complementary Measurements (NOAA, 1993a)
- Sampling and Analytical Methods of the National Status and Trends Program National Benthic Surveillance and Mussel Watch Projects 1984-92. Volume III. Comprehensive Descriptions of Elemental Analytical Methods (NOAA, 1993b)
- Sampling and Analytical Methods of the National Status and Trends Program National Benthic Surveillance and Mussel Watch Projects 1984-92. Volume IV. Comprehensive Descriptions of Trace Organic Analytical Methods (NOAA, 1993c)
- Separation of Seven Arsenic Compounds by High-performance Liquid Chromatography with On-line Detection by Hydrogen-Argon Flame Atomic Absorption Spectrometry and Inductively Coupled Plasma Mass Spectrometry (Hansen et al., 1992)
- Speciation of Selenium and Arsenic in Natural Waters and Sediments by Hydride Generation Followed by Atomic Absorption Spectroscopy (Crecelius et al., 1986)
- Standard Analytical Procedures of the NOAA National Analytical Facility (Krahn et al., 1988; MacLeod et al., 1985)
- Standard Methods for the Examination of Water and Wastewater (Greenburg et al., 1992)
- Test Methods for the Chemical Analysis of Municipal and Industrial Wastewater (U.S. EPA, 1982)
- Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods (SW-846) (U.S. EPA, 1986d)
- U.S. EPA Contract Laboratory Program Statement of Work for Inorganic Analysis (U.S. EPA, 1991b)
- U.S. EPA Contract Laboratory Program Statement of Work for Organic Analysis (U.S. EPA, 1991c)
- U.S. EPA Method 1613B: Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS (U.S. EPA, 1995b)
- U.S. EPA Method 1625: Semivolatile Organic Compounds by Isotope Dilution GC/MS (40 CFR 136, Appendix A)
- U.S. EPA Method 1631: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry (U.S. EPA, 1995c)
- U.S. EPA Method 1632: Determination of Inorganic Arsenic in Water by Hydride Generation Flame Atomic Absorption (U.S. EPA, 1995d)
- U.S. EPA Method 1637: Determination of Trace Elements in Ambient Waters by Chelation Preconcentration with Graphite Furnace Atomic Absorption (U.S. EPA, 1995e)
- U.S. EPA Method 1638: Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma-Mass Spectrometry (U.S. EPA, 1995f)
- U.S. EPA Method 1639: Determination of Trace Elements in Ambient Waters by Stabilized Temperature Graphite Furnace Atomic Absorption (U.S. EPA, 1995g)
- U.S. EPA Method 625: Base/Neutrals and Acids by GC/MS (40 CFR 136, Appendix A).
- U.S. EPA Method 8290: Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) (U.S. EPA, 1990b)
- U.S. EPA Method 1668: Draft Method 1668 Toxic Polychlorinated Biphenols by Isotope Dilution High Gas Chromatography/High Resolution Mass Spectrometry (U.S. EPA, 1997a)

techniques are most commonly used for the determination of the recommended target analytes. These techniques are listed in Table 8-3. As shown in Table 8-4, analytical methods employing these techniques have typically achievable detection and/or quantitation limits that are well below the recommended SVs for most target analytes, with the possible exception of dieldrin, heptachlor epoxide, toxaphene, PCBs, and dioxins/furans. Recommended procedures for determining method detection and quantitation limits are given in Section 8.3.3.3.

If lower SVs are used in a study (e.g., for susceptible populations), it is the responsibility of program managers to ensure that the detection and quantitation limits of the analytical methods are sufficiently low to allow reliable quantitation of target analytes at or below these SVs. If analytical methodology is not sensitive enough to reliably quantitate target analytes at or below selected SVs (e.g., dieldrin, heptachlor epoxide, toxaphene, PCBs, dioxins/furans), program managers must determine appropriate fish consumption guidance based on lowest detectable concentrations or provide justification for adjusting SVs to values at or above achievable method detection limits. It should be emphasized that when SVs are below detection limits, the failure to detect a target analyte cannot be assumed to mean that there is no cause for concern for human health effects.

The analytical techniques identified in Table 8-3 are recommended for use in state fish and shellfish contaminant monitoring programs. However, alternative techniques may be used if acceptable detection limits, accuracy, and precision can be demonstrated. **Note:** Neither rotenone, the most widely used piscicide in the United States, nor its biotransformation products (e.g., rotenolone, 6',7'-dihydro-6',7'-dihydroxyrotenone, 6',7'-dihydro-6',7'-dihydroxyrotenolone) would be expected to interfere with the analyses of organic target analytes using the recommended gas chromatographic methods of analysis. Furthermore, rotenone has a relatively short half-life in water (3.7, 1.3, and 5.2 days for spring, summer, and fall treatments, respectively) (Dawson et al., 1991) and does not bioaccumulate significantly in fish (bioconcentration factor= 26 in fish carcass) (Gingerich and Rach, 1985), so that tissue residues should not be significant.

Laboratories should select analytical methods for routine analyses of target analytes that are most appropriate for their programs based on available resources, experience, program objectives, and data quality requirements. A recent evaluation of current methods for the analyses of organic and trace metal target analytes in fish tissue provides useful guidance on method selection, validation, and data reporting procedures (Capuzzo et al., 1990).

The references in Table 8-2 should be consulted in selecting appropriate analytical methods. **Note:** Because many laboratories may have limited experience in determining inorganic arsenic, a widely accepted method for this analysis is included in Appendix H.

Table 8-3. Recommended Analytical Techniques for Target Analytes

Target analyte	Analytical technique
Metals	
Arsenic (inorganic)	HAA, or HPLC with ICP-MS
Cadmium	GFAA or ICP[a]
Mercury	CVAA
Selenium	GFAA, ICP, or HAA[a,b]
Tributyltin	GFAA or GC/FPD[c]
Organics	
PAHs	GC/MS or HRGC/HRMS[d]
PCBs	
Total Aroclors	GC/ECD[e,f,g,h]
Non-ortho coplanar PCBs	HRGC/HRMS[i]
Other cogeners/homologs	HRGC/LRMS
Organochlorine pesticides	GC/ECD[f,g]
Organophosphate pesticides	GC/MS, GC/FPD, or GC/NPD[j]
Chlorophenoxy herbicides	GC/ECD[f,g]
Dioxins/dibenzofurans	HRGC/HRMS[k,l]

CVAA	=	Cold vapor atomic absorption spectrophotometry.
GC/ECD	=	Gas chromatography/electron capture detection.
GC/FPD	=	Gas chromatography/flame photometric detection.
GC/MS	=	Gas chromatography/mass spectrometry.
GC/NPD	=	Gas chromatography/nitrogen-phosphorus detection.
GFAA	=	Graphite furnace atomic absorption spectrophotometry.
HAA	=	Hydride generation atomic absorption spectrophotometry.
HPLC	=	High-performance liquid chromatography.
HRGC/HRMS	=	High-resolution gas chromatography/high-resolution mass spectrometry.
ICP	=	Inductively coupled plasma emission spectrometry.
ICP-MS	=	Inductively coupled plasma mass spectrometry.
LRMS	=	Low resolution mass spectrometry.
PAHs	=	Polycyclic aromatic hydrocarbons.
PCBs	=	Polychlorinated biphenyls.

[a] Atomic absorption methods require a separate determination for each element, which increases the time and cost relative to the broad-scan ICP method. However, GFAA detection limits are typically more than an order of magnitude lower than those achieved with ICP.

[b] Use of HAA can lower detection limits for selenium by a factor of 10-100 (Crecelius, 1978; Skoog, 1985).

[c] GC/FDP is specific for tributyltin and the most widely accepted analytical method. GFAA is less expensive (see Table 8-5) but is not specific for tributyltin. Depending on the extraction scheme, mono-, di-, and tetrabutyltin and other alkyltins may be included in the analysis. Contamination of samples with tin may also be a potential problem, resulting in false positives (E. Crecelius, Battelle Pacific Northwest Laboratories, Marine Sciences Laboratory, Sequim, WA, personal communication, 1999).

[d] GC/MS is also recommended for base/neutral organic target analytes (except organochlorine pesticides and PCBs) that may be included in a study. Detection limits of less than 1 ppb can be achieved for PAHs using HRGC/HRMS. It is recommended that, in both screening and intensive studies, tissue samples be analyzed for benzo[a]pyrene and 14 other PAHs and that the relative potencies given for these PAHs (Nesbit and LaGoy, 1992; U.S. EPA, 1993c) be used to calculate PEC for each sample for comparison with the recommended SV for benzo[a]pyrene (see Section 5.3.2.4).

[e] Analysis of total PCBs, as the sum of PCB congeners or sum of Aroclors, is recommended for conducting human health risk assessments for PCBs. A standard method for Aroclor analyses is available (EPA Method 608). EPA is currently testing a draft method (1668) for PCB congener analysis; however, it has not been finalized.

(continued)

Table 8-3 (continued)

[f] GC/ECD does not provide definitive compound identification, and false positives due to interferences are commonly reported. Confirmation by an alternative GC column phase (with ECD), or by GC/MS with selected ion monitoring, is required for positive identification of PCBs, organochlorine pesticides, and chlorophenoxy herbicides.

[g] GC/MS with selected ion monitoring may be used for quantitative analyses of these compounds if acceptable detection limits can be achieved.

[h] PCB congener analysis using capillary GC columns is recommended (NOAA, 1989b; Dunn et al., 1984; Schwartz et al., 1984; Mullin et al., 1984; Stalling et al., 1987). An enrichment step, employing an activated carbon column, may also be required to separate and quantify coeluting congeners or congeners present at very low concentrations (Smith, 1981; Schwartz et al., 1993).

[i] Includes PCBs -77, -81, -126 and -169.

[j] Some of the chlorinated organophosphate pesticides (e.g., chlorpyrifos) may be analyzed by GC/ECD (USGS, 1987).

[k] The analysis of the 17 2,3,7,8-substituted congeners of tetra- through octa-chlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) using isotope dilution is recommended.

[l] Because of the toxicity of dioxins/furans and the difficulty and cost of these analyses, relatively few laboratories currently have the capability of performing these analyses. Contract laboratories experienced in conducting dioxin/furan analyses are listed in Table 8-1.

Table 8-4. Range of Detection and Quantitation Limits of Current Analytical Methods for Recommended Target Analytes[a]

Target analyte	Recreational SV	Subsistence SV[b]	Range of detection limits	Range of quantitation limits
Metals				
Arsenic (inorganic)	26 ppb	3.27 ppb	5-50 ppb[c]; 50-100 ppb[d]	5-25 ppb
Cadmium	4,000 ppb	491 ppb	5-46 ppb[e], 400 ppb[f]	5-500 ppb
Mercury	400 ppb	49 ppb	1.3-100 ppb[g]	2-10 ppb
Selenium	20,000 ppb	2,457 ppb	17-150 ppb[c]; 20 ppb[h], 600 ppb[f]	20-600 ppb
Tributyltin	1,200 ppb	147 ppb	2.5 ppb[e]; 2-5 ppb[i]	2-10 ppb
Organochlorine Pesticides[j]				
Chlordane (total)	—	—		
cis-Chlordane	114 ppb	14 ppb	1-5 ppb	2-20 ppb[j,k]
trans-Chlordane			1-5 ppb	2-15 ppb
cis-Nonachlor			1-5 ppb	2-15 ppb
trans-Nonachlor			1-7 ppb	2-15 ppb
Oxychlordane			1-5 ppb	2-15 ppb
DDT (total)	117 ppb	14.4 ppb		
4,4´-DDT			0.1-13 ppb	2-20 ppb
2,4´-DDT			0.1-10 ppb	2-15 ppb
4,4´-DDD			0.1-10 ppb	2-15 ppb
2,4´-DDD			0.1-10 ppb	2-15 ppb
4,4´-DDE			0.1-38 ppb	2-15 ppb[j,k]
2,4´-DDE			0.1-10 ppb	2-15 ppb
Dicofol	1,600 ppb	196 ppb	1-5 ppb	2-10 ppb
Dieldrin	2.50 ppb	0.307 ppb	0.1-5 ppb	2-15 ppb
Endosulfan (total)	24,000 ppb	2,949 ppb	5-70 ppb	10-70 ppb
Endosulfan I			5-10 ppb	2-15 ppb
Endosulfan II			5-70 ppb	10-70 ppb
Endrin	1,200 ppb	147 ppb	0.1-15 ppb	2-15 ppb[j,k]
Heptachlor epoxide	4.39 ppb	0.54 ppb	0.1-5 ppb	2-15 ppb[j,k]
Hexachlorobenzene	25 ppb	3.07 ppb	0.1-2 ppb	2-15 ppb[j,k]
Lindane	30 ppb	3.78 ppb	0.1-5 ppb	2-15 ppb[j,k]
Mirex	800 ppb	98 ppb	0.1-5 ppb	2-15 ppb[j,k]
Toxaphene	36 ppb	4.46 ppb	3-100 ppb	60-153 ppb
Organophosphate Pesticides[j]				
Chlorpyrifos	18,000 ppb	147 ppb	2-5 ppb	2-15 ppb[k]
Diazinon	4,200 ppb	344 ppb	2-5 ppb	2-15 ppb
Disulfoton	240 ppb	19 ppb	2-5 ppb	2-15 ppb
Ethion	3,000 ppb	245 ppb	2-5 ppb	2-15 ppb
Terbufos	120 ppb	9 ppb	2-5 ppb	2-15 ppb
Chlorophenoxy Herbicides				
Oxyfluorfen	546 ppb	679 ppb	10-20 ppb	20-200 ppb
PAHs[l]	5.47 ppb	0.67 ppb	1-10 ppt	2-20 ppt
PCBs total	20 ppb	2.45 ppb	—	—
(sum of Aroclors)[j]			(20-62 ppb)[m]	(110-170 ppb)[m]
Non-ortho coplanar PCBs[k]			2-5 ppt	2-10 ppt
Other congeners/ homologues[n]			2-5 ppb	10 ppb
Dioxins/furans[k] (total)	0.256 ppt	0.031 ppt	1.0 ppt	5-10 ppt
TCDD/TCDF			0.1 ppt	0.5 ppt
PeCDD/PeCDF			0.5 ppt	2.5 ppt
HxCDD/HxCDF			0.5 ppt	2.5 ppt
HpCDD/HpCDF			0.5 ppt	2.5 ppt
OCDD/OCDF			1.0 ppt	5 ppt

PAHs = Polycyclic aromatic hydrocarbons. PCBs = Polychlorinated biphenyls. SV = Screening value (wet weight).

(continued)

Table 8-4. (continued)

a Target analyte concentrations are given based on wet weight of fish tissue.

b From Tables 5-2 and 5-3. SVs shown here are for fish consumers using RfDs or CSFs available in the EPA IRIS (1999) database and assuming a consumption rate (CR) for recreational fishers of 12 g/d and for subsistence fishers of 124 g/d , average adult body weight (BW) = 72 kg, lifetime (70-yr) exposure, and, for carcinogens, a risk level (RL) = 10^{-5}. **Note:** Increasing CR, decreasing BW, and/or using an RL <10^{-5} will decrease the SV. Program managers must ensure that detection and quantitation limits of analytical methods are sufficient to allow reliable quantitation of target analytes at or below selected SVs. If analytical methodology is not sensitive enough to reliably quantitate target analytes at or below selected SVs (e.g., inorganic arsenic, dieldrin, heptachlor epoxide, toxaphene, PCBs, dioxins/furans), the program managers must determine appropriate fish consumption guidance based on lowest detectable concentrations or provide justification for adjusting SVs to values at or above achievable method detection or quantitation limits. It should be emphasized that when SVs are below method detection limits, the failure to detect a target analyte cannot be assumed to indicate that there is no cause for concern for human health effects.

c Analysis by hydride generation atomic absorption spectrophotometry (HAA) with preconcentration (E. Crecelius, Battelle Pacific Northwest Laboratories, Marine Sciences Laboratory, Sequim, WA, personal communication, July 1999).

d Analysis by high-performance liquid chromatography/mass spectrometry (HPLC/MS) (E. Crecelius, Battelle Pacific Northwest Laboratories, Marine Sciences Laboratory, Sequim, WA, personal communication, July 1999).

e Analysis by graphite furnace atomic absorption spectrophotometry (GFAA). **Note:** This method is not specific for tributyltin. Depending on the extraction procedure, mono-, di-, and tetrabutyltin may also be included in the analysis. Also, this method does not distinguish between butyltins and other alkyltins (E. Crecelius, Battelle Pacific Northwest Laboratories, Marine Sciences Laboratory, Sequim, WA, personal communication, July 1999).

f Analysis by inductively coupled plasma atomic emission spectrophotometry (ICP).

g Analysis by cold vapor atomic absorption spectrophotometry (CVAA).

h Analysis by HAA.

i Analysis by gas chromatography/flame photometric detection (GC/FPD) (E. Crecelius, Battelle Pacific Northwest Laboratories, Marine Sciences Laboratory, Sequim, WA, personal communication, July 1999).

j Analysis by gas chromatography/electron capture detection (GC/ECD), except where otherwise noted.

k Analysis by high-resolution GC/high-resolution mass spectrometry (HRGC/HRMS).

l Analysis by gas chromatography/mass spectrometry. Detection limits of less than 1 ppb can be achieved using high-resolution gas chromatography/mass spectrometry (HRGC/HRMS).

m Values in parentheses represent ranges for individual Aroclors.

n Analysis by high-resolution GC/low resolution mass spectrometry (HRGC/LRMS).

An additional resource for method selection is the EPA Environmental Monitoring Methods Index System (EMMI), an automated inventory of information on environmentally significant analytes and methods for their analysis (U.S. EPA, 1991f). The EMMI database includes information on more than 4,000 analytes from over 80 regulatory and nonregulatory lists and more than 900 analytical methods in a variety of matrices, including tissue. This searchable database provides a comprehensive cross-reference between analytes and analytical methods with detailed information on each analytical method, including sponsoring organization, sample matrix, and estimates of detection limits, accuracy, and precision.

EMMI is available from the EPA Sample Control Center for all EPA personnel and from National Technical Information Service (NTIS) for all other parties. EMMI is also available through the EPA Local Area Network (LAN).

The private sector may purchase EMMI Version 2.0 through the:

> National Technical Information Service (NTIS)
> 5285 Port Royal Road
> Springfield, VA 22161
> USA
> Phone: (703) 605-6000
> Fax: (703) 605-6900
> Rush Orders: (800) 553-NTIS
> Online Orders: http:\\www.ntis.gov

The order number is PB97-5026371NC for a single user, PB97-502645INC for a five-user LAN package, and PB97-502652INC for an unlimited user LAN package. Further information may be obtained by contacting:

> EMMI User Support
> Tech Calls
> EPA Assistant Administrator for Water
> Office of Science and Technology
> (703) 461-2104
> Alexandria, VA 22313

Because chemical analysis is frequently one of the most expensive components of a sampling and analysis program, the selection of an analytical method often will be influenced by its cost. In general, analytical costs increase with increased sensitivity (i.e., lower detection limits) and reliability (i.e., accuracy and precision). Analytical costs will also be dependent on the number of samples to be analyzed, the requested turnaround time, the number and type of analytes requested, the level of QC effort, and the amount of support documentation requested (Puget Sound Estuary Program, 1990d). However, differences in protocols, laboratory experience, and pricing policies of laboratories often introduce large variation into analytical costs. Approximate costs per sample for the analysis of target analytes by the recommended analytical techniques are provided in Table 8-5.

8.3 QUALITY ASSURANCE AND QUALITY CONTROL CONSIDERATIONS

Quality assurance and quality control must be integral parts of each chemical analysis program. The QA process consists of management review and oversight at the planning, implementation, and completion stages of the analytical data collection activity to ensure that data provided are of the quality required. The QC process includes those activities required during data collection to produce the data quality desired and to document the quality of the collected data.

During the planning of a chemical analysis program, QA activities focus on defining data quality criteria and designing a QC system to measure the quality of data being generated. During the implementation of the data collection effort, QA activities ensure that the QC system is functioning effectively and that the

**Table 8-5. Approximate Range of Costs per Sample for
Analysis of Recommended Target Analytes[a]**

Target analyte	Approximate cost range (1999 $)
Metals[b]	
Arsenic (inorganic)[c]	200 - 400
Cadmium	55 - 60
Mercury (total)	45 - 60
Selenium	35 - 60
Tributyltin[d]	200 - 400
Organochlorine pesticides[e,f]	285 - 500
Organophosphate pesticides[g]	250 - 500
Chlorophenoxy herbicides[h]	250 - 500
PAHs[i]	250 - 525
PCBs	
Total Aroclors[e]	210 - 500
Non-ortho coplanar PCBs[j]	1,000 - 2,000
Other cogeners/homologs[k]	800 - 1,000
Dioxins/furans[j]	
TCDD/TCDF only	600 - 1,000
TCDD/TCDF through OCDD/OCDF isomers	800 - 1,600
2,3,7,8-substituted dioxins/furans	1,000 - 2,000
Lipid	30 - 40

OCDD = Octachlorodibenzo-*p*-dioxin.   PCBs = Polychlorinated biphenyls.
OCDF = Octachlorodibenzofuran.   TCDD = 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin.
PAHs = Polycyclic aromatic hydrocarbons.   TCDF = 2,3,7,8-Tetrachlorodibenzofuran.

[a] These costs include sample digestion or extraction and cleanup, but not sample preparation (i.e., resection, grinding, homogenization, compositing). Estimated cost of sample preparation for a composite homogenate of five fish is $200 to $500.

[b] Analysis of inorganic arsenic by hydride generation atomic absorption spectroscopy (HAA) or high-performance liquid chromatography-inductively coupled plasma mass spectrometry (HPLC-ICP/MS). Analysis of cadmium by graphite furnace atomic absorption spectrophotometry (GFAA). Analysis of selenium by GFAA or HAA. Analysis of mercury by cold vapor atomic absorption spectrophotometry (CVAA). Analysis of tributyltin by GFAA or gas chromatography/flame photometric detection (GC/FPD).

[c] Estimated costs are for total inorganic arsenic. Estimated cost of analysis by HAA is $200. Estimated cost of analysis by HPLC-ICP/MS is $400.

[d] Estimated cost of analysis by GFAA is $200. Estimated cost of analysis by GC/FPD is $400. **Note:** Analysis by GFAA is not specific for tributyltin. Depending on the extraction procedure, other butyl- and alkyltin species may be detected.

[e] Analysis by gas chromatography/electron capture detection (GC/ECD).

[f] Estimated costs are for analysis of all recommended target analyte organochlorine pesticides (see Table 4-1).

[g] Analysis by GC/FPD or gas chromatography/nitrogen-phosphorus detection (GC/NPD). Some of the chlorinated organophosphate pesticides (e.g., chlorpyrifos) may be analyzed as organochlorine pesticides by GC/ECD (USGS, 1987).

[h] Analysis by GC/ECD.

[i] Costs are for analysis by gas chromatography/mass spectrometry (GC/MS) or gas chromatography/flame ionization detection (GC/FID). Cost for analysis by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) is approximately $1,000 per sample.

[j] Analysis by HRGC/HRMS.

[k] Analysis by HRGC/low resolution mass spectrometry (LRMS).

deficiencies uncovered by the QC system are corrected. After the analytical data are collected, QA activities focus on assessing the quality of data obtained to determine its suitability to support decisions for further monitoring, risk assessments, or issuance of advisories.

The purpose of this section is to describe the general QA and QC requirements for chemical analysis programs.

8.3.1 QA Plans

Each laboratory performing chemical analyses in fish and shellfish contaminant monitoring programs must have an adequate QA program (U.S. EPA, 1984b). The QA program should be documented fully in a QA plan or in a combined Work/QA Project Plan (U.S. EPA, 1980b). (See Appendix I.) Each QA and QC requirement or procedure should be described clearly. Documentation should clearly demonstrate that the QA program meets overall program objectives and data quality requirements. The QA guidelines in the Puget Sound Estuary Program (1990d, 1990e), the NOAA Status and Trends Program (Battelle, 1989b; Cantillo, 1991; NOAA, 1987), the EPA 301(h) Monitoring Programs (U.S. EPA, 1987e), the EPA EMAP Near Coastal (EMAP-NC) Program (U.S. EPA, 1991e), and the EPA Contract Laboratory (CLP) Program (U.S. EPA, 1991b, 1991c) are recommended as a basis for developing program-specific QA programs. Additional method-specific QC guidance is given in references in Table 8-2.

8.3.2 Method Documentation

Methods used routinely for the analyses of contaminants in fish and shellfish tissues must be documented thoroughly, preferably as formal standard operating procedures (U.S. EPA, 1984b). Recommended contents of an analytical SOP are shown in Figure 8-1. Analytical SOPs must be followed exactly as written. A published method may serve as an analytical SOP only if the analysis is performed exactly as described. Any significant deviations from analytical SOPs must be documented in the laboratory records (signed and dated by the responsible person) and noted in the final data report. Adequate evidence must be provided to demonstrate that an SOP deviation did not adversely affect method performance (i.e., detection or quantitation limits, accuracy, precision). Other-wise, the effect of the deviation on data quality must be assessed and documented and all suspect data must be identified.

8.3.3 Minimum QA and QC Requirements for Sample Analyses

The guidance provided in this section is derived primarily from the protocols developed for the Puget Sound Estuary Program (1990d, 1990e). These protocols have also provided the basis for the EPA EMAP-NC QA and QC requirements (U.S. EPA, 1991e). QA and QC recommendations specified in this document are intended to provide a uniform performance standard for all analytical protocols used in state fish and shellfish contaminant monitoring

- Scope and application
- Method performance characteristics (accuracy, precision, method detection and quantitation limits) for each analyte
- Interferences
- Equipment, supplies, and materials
- Sample preservation and handling procedures
- Instrument calibration procedures
- Sample preparation (i.e., extraction, digestion, cleanup) procedures
- Sample analysis procedures
- Quality control procedures
- Corrective action procedures
- Data reduction and analysis procedures (with example calculations)
- Recordkeeping procedures (with standard data forms, if applicable)
- Safety procedures and/or cautionary notes
- Disposal procedures
- References

Figure 8-1. Recommended contents of analytical standard operating procedures (SOPs).

programs and to enable an assessment of the comparability of results generated by different laboratories and different analytical procedures. These recommendations are intended to represent minimum QA and QC procedures for any given analytical method. Additional method-specific QC procedures should always be followed to ensure overall data quality.

For sample analyses, minimum QA and QC requirements consist of (1) initial demonstration of laboratory capability and (2) routine analyses of appropriate QA and QC samples to demonstrate continued acceptable performance and to document data quality.

Initial demonstration of laboratory capability (prior to analysis of field samples) should include

- Instrument calibration
- Documentation of detection and quantitation limits
- Documentation of accuracy and precision
- Analysis of an accuracy-based performance evaluation sample provided by an external QA program.

Ongoing demonstration of acceptable laboratory performance and documentation of data quality should include

- Routine calibration and calibration checks
- Routine assessment of accuracy and precision
- Routine monitoring of interferences and contamination
- Regular assessment of performance through participation in external QA interlaboratory comparison exercises, when available.

The QA and QC requirements for the analyses of target analytes in tissues should be based on specific performance criteria (i.e., warning or control limits) for data quality indicators such as accuracy and precision. **Warning limits** are numerical criteria that serve to alert data reviewers and data users that data quality may be questionable. A laboratory is not required to terminate analyses when a warning limit is exceeded, but the reported data may be qualified during subsequent QA review. **Control limits** are numerical data criteria that, when exceeded, require

suspension of analyses and specific corrective action by the laboratory before the analyses may resume.

Typically, warning and control limits for accuracy are based on the historical mean recovery plus or minus two or three standard deviation units, respectively. Warning and control limits for precision are typically based on the historical standard deviation or coefficient of variation (or mean relative percent difference for duplicate samples) plus two or three standard deviation units, respectively. Procedures incorporating control charts (ASTM, 1976; Taylor, 1985) and/or tabular presentations of historical data should be in place for routine monitoring of analytical performance. Procedures for corrective action in the event of excursion outside warning and control limits should also be in place.

The results for the various QC samples analyzed with each batch of samples should be reviewed by qualified laboratory personnel immediately following the analysis of each sample batch to determine when warning or control limits have been exceeded. When established control limits are exceeded, appropriate corrective action should be taken and, if possible, all suspect samples reanalyzed before resuming routine analyses. If reanalyses cannot be performed, all suspect data should be identified clearly. **Note:** For the purposes of this guidance manual, a batch is defined as any group of samples from the same source that is processed at the same time and analyzed during the same analytical run.

Recommended QA and QC samples (with definitions and specifications), frequencies of analyses, control limits, and corrective actions are summarized in Table 8-6.

Note: EPA recognizes that resource limitations may prevent some states from fully implementing all recommended QA and QC procedures. Therefore, as additional guidance, the minimum numbers of QA and QC samples recommended for routine analyses of target analytes are summarized in Table 8-7. It is the responsibility of each program manager to ensure that the analytical QC program is adequate to meet program data quality objectives for method detection limits, accuracy, precision, and comparability.

Recommended QA and QC procedures and the use of appropriate QA and QC samples are discussed in Sections 8.3.3.2 through 8.3.3.8. Recommended procedures for documenting and reporting analytical and QA and QC data are given in Section 8.4. Because of their importance in assessing data quality and interlaboratory comparability, reference materials are discussed separately in the following section.

Table 8-6. Recommended Quality Assurance and Quality Control Samples

Sample type (definition; specifications)	Objective	Recommended frequency of analysis[a]	Recommended control limits[b]	Recommended corrective action
External Calibration				
Calibration standards (3-5 standards over the expected range of sample target analyte concentrations, with the lowest concentration standard at or near the MDL; see Section 8.3.3.2.1)	Full calibration: Establish relationship between instrument response and target analyte concentration. Used for organics analysis by GC/ECD and for metals analysis.	Instrument/method-dependent; follow manufacturer's recommendations or procedures in specific analytical protocols. At a minimum, perform a 3-point calibration each time an instrument is set up for analysis, after each major equipment change or disruption, and when routine calibration check exceeds specific control limits.	*Organics:* RSD of RFs of calibration standards $\leq$20%. *Metals:* %R of all calibration standards = 95-105.	Determine cause of problem (e.g., instrument instability or malfunction, contamination, inaccurate preparation of calibration standards) and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.
Internal Standard Calibration				
Instrument internal standards (e.g., 2,2'-difluorobiphenyl) (see Section 8.3.3.2.1 for definition)	Full calibration: Determine RRFs of organic target analytes for quantitative analysis. Required for internal calibration of GC/MS systems. Optional calibration technique for GC/ECD.	In every calibration standard, sample, and blank analyzed; added to final sample extract. Internal standard calibration performed at same frequency recommended for external calibration.	RSD of RRFs of calibration standards $\leq$30%.	Determine cause of problem (e.g., instrument instability or malfunction, contamination, inaccurate preparation of internal standards or calibration standards) and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.
Calibration Verification				
Calibration check standards (minimum of one mid-range standard prepared independently from initial calibration standards; an instrument internal standard must be added to each calibration check standard when internal standard calibration is being used; see Section 8.3.3.2.1)	Verify calibration.	*Organics (GC/MS):* After initial calibration or recalibration. At beginning and end of each work shift, and once every 12 h (or every 10-12 analyses, whichever is more frequent). *Organics (GC/ECD):* After initial calibration or recalibration. At beginning and end of each work shift, and once every 6 h (or every 6 samples, whichever is less frequent). *Metals:* After initial calibration or recalibration. Every 10 samples or every 2 h, whichever is more frequent.	*Organics:* Percent difference between the average RF (or RRF) from initial calibration and the RF (or RRF) from the calibration check $\leq$25%. *Mercury:* %R = 80-120. *Other Metals:* %R = 90-110.	Determine cause of problem (e.g., instrument instability or malfunction, contamination, inaccurate preparation of calibration standards) and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.

(continued)

Table 8-6. (continued)

Sample type (definition; specifications)	Objective	Recommended frequency of analysis[a]	Recommended control limits[b]	Recommended corrective action
Method Detection Limit Determination				
Spiked matrix samples (analyte-free tissue samples to which known amounts of target analytes have been added; one spike for each target analyte at 3-5 times the estimated MDL; see Section 8.3.3.1)	Establish or confirm MDL for analyte of interest (Keith, 1991a; Keith et al., 1983).	Seven replicate analyses prior to use of method for routine analyses, and after any significant change to a method currently in use. Reevaluation of MDL annually.	Determined by program manager.	Redetermine MDL.
Accuracy and Precision Assessment				
Reference materials[c] (see Section 8.3.3.1 for definitions) (SRMs or CRMs, prepared from actual contaminated fish or shellfish tissue if possible, covering the range of expected target analyte concentrations.	Assess method performance (initial method validation and routine accuracy assessment).	*Method validation:* As many as required to assess accuracy (and precision) of method before routine analysis of samples (i.e., when using a method for the first time or after any method modification). *Routine accuracy assessment:* one (preferably blind) per 20 samples or one per batch, whichever is more frequent.	*Organics:* Measured value <95% confidence intervals, if certified. Otherwise, %R = 70-130.[d] *Metals:* %R = 85-115.[d] *Organics:* Measured value <95% confidence intervals, if certified. Otherwise, %R = 70-130.[d] *Metals:* %R = 85-115.[d]	NA Determine cause of problem (e.g., inaccurate calibration, contamination), take appropriate corrective action, and reanalyze all suspect samples or flag all suspect data.
Laboratory control samples (Accuracy-based samples consisting of fish or shellfish tissue homogenates spiked with target analytes of interest; may be SRMs or CRMs; sometimes referred to as QC samples. When available, CRMs are recommended for routine use as laboratory control samples; see Appendix M)	Assess method performance (initial method validation and routine accuracy assessment). Used for initial accuracy assessment only if reference materials prepared from actual contaminated fish or shellfish tissue are not available.	*Method validation:* As many as required to assess accuracy (and precision) of method before routine analysis of samples (i.e., when using a method for the first time or after any method modification). *Routine accuracy assessment.* One per 20 samples or one per batch, whichever is more frequent.	Determined by program manager. *Organics:* %R = 70-130.[d] *Metals:* %R = 85-115.[d]	NA Determine cause of problem (e.g., inaccurate calibration, inaccurate preparation of control samples), take appropriate corrective action, and reanalyze all suspect samples or flag all suspect data. Zero percent recovery requires rejection of all suspect data.

(continued)

Table 8-6. (continued)

Sample type (definition; specifications)	Objective	Recommended frequency of analysis[a]	Recommended control limits[b]	Recommended corrective action
Matrix spikes (composite tissue homogenates of field samples to which known amounts of target analytes have been added; 0.5 to 5 times the concentration of the analyte of interest or 5 times the MQL)	Assess matrix effects and accuracy (%R) routinely.	One per 20 samples or one per batch, whichever is more frequent.	*Organics:* %R ≥50 with good precision. *Metals:* %R = 75-125.	Determine cause of problem (e.g., incomplete extraction or digestion, contamination), take appropriate corrective action, and reanalyze all suspect samples or flag all suspect data. Zero percent recovery requires rejection of all suspect data.
Matrix spike replicates (replicate aliquots of matrix spike samples; 0.5 to 5 times the concentration of the analyte of interest or 5 times the MQL)	Assess method precision routinely.	One duplicate per 20 samples or one per batch, whichever is more frequent.	*Organics:* A difference of no more than a factor of 2 among replicates (i.e., approximately 50% coefficient of variation). **Note:** Pooling of variances in duplicate analyses from different sample batches is recommended for estimating the standard deviation or coefficient of variation of replicate analyses. *Metals:* IRPDI ≤20 for duplicates.	Determine cause of problem (e.g., incomplete extraction or digestion, contamination, instrument instability or malfunction), take appropriate corrective action, and reanalyze all suspect samples or flag all suspect data.
Laboratory replicates[e] (replicate aliquots of composite tissue homogenates of field samples)	Assess method precision routinely.	One blind duplicate sample per 20 samples or one per batch, whichever is more frequent.	*Organics:* A difference of no more than a factor of 2 among replicates (i.e., approximately 50% coefficient of variation). **Note:** Pooling of variances in duplicate analyses from different sample batches is recommended for estimating the standard deviation or coefficient of variation of replicate analyses. *Metals:* IRPDI ≤20 for duplicates.	Determine cause of problem (e.g., composite sample not homogeneous, instrument instability or malfunction), take appropriate corrective action, and reanalyze all suspect samples or flag all suspect data.
Analytical Replicates (replicate aliquots of final sample extract or digestate)	Assess analytical precision.	Duplicate injections for all metal analyses.[f]	Determined by program manager.[g]	Determine cause of problem (e.g., instrument instability or malfunction), take appropriate corrective action, and reanalyze sample.

(continued)

Table 8-6. (continued)

Sample type (definition; specifications)	Objective	Recommended frequency of analysis[a]	Recommended control limits[b]	Recommended corrective action
Field replicates (replicate composite tissue samples)	Assess total variability (i.e., population variability, field or sampling variability, and analytical method variability).	*Screening studies*: **OPTIONAL;** if program resources allow, a minimum of one blind replicate (i.e., duplicate) for each primary target species at 10 percent of screening sites.[g]	Determined by program manager.[g]	Determined by program manager.
		Intensive studies: Blind replicate samples for each target species (and size, age or sex class, if appropriate) at each sampling site. Number of replicates determined by program manager (see Section 6.1.2.7).	Determined by program manager.[g]	Determined by program manager.
Contamination Assessment				
Blanks (field, method, processing, bottle, reagent) (see Section 8.3.3.6 for definitions)	Assess contamination from equipment, reagents, etc.	One field blank per sampling site. One method blank per 20 samples or one per batch, whichever is more frequent. At least one processing blank per study. At least one bottle blank per lot or per batch of samples, whichever is more frequent. One reagent blank prior to use of a new batch of reagent and whenever method blank exceeds control limits.	Concentration of any analyte <MDL or MQL, as determined by program manager.	Determine cause of problem (e.g., contaminated reagents, equipment), remove sources of contamination, and reanalyze all suspect samples or flag all suspect data.
Routine Monitoring of Method Performance for Organic Analyses				
Surrogate spikes (see Section 8.3.7.1 for definition)				
Prepared from isotopically labeled target analytes	Assess method performance and estimate recovery of organic target analytes analyzed by GC/MS. Determine RRFs of organic target analytes quantitated by isotope dilution techniques.	In every calibration standard, sample, and blank analyzed for organics by isotope dilution GC/MS; added to samples prior to extraction.	Determined by program manager.	Determine cause of problem (e.g., incomplete extraction or digestion, contamination, inaccurate preparation of internal standard), take appropriate corrective action, and reanalyze all suspect samples or flag all suspect data.

(continued)

Table 8-6. (continued)

Sample type (definition; specifications)	Objective	Recommended frequency of analysis[a]	Recommended control limits[b]	Recommended corrective action
Prepared from other surrogate compounds	Assess method performance and estimate the recovery of organic target analytes analyzed by GC/MS or GC/ECD.	In every calibration standard, sample, and blank analyzed for organics, unless isotope dilution technique is used: *Semivolatiles:* 3 for neutral fraction 2 for acid fraction *Volatiles:* 3 *Pesticides/PCBs:* 1 Added to samples prior to extraction.	Determined by program manager according to most recent EPA CLP guidelines.[h]	Determine cause of problem (e.g., incomplete extraction or digestion, contamination, inaccurate preparation of surrogates), take appropriate corrective action, and reanalyze all suspect samples or flag all suspect data.
External QA Assessment				
Accuracy-based performance evaluation samples (QA samples from NOAA interlaboratory comparison program; see Section 8.3.3.8.1)	Initial demonstration of laboratory capability.	Once prior to routine analysis of field samples (blind).	*Organics:* %R=70-130.[d] *Metals:* %R=85-115.[d]	Determine cause of problem and reanalyze sample. Do not begin analysis of field samples until performance evaluation sample results are acceptable.
	Ongoing demonstration of laboratory capability.	One exercise (four to six samples) per year (blind).	Determined by NOAA. Based on consensus value of all participating laboratories.	Determine cause of problem. Do not continue analysis of field samples until laboratory capability is clearly demonstrated.

(continued)

Table 8-6. (continued)

Sample type (definition; specifications)	Objective	Recommended frequency of analysis[a]	Recommended control limits[b]	Recommended corrective action
Split samples (laboratory replicates analyzed by different laboratories; see Section 8.3.3.8.2)	Assess interlaboratory comparability.	5-10% of composite homogenates split between states and/or Regions that routinely share monitoring results, or as determined by program managers.[g]	Determined by program managers.	Review sampling and analytical methods. Identify sources of noncomparability. Standardize and validate methods to document comparability.

CLP = Contract laboratory program.
CRM = Certified reference material (see Section 8.3.3.1).
GC/ECD = Gas chromatography/electron capture detection.
GC/MS = Gas chromatography/mass spectrometry.
MDL = Method detection limit (see Section 8.3.3.1).
MQL = Method quantitation limit (see Section 8.3.3.2).

NA = Not applicable.
NOAA = National Oceanic and Atmospheric Administration.
PCBs = Polychlorinated biphenyls.
QA = Quality assurance.
%R = Percent recovery (see Sections 8.3.3.4 and 8.3.3.7.1).
RF = Response factor (see Section 8.3.3.2.1).

RPD = Relative percent difference (see Section 8.3.3.5).
RRF = Relative response factor (see Section 8.3.3.2.1).
RSD = Relative standard deviation (see Section 8.3.3.5).
SRM = Standard reference material (see Section 8.3.3.1).

a Recommended frequencies are based primarily on recommendations in U.S. EPA (1986d, 1987e, 1989c, 1991b, 1991c), Puget Sound Estuary Program (1990d, 1990e), and Battelle (1989b).
b From Puget Sound Estuary Program (1990d, 1990e) action limits, except where otherwise noted. **Note:** Individual programs may require more stringent control limits. It is the responsibility of each program manager to set control limits that will ensure that the measurement data meet program data quality objectives.
c As available (see Table 8-8 and Appendix M).
d From U.S.EPA (1991e).
e Sometimes referred to as analytical replicates (e.g., in Puget Sound Estuary Program, 1990d).
f From U.S. EPA (1987e).
g Recommended by EPA for this guidance document.
h From U.S. EPA (1991b, 1991c).

(continued)

**Table 8-7. Minimum Recommended QA and QC Samples for
Routine Analysis of Target Analytes[a]**

Sample Type	Target analyte	
	Metals	Organics
Accuracy-based performance evaluation sample[b]	Once prior to routine analysis of field samples, plus one exercise (four to six samples) per year.	Once prior to routine analysis of field samples, plus one exercise (four to six samples) per year.
Method blank	1	1
Laboratory duplicate	1	1
Matrix spike/matrix spike replicate	1	1
Laboratory control sample (SRM or CRM, if available)	1	1
Calibration check standard	2[c]	2[c]
Surrogate spike (isotopically labeled target analyte or other surrogate compound added prior to extraction)	NA	Each sample
Instrument (injection) internal standard; added prior to injection	NA	Each calibration or calibration check standard and each sample or blank analyzed by GC/MS[d]

CRM   = Certified reference material (see Section 8.3.3.1).
GC/MS = Gas chromatography/mass spectroscopy.
NA   = Not applicable.

QA   = Quality assurance.
QC   = Quality control.
SRM = Standard reference material (see Section 8.3.3.1).

[a] Unless otherwise specified, the number given is the recommended number of QC samples per 20 samples or per batch, whichever is more frequent. Additional method-specific QC requirements should always be followed provided these minimum requirements have been met.

[b] QA samples from National Oceanic and Atmospheric Administration interlaboratory comparison program (see Section 8.3.3.8.1).

[c] One every 10 samples (plus one at beginning and end of each analytical run).

[d] Optional for analyses by GC/electron capture detection (ECD), GC/flame ionization detection (FID), or GC with other nonspecific detectors.

8.3.3.1 Reference Materials—

The appropriate use of reference materials is an essential part of good QA and QC practices for analytical chemistry. The following definitions of reference materials (Puget Sound Estuary Program, 1990d) are used in this guidance document:

- A **reference material** is any material or substance of which one or more properties have been sufficiently well established to allow its use for instrument calibration, method evaluation, or characterization of other materials.

- A **certified reference material (CRM)** is a reference material of which the value(s) of one or more properties has (have) been certified by a variety of technically valid procedures. CRMs are accompanied by or traceable to a certificate or other documentation that is issued by the certifying organization (e.g., U.S. EPA, NIST, National Research Council of Canada [NRCC]).

- A **standard reference material (SRM)** is a CRM issued by the NIST.

Reference materials may be used to (1) provide information on method accuracy and, when analyzed in replicate, on precision, and (2) obtain estimates of intermethod and/or interlaboratory comparability. An excellent discussion of the use of reference materials in QA and QC procedures is given in Taylor (1985). The following general guidelines should be followed to ensure proper use of reference materials (NOAA, 1992):

- When used to assess the accuracy of an analytical method, the matrix of the reference material should be as similar as possible to that of the samples of interest. If reference materials in matrices other than fish or shellfish tissue are used, possible matrix effects should be addressed in the final data analysis or interpretation.

- Concentrations of reference materials should cover the range of possible concentrations in the samples of interest. **Note:** Because of a lack of low- and high-concentration reference materials for most analytes in fish and shellfish tissue matrices, potential problems at low or high concentrations often cannot be documented.

- Reference materials should be analyzed prior to beginning the analyses of field samples to assess laboratory capability and regularly thereafter to detect and document any changes in laboratory performance over time. Appropriate corrective action should be taken whenever changes are observed outside specified performance limits (e.g., accuracy, precision).

- If possible, reference material samples should be introduced into the sample stream as double blinds, that is, with identity and concentration unknown to the analyst. However, because of the limited number of certified fish and

shellfish tissue reference materials available, the results of analyses of these materials may be biased by an analyst's increasing ability to recognize these materials with increased use.

• Results of reference material analyses are essential to assess interlaboratory or intermethod comparability. However, the results of sample analyses should not be corrected based on percent recoveries of reference materials. Final reported results should include both uncorrected sample results and percent recoveries of reference materials.

Sources of reference materials for the analysis of priority pollutants and selected related compounds in fish and shellfish tissues are given in Appendix M. Available marine or estuarine tissue reference materials that may be appropriate for use by analytical laboratories in fish and shellfish contaminant monitoring programs are given in Table 8-8.

8.3.3.2 Calibration and Calibration Checks—

General guidelines for initial calibration and routine calibration checks are provided in this section. Method-specific calibration procedures are included in the references in Table 8-2. It is the responsibility of each program manager to ensure that proper calibration procedures are developed and followed for each analytical method to ensure the accuracy of the measurement data.

All analytical instruments and equipment should be maintained and calibrated properly to ensure optimum operating conditions throughout a measurement program. Calibration and maintenance procedures should be performed according to SOPs based on the manufacturers' specifications and the requirements of specific analytical procedures. Calibration procedures must include provisions for documenting calibration frequencies, conditions, standards, and results to describe adequately the calibration history of each measurement system. Calibration records should be inspected regularly to ensure that these procedures are being performed at the required frequency and according to established SOPs. Any deficiencies in the records or deviations from established procedures should be documented and appropriate corrective action taken.

Calibration standards of known and documented accuracy must be used to ensure the accuracy of the analytical data. Each laboratory should have a program for verifying the accuracy and traceability of calibration standards against the highest quality standards available. If possible, NIST-SRMs or other certified reference standards should be used for calibration standards (see Section 8.3.3.4 and Appendix M). A log of all calibration materials and standard solutions should be maintained. Appropriate storage conditions (i.e., container specifications, shelf-life, temperature, humidity, light condition) should be documented and maintained.

Table 8-8. Fish and Shellfish Tissue Reference Materials

Identification code	Analytes	Source	Matrix
DOLT-1	Elements	NRCC	Dogfish liver (freeze-dried)
DORM-1	Elements	NRCC	Dogfish muscle (freeze-dried)
LUTS-1	Elements	NRCC	Non-defatted lobster hepatopancreas
TORT-1	Elements	NRCC	Lobster hepatopancreas
GBW-08571	Elements	NRCCRM	Mussel tissue (freeze-dried)
GBW-08572	Elements	NRCCRM	Prawn tissue
MA-A-1/OC	Organic compounds	IAEA	Copepod homogenate (freeze-dried)
MA-A-3/OC	Organic compounds	IAEA	Shrimp homogenate (freeze-dried)
MA-B-3/OC	Organic compounds	IAEA	Fish tissue (freeze-dried)
MA-M-2/OC	Organic compounds	IAEA	Mussel tissue
MA-A-1/TM	Elements	IAEA	Copepod homogenate (freeze-dried)
MA-A-2/TM	Elements	IAEA	Fish flesh homogenate
MA-B-3/TM	Elements	IAEA	Fish tissue (freeze-dried)
MA-B-3/RN	Isotopes	IAEA	Fish tissue (freeze-dried)
IAEA-350	Elements	IAEA	Tuna homogenate (freeze-dried)
IAEA-351	Organic compounds	IAEA	Tuna homogenate (freeze-dried)
IAEA-352	Isotopes	IAEA	Tuna homogenate (freeze-dried)
CRM-278	Elements	BCR	Mussel tissue (freeze-dried)
CRM-422	Elements	BCR	Cod muscle (freeze-dried)
EPA-FISH	Pesticides	EPA1	Fish tissue
EPA-SRS903	Chlordane	EPA2	Fish tissue
EPA-0952	Mercury	EPA1	Fish tissue
EPA-2165	Mercury	EPA1	Fish tissue
RM-50	Elements	NIST	Albacore tuna (freeze-dried)
SRM-1566a	Elements	NIST	Oyster tissue (freeze-dried)
SRM-1974	Organic compounds	NIST	Mussel tissue (frozen)
SRM-2974	Organic compounds	NIST	Mussel tissue (freeze-dried)
NIES-6	Elements	NIES	Mussel tissue

Sources:

BCR = Community Bureau of Reference, Commission of the European Communities, Directorate General for Science, Research and Development, 200 rue de la Loi, B-1049 Brussels, Belgium.
EPA = U.S. Environmental Protection Agency, Quality Assurance Branch, EMSL-Cincinnati, Cincinnati, OH, 45268, USA. (EPA1: Material available from Supelco, Inc., Supelco Park, Bellefonte, PA, 16823-0048, USA. EPA2: Material available from Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219.)
IAEA = International Atomic Energy Agency, Analytical Quality Control Service, Laboratory Seibersdorf, P. O. Box 100, A-1400 Vienna, Austria.
NRCCRM = National Research Center for CRMs, Office of CRMs, No. 7, District 11, Hepingjie, Chaoyangqu, Beijing, 100013, China.
NRCC = National Research Council of Canada, Institute for Environmental Chemistry, Marine Analytical Chemistry Standards Program, Division of Chemistry, Montreal Road, Ottawa, Ontario K1A 0R9, Canada.
NIST = National Institute of Standards and Technology, Office of Standard Reference Materials, Gaithersburg, MD, 20899, USA.
NIES = National Institute for Environmental Studies, Yatabe-machi, Tsukuba, Ibaraki, 305, Japan.

8.3.3.2.1   Initial and routine calibration

Prior to beginning routine analyses of samples, a minimum of three (and preferably five) calibration standards should be used to construct a calibration curve for each target analyte, covering the normal working range of the instrument or the expected target analyte concentration range of the samples to be analyzed. The lowest-concentration calibration standard should be at or near the estimated method detection limit (see Section 8.3.3.3.1). Calibration standards should be prepared in the same matrix (i.e., solvent) as the final sample extract or digestate. Criteria for acceptable calibration (e.g., acceptable limits for r^2, slope, intercept, percent recovery, response factors) should be established for each analytical method. If these control limits are exceeded, the source of the problem (e.g., inaccurate standards, instrument instability or malfunction) should be identified and appropriate corrective action taken. No analyses should be performed until acceptable calibration has been achieved and documented.

In addition to the initial calibration, an established schedule for the routine calibration and maintenance of analytical instruments should be followed, based on manufacturers' specifications, historical data, and specific procedural require-ments. At a minimum, calibration should be performed each time an instrument is set up for analysis, after any major disruption or failure, after any major maintenance, and whenever a calibration check exceeds the recommended control limits (see Table 8-6).

Two types of calibration procedures are used in the analytical methods recom-mended for the quantitation of target analytes: external calibration and internal standard calibration.

External calibration

In external calibration, calibration standards with known concentrations of target analytes are analyzed, independent of samples, to establish the relationship between instrument response and target analyte concentration.   External calibration is used for the analyses of metals and, at the option of the program manager, for the analyses of organics by gas chromatography/electron capture detection (GC/ECD), gas chromatography/flame ionization detection (GC/FID), or GC methods using other nonspecific detectors.

External calibration for metals analysis is considered acceptable if the percent recovery of all calibration standards is between 95 and 105 percent; external calibration for organic analyses is considered acceptable if the relative standard deviation (RSD) of the response factors (RFs) is $\leq$20 percent (see Table 8-6). If these limits are exceeded, the initial calibration should be repeated.

Internal standard calibration

Calibration of GC/mass spectrometry (MS) systems used for the analysis of organic target analytes requires the addition of an **internal standard** to each calibration standard and determination of the response of the target analyte of interest relative to that of the internal standard. Internal standard calibration may also be used with nonspecific detector GC methods such as GC/ECD and GC/FID. Internal standards used to determine the relative response factors (RRFs) are termed instrument or injection internal standards (Puget Sound Estuary Program, 1990d; U.S. EPA, 1991e). The addition of instrument internal standards to both calibration standards and sample extracts ensures rigorous quantitation, particularly accounting for shifts in retention times of target analytes in complex sample extracts relative to calibration standards. Recommended instrument internal standards for semivolatile organic compounds are included in analytical methods for these compounds (see references in Table 8-2).

The RRF for each target analyte is calculated for each calibration standard as follows:

$$RRF_t = (A_t) (C_{is}) / (A_{is}) (C_t) \tag{8-1}$$

where

A_t = Measured response (integrated peak area) for the target analyte

C_{is} = Concentration of the instrument internal standard in the calibration standard

A_{is} = Measured response (integrated peak area) for the instrument internal standard

C_t = Concentration of the target analyte in the calibration standard.

If the RSD of the average RRF_t for all calibration standards ($\overline{RRF_t}$) is ≤30 percent, $\underline{RRF_t}$ can be assumed to be constant across the working calibration range and $\overline{RRF_t}$ can be used to quantitate target analyte concentrations in the samples as follows:

$$C_t \text{ (ppm or ppb, wet weight)} = (A_t) (C_{is}) (V_e) / (A_{is}) (\overline{RRF_t}) (W) \tag{8-2}$$

where

C_t = Concentration of the target analyte in the sample

C_{is} = Concentration of the instrument internal standard in the sample extract

V_e = Volume of the final sample extract (mL)

W = Weight of sample extracted (g)

and A_t, A_{is}, and $\overline{RRF}_t$ are defined as in Equation (8-1).

If the RSD of $\overline{RRF}_t$ for all calibration standards is >30 percent, the initial calibration should be repeated (see Table 8-6).

8.3.3.2.2   Routine calibration checks

After initial calibration has been achieved and prior to the routine analyses of samples, the accuracy of the calibration should be verified by the analysis of a calibration check standard. A **calibration check standard** is a mid-range calibration standard that has been prepared independently (i.e., using a different stock) from the initial calibration standards. When internal standard calibration is being used, an instrument internal standard must be added to each calibration check standard.

Routine calibration checks should be conducted often enough throughout each analysis run to ensure adequate maintenance of instrument calibration (see Table 8-6). A calibration check should always be performed after analyzing the last sample in a batch and at the end of each analysis run.

If a calibration check does not fall within specified calibration control limits, the source of the problem should be determined and appropriate corrective action taken (see Table 8-6). After acceptable calibration has been reestablished, all suspect analyses should be repeated. If resources permit, it is recommended that all samples after the last acceptable calibration check be reanalyzed. Otherwise, the last sample analyzed before the unacceptable calibration check should be reanalyzed first and reanalysis of samples should continue in reverse order until the difference between the reanalysis and initial results is within the control limits specified in Table 8-6. If reanalysis is not possible, all suspect data (i.e., since the last acceptable calibration check) should be identified clearly in the laboratory records and the data report.

8.3.3.2.3   Calibration range and data reporting

As noted in Section 8.3.2.1, the lowest-concentration calibration standard should be at or near the method detection limit. The highest-concentration calibration standard should be selected to cover the full range of expected concentrations of the target analyte in fish and shellfish tissue samples. If a sample concentration occurs outside the calibration range, the sample should be diluted or concentrated as appropriate and reanalyzed or the calibration range should be extended. Extremely high concentrations of organic compounds may indicate that the extraction capabilities of the method have been saturated and extraction of a smaller sample or modification of the extraction procedure may be required.

All reported concentrations must be within the upper limit of the demonstrated working calibration range. Procedures for reporting data, with appropriate

qualifications for data below method detection and quantitation limits, are given in Section 8.3.3.3.3.

8.3.3.3   Assessment of Detection and Quantitation Limits—

It is the responsibility of each laboratory to determine appropriate detection and quantitation limits for each analytical method for each target analyte in a fish or shellfish tissue matrix. When available scientific literature demonstrates that the selected SVs are analytically attainable, the laboratory is responsible for ensuring that these limits are sufficiently low to allow reliable quantitation of the analyte at or below the selected SVs (see Section 5.2). Detection and quantitation limits must be determined prior to the use of any method for routine analyses and after any significant changes are made to a method during routine analyses. Several factors influence achievable detection and quantitation limits regardless of the specific analytical procedure. These include amount of sample available, matrix interferences, and stability of the instrumentation. The limits of detection given in Table 8-4 are considered to be representative of typically attainable values. Depending upon individual laboratory capabilities and fish tissue matrix properties, it should be noted that SVs for some recommended target analytes (e.g., inorganic arsenic, dieldrin, heptachlor epoxide, toxaphene, PCBs, and dioxins/ furans) may not always be analytically attainable quantitation limits. In these instances, all historic and current data on contaminant sources and on water, sediment, and fish and shellfish contaminant tissue data should be reviewed to provide additional information that could aid in the risk assessment process and in making risk management decisions.

The EPA has previously issued guidance on detection limits for trace metal and organic compounds for analytical methods used in chemical contaminant monitoring programs (U.S. EPA, 1985a). However, at present there is no clear consensus among analytical chemists on a standard procedure for determining and reporting the limits of detection and quantitation of analytical procedures. Furthermore, detection and quantitation limits reported in the literature are seldom clearly defined. Reported detection limits may be based on instrument sensitivity or determined from the analyses of method blanks or low-level matrix spikes; quantitation limits may be determined from the analyses of method blanks or low-level matrix spikes (Puget Sound Estuary Program, 1990d).

8.3.3.3.1   Detection limits

The EPA recommends that the method detection limit (MDL) defined below and determined according to 40 CFR 136, Appendix B, be used to establish the limits of detection for the analytical methods used for analyses of all target analytes:

•   **Method Detection Limit**: The minimum concentration of an analyte in a given matrix (i.e., fish or shellfish tissue homogenates for the purposes of this guidance) that can be measured and reported with 99 percent confidence that the concentration is greater than zero. The MDL is determined by multiplying

the appropriate (i.e., n-1 degrees of freedom) one-sided 99 percent Student's t-statistic **($t_{0.99}$)** by the standard deviation **(S)** obtained from a minimum of seven replicate analyses of a **spiked matrix sample** containing the analyte of interest at a concentration three to five times the estimated MDL (Glaser et al., 1981; 40 CFR 136, Appendix B):

$$MDL = (t_{0.99})\ (S). \tag{8-3}$$

It is important to emphasize that all sample processing steps of the analytical method (e.g., digestion, extraction, cleanup) must be included in the determination of the MDL.

In addition to the MDL, three other types of detection limits have been defined by the American Chemical Society Committee on Environmental Improvement (Keith, 1991a):

• **Instrument Detection Limit (IDL)**: The smallest signal above background noise that an instrument can detect reliably.

• **Limit of Detection (LOD)**: The lowest concentration that can be determined to be statistically different from a method blank at a specified level of confidence. The recommended value for the LOD is three times the standard deviation of the blank in replicate analyses, corresponding to a 99 percent confidence level.

• **Reliable Detection Limit (RDL):** The concentration level of an analyte in a given matrix at which a detection decision is extremely likely. The RDL is generally set higher than the MDL. When RDL=MDL, the risk of a false positive at 3σ from zero is <1 percent, whereas the corresponding risk of a false negative is 50 percent. When RDL=2MDL, the risk of either a false positive or a false negative at 3σ from zero is <1 percent.

Each of these estimates has its practical limitations. The IDL does not account for possible blank contaminants or matrix interferences. The LOD accounts for blank contaminants but not for matrix effects or interferences. In some instances, the relatively high value of the MDL or RDL may be too stringent and result in the rejection of valid data; however, these are the only detection limit estimates that account for matrix effects and interferences and provide a high level of statistical confidence in sample results. The MDL is the recommended detection limit in the EPA EMAP-NC Program (U.S. EPA, 1991e).

The MDL, expressed as the concentration of target analyte in fish tissue, is calculated from the measured MDL of the target analyte in the sample extract or digestate according to the following equation:

$$MDL_{tissue}\ (ppm\ or\ ppb) = (MDL_{extract} \bullet V)\ /W \tag{8-4}$$

where

V = Final extract or digestate volume, after dilution or concentration (mL)
W = Weight of sample digested or extracted (g).

Equation 8-4 clearly illustrates that the MDL in tissue may be improved (reduced) by increasing the sample weight (W) and/or decreasing the final extract or digestate volume (V).

The initial MDL is a statistically derived empirical value that may differ in actual samples depending on several factors, including sample size, matrix effects, and percent moisture. Therefore, it is recommended that each laboratory reevaluate annually all MDLs for the analytical methods used for the sample matrices typically encountered (U.S. EPA, 1991e).

Experienced analysts may use their best professional judgment to adjust the measured MDL to a lower "typically achievable" detection limit (Puget Sound Estuary Program, 1990e; U.S. EPA, 1985a) or to derive other estimates of detection limits. For example, EPA recommends the use of lower limits of detection (LLDs) for GG/MS methods used to analyze organic pollutants in bioaccumulation monitoring programs (U.S. EPA, 1986a). Estimation of the LLD for a given analyte involves determining the noise level in the retention window for the quantitation mass of the analyte for at least three field samples in the sample set being analyzed.   The LLD is then estimated as the concentration corresponding to the signal required to exceed the average noise level observed by at least a factor of 2. Based on the best professional judgment of the analyst, this LLD is applied to samples in the set with comparable or lower interference; samples with significantly higher interferences (i.e., by at least a factor of 2) are assigned correspondingly higher LLDs. LLDs are greater than IDLs but usually are less than the more rigorously defined MDLs. Thus, data quantified between the LLD and the MDL have a lower statistical confidence associated with them than data quantified above the MDL. However, these data are considered valid and useful in assessing low-level environmental contamination.

If estimates of detection limits other than the MDL are developed and used to qualify reported data, they should be clearly defined in the analytical SOPs and in all data reports, and their relationship to the MDL should be clearly described.

8.3.3.3.2   Quantitation limits

In addition to the MDL, a method quantitation limit (MQL), or minimum concentration allowed to be reported at a specified level of confidence without qualifications, should be derived for each analyte. Ideally, MQLs should account for matrix effects and interferences. The MQL can be greater than or equal to the MDL. At present, there is no consistent guidance in the scientific literature for determining MQLs; therefore, it is not possible to provide specific recommendations for determining these limits at this time.

The American Chemical Society Committee on Environmental Improvement (Keith, 1991b; Keith et al., 1983) has defined one type of quantitation limit:

• **Limit of Quantitation (LOQ)**: The concentration above which quantitative results may be obtained with a specified degree of confidence. The recommended value for the LOQ is 10 times the standard deviation of a method blank in replicate analyses, corresponding to an uncertainty of ±30 percent in the measured value ($10\sigma \pm 3\sigma$) at the 99 percent confidence level.

The LOQ is the recommended quantitation limit in the EPA EMAP-NC Program (U.S. EPA, 1991e). However, the LOQ does not account for matrix effects or interferences.

The U.S. EPA (1986d) has defined another type of quantitation limit:

• **Practical Quantitation Limit (PQL):** The lowest concentration that can be reliably reported within specified limits of precision and accuracy under routine laboratory operating conditions.

The Puget Sound Estuary Program (1990d) and the National Dioxin Study (U.S. EPA, 1987d) used a PQL based on the lowest concentration of the initial calibration curve (C, in μg/mL), the amount of sample typically analyzed (W, in g), and the final extract volume (V, in mL) of that method:

$$PQL\ (\mu g\,/\,g[ppm]) = \frac{C\,(\mu g\,/\,mL) \bullet V(mL)}{W\ (g)} \qquad (8\text{-}5)$$

However, this PQL is also applicable only to samples without substantial matrix effects or interferences.

A reliable detection limit (RDL) equal to 2 MDL may also be used as an estimate of the MQL (see Section 8.3.3.3.1). The RDL accounts for matrix effects and provides a high level of statistical confidence in analytical results.

Analysts must use their expertise and professional judgment to determine the best estimate of the MQL for each target analyte. MQLs, including the estimated degree of confidence in analyte concentrations above the quantitation limit, should be clearly defined in the analytical SOPs and in all data reports.

8.3.3.3.3   Use of detection and quantitation limits in reporting data

The analytical laboratory does not have responsibility or authority to censor data. Therefore, all data should be reported with complete documentation of limitations and problems. Method detection and quantitation limits should be used to qualify reported data for each composite sample as follows (Keith, 1991b):

- "Zero" concentration (no observed response) should be reported as not detected (ND) with the MDL noted, e.g., "ND(MDL=X)".

- Concentrations below the MDL should be reported with the qualification that they are below the MDL.

- Concentrations between the MDL and the MQL should be reported with the qualification that they are below the quantitation limit.

- Concentrations at or above the MQL may be reported and used without qualification.

The use of laboratory data for comparing target analyte concentrations to SVs in screening and intensive studies is discussed in Sections 9.1.1 and 9.1.2.

8.3.3.4 Assessment of Method Accuracy—

The accuracy of each analytical method should be assessed and documented for each target analyte of interest, in a fish or shellfish tissue matrix, prior to beginning routine analyses and on a regular basis during routine analyses.

Method accuracy may be assessed by analysis of appropriate reference materials (i.e., SRMs or CRMs prepared from actual contaminated fish or shellfish tissue, see Table 8-8, **laboratory control samples** (i.e., accuracy-based samples consisting of fish and shellfish tissue homogenates spiked with compounds representative of the target analytes of interest), and/or **matrix spikes**. If possible, laboratory control samples should be SRMs or CRMs. **Note:** Only the analysis of fish or shellfish tissue SRMs or CRMs prepared from actual contaminated fish or shellfish tissue allows rigorous assessment of total method accuracy, including the accuracy with which an extraction or digestion procedure isolates the target analyte of interest from actual contaminated fish or shellfish. The analysis of spiked laboratory control samples or matrix spikes provides an assessment of method accuracy including sample handling and analysis procedures but does not allow rigorous assessment of the accuracy or efficiency of extraction or digestion procedures for actual contaminated fish or shellfish. Consequently, these samples should not be used for the primary assessment of total method accuracy unless SRMs or CRMs prepared from actual contaminated fish or shellfish tissue are not available.

The concentrations of target analytes in samples used to assess accuracy should fall within the range of concentrations found in the field samples; however, this may not always be possible for reference materials or laboratory control samples because of the limited number of these samples available in fish and shellfish tissue matrices (see Table 8-8). Matrix spike samples should be prepared using spike concentrations approximately equal to the concentrations found in the unspiked samples. An acceptable range of spike concentrations is 0.5 to 5 times

the expected sample concentrations (U.S. EPA, 1987e). Spikes should always be added to the sample homogenates prior to digestion or extraction.

Accuracy is calculated as percent recovery from the analysis of reference materials, or laboratory control samples, as follows:

$$\% \text{ Recovery} = 100 \ (M/T) \qquad (8\text{-}6)$$

where

M = Measured value of the concentration of target analyte
T = "True" value of the concentration of target analyte.

Accuracy is calculated as percent recovery from the analysis of matrix spike samples as follows:

$$\% \text{ Recovery} = [(M_s - M_u)/T_s] \times 100 \qquad (8\text{-}7)$$

where

M_s = Measured concentration of target analyte in the spiked sample
M_u = Measured concentration of target analyte in the unspiked sample
T_s = "True" concentration of target analyte added to the spiked sample.

When sample concentrations are less than the MDL, the value of one-half the MDL should be used as the concentration of the unspiked sample (M_u) in calculating spike recoveries.

8.3.3.4.1 Initial assessment of method accuracy

As discussed above, method accuracy should be assessed initially by analyzing appropriate SRMs or CRMs that are prepared from actual contaminated fish or shellfish tissue. The number of reference samples required to be analyzed for the initial assessment of method accuracy should be determined by each laboratory for each analytical procedure with concurrence of the program manager. If such SRMs or CRMs are not available, laboratory control samples or matrix spikes may be used for initial assessment of method accuracy.

8.3.3.4.2 Routine assessment of method accuracy

Laboratory control samples and matrix spikes should be analyzed for continuous assessment of accuracy during routine analyses. It is recommended that one laboratory control sample and one matrix spike sample be analyzed with every 20 samples or with each sample batch, whichever is more frequent (Puget Sound Estuary Program, 1990d, 1990e). Ideally, CRMs or SRMs should also be analyzed at this recommended frequency; however, limited availability and cost of these materials may make this impractical.

For organic compounds, isotopically labeled or surrogate recovery standards that must be added to each sample to monitor overall method performance also provide an assessment of method accuracy (see Section 8.3.3.7.1).

Percent recovery values for spiked samples must fall within established control limits (see Table 8-6). If the percent recovery falls outside the control limit, the analyses should be discontinued, appropriate corrective action taken, and, if possible, the samples associated with the spike reanalyzed. If reanalysis is not possible, all suspect data should be clearly identified.

Note: Reported data should not be corrected for percent recoveries. Recovery data should be reported for each sample to facilitate proper evaluation and use of analytical results.

Poor performance on the analysis of reference materials or poor spike recovery may be caused by inadequate mixing of the composite homogenate sample before aliquotting, inconsistent digestion or extraction procedures, matrix interferences, or instrumentation problems. If replicate analyses are acceptable (see Section 8.3.3.5), matrix interferences or loss of target analytes during sample preparation are indicated. To check for loss of target analytes during sample preparation, a step-by-step examination of the procedure using spiked blanks should be conducted. For example, to check for loss of metal target analytes during digestion, a postdigestion spike should be prepared and analyzed and the results compared with those from a predigestion spike. If the results are significantly different, the digestion technique should be modified to obtain acceptable recoveries. If there is no significant difference in the results of pre- and postdigestion spikes, the sample should be diluted by at least a factor of 5 and reanalyzed. If spike recovery is still poor, then the method of standard additions or use of a matrix modifier is indicated (U.S. EPA, 1987e).

8.3.3.5 Assessment of Method Precision—

The precision of each analytical method should be assessed and documented for each target analyte prior to the performance of routine analyses and on a regular basis during routine analysis.

Precision is defined as the agreement among a set of replicate measurements without assumption of knowledge of the true value. Method precision (i.e., total variability due to sample preparation and analysis) is estimated by means of the analyses of duplicate or replicate tissue homogenate samples containing concentrations of the target analyte of interest above the MDL. All samples used for assessment of total method precision must be carried through the complete analytical procedure, including extraction or digestion.

The most commonly used estimates of precision are the relative standard deviation or coefficient of variation (CV) for multiple samples, and the relative percent

difference (RPD) when only two samples are available. These are defined as follows:

$$RSD = CV = 100\ S/\bar{x}_i \tag{8-8}$$

where

      S = Standard deviation of the x_i measurements
      $\bar{x}_i$ = Arithmetic mean of the x_i measurements

and

$$RPD = 100\ \{(x_1 - x_2)/[(x_1 + x_2)/2]\}\ . \tag{8-9}$$

8.3.3.5.1 Initial assessment of method precision

Method precision should be assessed prior to routine sample analyses by analyzing replicate samples of the same reference materials, laboratory control samples, and/or matrix spikes that are used for initial assessment of method accuracy (see Section 8.3.3.4.1). The number of replicates required to be analyzed for the initial assessment of method precision should be determined by each laboratory for each analytical procedure with concurrence of the program manager. Because precision may be concentration-dependent, initial assessments of precision across the estimated working range should be obtained.

8.3.3.5.2 Routine assessment of method precision

Ongoing assessment of method precision during routine analysis should be performed by analyzing replicate aliquots of tissue homogenate samples taken prior to sample extraction or digestion (i.e., **laboratory replicates**) and **matrix spike replicates**. Matrix spike concentrations should approximate unspiked sample concentrations; an acceptable range for spike concentrations is 0.5 to 5 times the sample concentrations (U.S. EPA, 1987e).

For ongoing assessment of method precision, it is recommended that one laboratory duplicate and one matrix spike duplicate be analyzed with every 20 samples or with each sample batch, whichever is more frequent. In addition, it is recommended that a **laboratory control sample** be analyzed at the above frequency to allow an ongoing assessment of method performance, including an estimate of method precision over time. Specific procedures for estimating method precision by laboratory and/or matrix spike duplicates and laboratory control samples are given in ASTM (1983). This reference also includes procedures for estimating method precision from spike recoveries and for testing for significant change in method precision over time.

Precision estimates obtained from the analysis of laboratory duplicates, matrix spike duplicates, and repeated laboratory control sample analyses must fall within

specified control limits (see Table 8-6). If these values fall outside the control limits, the analyses should be discontinued, appropriate corrective action taken, and, if possible, the samples associated with the duplicates reanalyzed. If reanalysis is not possible, all suspect data should be clearly identified.

Unacceptable precision estimates derived from the analysis of duplicate or replicate samples may be caused by inadequate mixing of the sample before aliquotting; inconsistent contamination; inconsistent digestion, extraction, or cleanup procedures; or instrumentation problems (U.S. EPA, 1987e).

8.3.3.5.3 Routine assessment of analytical precision

The analysis of replicate aliquots of final sample extracts or digestates **(analytical replicates)** provides an estimate of analytical precision only; it does not provide an estimate of total method precision. For organic target analytes, analytical replicates may be included at the discretion of the program manager or laboratory supervisor. For the analysis of target metal analytes by graphite furnace atomic absorption spectrophotometry (GFAA) and cold vapor atomic absorption spectrophotometry (CVAA), it is recommended that duplicate injections of each sample be analyzed and the mean concentration be reported. The RPD should be within control limits established by the program manager or laboratory supervisor, or the sample should be reanalyzed (U.S. EPA, 1987e).

8.3.3.5.4 Assessment of overall variability

Estimates of the overall variability of target analyte concentrations in a sample fish or shellfish population and of the sampling and analysis procedures can be obtained by collecting and analyzing **field replicates**. Replicate field samples are optional in screening studies; however, if resources permit, it is recommended that duplicate samples be collected at 10 percent of the screening sites as a minimal QC check. Analysis of replicate field samples provides some degree of variability in that the samples themselves are typically collected and exposed to the same environmental conditions and contaminants. There are many points of potential dissimilarity between samples of the type described here; however, this variability is reduced when well-homogenized composite samples are analyzed. In intensive studies, replicate samples should be collected at each sampling site (see Section 6.1.2.7). Although the primary purpose of replicate field samples in intensive studies is to allow more reliable estimates of the magnitude of contamination, extreme variability in the results of these samples may also indicate that sampling and/or analysis procedures are not adequately controlled.

8.3.3.6 Routine Monitoring of Interferences and Contamination—

Because contamination can be a limiting factor in the reliable quantitation of target contaminants in tissue samples, the recommendations for proper materials and handling and cleaning procedures given in Sections 6.2.2 and 7.2 should be followed carefully to avoid contamination of samples in the field and laboratory.

Many metal contamination problems are due to airborne dust. High zinc blanks may result from airborne dust or galvanized iron, and high chromium and nickel blanks often indicate contamination from stainless steel. Mercury thermometers should not be used in the field because broken thermometers can be a source of significant mercury contamination. In the laboratory, samples to be analyzed for mercury should be isolated from materials and equipment (e.g., polarographs) that are potential sources of mercury contamination. Cigarette smoke is a source of cadmium. Consequently, care should be taken to avoid the presence of cigarette smoke during the collection, handling, processing, and analysis of samples for cadmium. In organic analyses, phthalates, methylene chloride, and toluene are common laboratory contaminants that are often detected in blanks at concentrations above the MDL (U.S. EPA, 1987e).

Cross-contamination between samples should be avoided during all steps of analysis of organic contaminants by GC-based methods. Injection micro-syringes must be cleaned thoroughly between uses. If separate syringes are used for the injection of solutions, possible differences in syringe volumes should be assessed and, if present, corrected for. Particular care should be taken to avoid carryover when high- and low-level samples are analyzed sequentially. Analysis of an appropriate method blank may be required following the analysis of a high-level sample to assess carryover (U.S. EPA, 1987e).

To monitor for interferences and contamination, the following blank samples should be analyzed prior to beginning sample collection and analyses and on a routine basis throughout each study (U.S. EPA, 1987e):

- **Field blanks** are rinsates of empty field sample containers (i.e., aluminum foil packets and plastic bags) that are prepared, shipped, and stored as actual field samples. Field blanks should be analyzed to evaluate field sample packaging materials as sources of contamination. Each rinsate should be collected and the volume recorded. The rinsate should be analyzed for target analytes of interest and the total amount of target analyte in the rinsate recorded. It is recommended that one field blank be analyzed with every 20 samples or with each batch of samples, whichever is more frequent.

- **Processing blanks** are rinsates of utensils and equipment used for dissecting and homogenizing fish and shellfish. Processing blanks should be analyzed, using the procedure described above for field blanks, to evaluate the efficacy of the cleaning procedures used between samples. It is recommended that processing blanks be analyzed at least once at the beginning of a study and preferably once with each batch of 20 or fewer samples.

- **Bottle blanks** are rinsates of empty bottles used to store and ship sample homogenates. Bottle blanks should be collected after the bottles are cleaned prior to use for storage or shipment of homogenates. They should be analyzed, using the procedure described above for field blanks, to evaluate their potential as sources of contamination. It is recommended that one bottle

blank be analyzed for each lot of bottles or with each batch of 20 or fewer samples, whichever is more frequent.

- **Method blanks** are samples of extraction or digestion solvents that are carried through the complete analytical procedure, including extraction or digestion; they are also referred to as **procedural blanks.** Method blanks should be analyzed to evaluate contaminants resulting from the total analytical method (e.g., contaminated glassware, reagents, solvents, column packing materials, processing equipment). It is recommended that one method blank be analyzed with every 20 samples or with each batch of samples, whichever is more frequent.

- **Reagent blanks** are samples of reagents used in the analytical procedure. It is recommended that each lot of analytical reagents be analyzed for target analytes of interest prior to use to prevent a potentially serious source of contamination. For organic analyses, each lot of alumina, silica gel, sodium sulfate, or Florasil used in extract drying and cleanup should also be analyzed for target analyte contamination and cleaned as necessary. Surrogate mixtures used in the analysis of organic target analytes have also been found to contain contaminants and the absence of interfering impurities should be verified prior to use (U.S. EPA, 1987e).

Because the contamination in a blank sample may not always translate into contamination of the tissue samples, analysts and program managers must use their best professional judgment when interpreting blank analysis data. Ideally, there should be no detectable concentration of any target analyte in any blank sample (i.e., the concentration of target analytes in all blanks should be less than the MDL). However, program managers may set higher control limits (e.g., $\leq$MQL) depending on overall data quality requirements of the monitoring program. If the concentration of a target analyte in any blank is greater than the established control limit, all steps in the relevant sample handling, processing, and analysis procedures should be reviewed to identify the source of contamination and appropriate corrective action should be taken. If there is sufficient sample material, all samples associated with the unacceptable blank should be reanalyzed. If reanalysis is not possible, all suspect data should be identified clearly.

Note: Analytical data should not be corrected for blank contamination by the reporting laboratory; however, blank concentrations should always be reported with each associated sample value.

8.3.3.7 Special QA and QC Procedures for the Analysis of Organic Target Analytes—

8.3.3.7.1   Routine monitoring of method performance

To account for losses during sample preparation (i.e., extraction, cleanup) and to monitor overall method performance, a standard compound that has chemical and physical properties as similar as possible to those of the target analyte of interest should be added to each sample prior to extraction and to each calibration standard. Such compounds may be termed **surrogate recovery standards**. A stable, **isotopically labeled analog of the target analyte** is an ideal surrogate recovery standard for GC/MS analysis.

If resources permit, an isotope dilution GC/MS technique such as EPA Method 1625 (40 CFR 136, Appendix A) is recommended for the analysis of organic target analytes for which isotopically labeled analogs are available.   In this technique, RRFs used for quantitation may be calculated from measured isotope ratios in calibration standards and not from instrument internal standards. However, an instrument internal standard still must be added to the final sample extract prior to analysis to determine the percent recoveries of isotopically labeled recovery standards added prior to extraction. Thus, in isotope dilution methods, instrument internal standards may be used only for QC purposes (i.e., to assess the quality of data) and not to quantify analytes. Control limits for the percent recovery of each isotopically labeled recovery standard should be established by the program manager, consistent with program data quality requirements. Control limits for percent recovery and recommended corrective actions given in EPA Method 1625 (40 CFR 136, Appendix A) should be used as guidance.

If isotopically labeled analogs of target analytes are not available or if the isotope dilution technique cannot be used (e.g., for chlorinated pesticides and PCBs analyzed by GC/ECD), other surrogate compounds should be added as recovery standards to each sample prior to extraction and to each calibration standard. These surrogate recovery standards should have chemical and physical properties similar to the target analytes of interest and should not be expected to be present in the original samples. Recommended surrogate recovery standards are included in the methods referenced in Table 8-2 and in EMMI (U.S. EPA, 1991f).

Samples to which surrogate recovery standards have been added are termed **surrogate spikes**. The percent recovery of each surrogate spike (% R_s) should be determined for all samples as follows:

$$\% \ R_s = 100 \ (C_m/C_a) \tag{8-10}$$

where

$\% \ R_s$ = Surrogate spike percent recovery
C_m = Measured concentration of surrogate recovery standard

C_a = Actual concentration of surrogate recovery standard added to the sample.

Control limits for the percent recovery of each surrogate spike should be established by the program manager consistent with program data quality requirements. The control limits in the most recent EPA CLP methods (U.S. EPA, 1991c) are recommended for evaluating surrogate recoveries.

Note: Reported data should not be corrected for percent recoveries of surrogate recovery standards. Recovery data should be reported for each sample to facilitate proper evaluation and use of the analytical results.

8.3.3.7.2 Other performance evaluation procedures

The following additional procedures are required to evaluate the performance of GC-based analytical systems prior to the routine analysis of field samples (U.S. EPA, 1989c; U.S. EPA, 1991c). It is the responsibility of each program manager to determine specific evaluation procedures and control limits appropriate for their data quality requirements.

Evaluation of the GC system

GC system performance should be evaluated by determining the number of theoretical plates of resolution and the relative retention times of the internal standards.

Column Resolution: The number of theoretical plates of resolution, N, should be determined at the time the calibration curve is generated (using chrysene-d_{10}) and monitored with each sample set. The value of N should not decrease by more than 20 percent during an analysis session. The equation for N is given as follows:

$$N = 16 \ (RT/W)^2 \tag{8-11}$$

where

RT = Retention time of chrysene-d_{10} (s)
W = Peak width of chrysene-d_{10} (s).

Relative Retention Time: Relative retention times of the internal standards should not deviate by more than ±3 percent from the values calculated at the time the calibration curve was generated.

If the column resolution or relative retention times are not within the specified control limits, appropriate corrective action (e.g., adjust GC parameters, flush GC column, replace GC column) should be taken.

Evaluation of the MS system

The performance of the mass spectrometer should be evaluated for sensitivity and spectral quality.

Sensitivity: The signal-to-noise value should be at least 3.0 or greater for m/z 198 from an injection of 10 ng decafluorotriphenylphosphine (DFTPP).

Spectral Quality: The intensity of ions in the spectrum of a 50-ng injection of DFTPP should meet the following criteria (U.S. EPA, 1991c):

m/z	Criteria
51	30-80% mass 198
68	<2% mass 69
69	present
70	<2% mass 69
127	25-75% mass 198
197	<1% mass 198
198	base peak, 100% relative abundance
199	5-9% mass 198
275	10-30% mass 198
365	>0.75% mass 198
441	present and <mass 443
442	40-110% mass 198
443	15-24% mass 442

If the control limits for sensitivity or spectral quality are not met, appropriate corrective action (e.g., clean MS, retune MS) should be taken.

Evaluation of cleanup columns

Because the fatty content of many tissue samples may overload the cleanup columns, these columns should be calibrated and monitored regularly to ensure that target analytes are consistently collected in the proper fraction. Gel permeation columns should be monitored by visual inspection (for column discoloration, leaks, cracks, etc.) and by measurement of flow rate, column resolution, collection cycle, and method blanks (see Section 8.3.3.6). Silica gel columns should be evaluated by their ability to resolve cholesterol from a selected target analyte.

8.3.3.8   External QA Assessment of Analytical Performance—

Participation in an external QA program by all analytical laboratories in state fish and shellfish consumption advisory programs is strongly recommended for several reasons:

- To demonstrate laboratory capability prior to conducting routine analyses of field samples

- To provide an independent ongoing assessment of each laboratory's capability to perform the required analyses

- To enhance the comparability of data between states and Regions.

Two types of external QA programs are recommended: **round-robin interlaboratory comparisons** (often referred to as **interlaboratory calibration programs**) and **split-sample interlaboratory comparisons**.

8.3.3.8.1   Round-robin analysis interlaboratory comparison program

At present, the only external round-robin QA program available for analytical laboratories conducting fish and shellfish tissue analyses for environmental pollutants is administered by NOAA in conjunction with its National Status and Trends (NS&T) Program (Cantillo, 1991). This QA program has been designed to ensure proper documentation of sampling and analysis procedures and to evaluate both the individual and collective performance of participating laboratories. Recently, NOAA and EPA have agreed to conduct the NS&T Program and the EMAP-NC Program as a coordinated effort. As a result, EMAP-NC now cosponsors and cooperatively funds the NS&T QA Program, and the interlaboratory comparison exercises include all EMAP-NC laboratories (U.S. EPA, 1991e).

Note: Participation in the NS&T QA program by all laboratories performing chemical analyses for state fish and shellfish contaminant monitoring programs is recommended to enhance the credibility and comparability of analytical data among the various laboratories and programs.

Each laboratory participating in the NS&T QA program is required to demonstrate its analytic capability prior to the analysis of field samples by the blind analysis of a fish and shellfish tissue sample that is uncompromised, homogeneous, and contains the target analytes of interest at concentrations of interest. A laboratory's performance generally will be considered acceptable if its reported results are within ±30 percent (for organics) and ±15 percent (for metals) of the actual or certified concentration of each target analyte in the sample (U.S. EPA, 1991e). If any of the results exceed these control limits, the laboratory will be required to repeat the analysis until all reported results are within the control limits. Routine analysis of field samples will not be allowed until initial demonstration of laboratory capability is acceptable.

Following the initial demonstration of laboratory capability, each participating laboratory is required to participate in one intercomparison exercise per year as a continuing check on performance. This intercomparison exercise includes both organic and inorganic (i.e., trace metals) environmental and standard reference

samples. The organic analytical intercomparison program is coordinated by NIST, and the inorganic analytical intercomparison program is coordinated by the NRCC. Sample types and matrices vary yearly. Performance evaluation samples used in the past have included accuracy-based solutions, sample extracts, and representative matrices (e.g., tissue or sediment samples). Laboratories are required to analyze the performance evaluation samples blind and to submit their results to NIST or NRCC, as instructed. Individual laboratory performance is evaluated against the consensus values (i.e., grand means) of the results reported by all participating laboratories. Laboratories that fail to achieve acceptable performance must take appropriate corrective action. NIST and NRCC will provide technical assistance to participating laboratories that have problems with the intercomparison analyses. At the end of each calendar year, the results of the intercomparison exercises are reviewed at a workshop sponsored by NIST and NRCC. Representatives from each laboratory are encouraged to participate in these workshops, which provide an opportunity for discussion of analytical problems encountered in the intercomparison exercises.

Note: Nonprofit laboratories (e.g., EPA and other federal laboratories, state, municipal, and nonprofit university laboratories) may participate in the NS&T QA program at no cost on a space-available basis. The cost of participation in the NIST Intercomparison Exercise Program for Organic Contaminants in the Marine Environment is $2,500 for private laboratories within and outside the United States. This cost covers samples for one exercise per year. Samples may be obtained directly from NIST by contacting Ms. Michele Shantz, NIST, 100 Bureau Drive, Stop 8392, Gaithersburg, MD 20899-8392; Tel: 301-975-3106, FAX: 301-997-0685. Trace inorganic samples are available directly from NRCC by contacting Mr. Scott Willis, NRCC, Ottawa, Ontario, Canada K1A029, e-mail: scott.willie@NRC.CA, Tel: 613-993-4969.

To obtain additional information about participation in the NS&T QA program, contact Dr. Adriana Cantillo, QA Manager, NOAA/National Status and Trends Program, NYSCI1, 1305 East West Highway, Silver Spring, MD 20910; Tel: 301-713-3028, ext. 147, FAX: 301-713-4388.

8.3.3.8.2   Split sample analysis interlaboratory comparison programs

Another useful external QA procedure for assessing interlaboratory comparability of analytical data is a split-sample analysis program in which a percentage (usually 5 to 10 percent) of all samples analyzed by each state or Region are divided and distributed for analyses among laboratories from other states or Regions. Because actual samples are used in a split-sample analysis program, the results of the split-sample analyses provide a more direct assessment of the comparability of the reported results from different states or Regions.

The NS&T QA program does not include an interlaboratory split-sample analysis program. However, it is recommended that split-sample analysis programs be established by states and/or Regions that routinely share results.

8.4 Documentation and Reporting of Data

The results of all chemical analyses must be documented adequately and reported properly to ensure the correct evaluation and interpretation of the data.

8.4.1 Analytical Data Reports

The documentation of analytical data for each sample should include, at a minimum, the following information:

- Study identification (e.g., project number, title, phase)

- Description of the procedure used, including documentation and justification of any deviations from the standard procedure

- Method detection and quantitation limits for each target analyte

- Method accuracy and precision for each target analyte

- Discussion of any analytical problems and corrective action taken

- Sample identification number

- Sample weight (wet weight)

- Final dilution volume/extract volume

- Date(s) of analysis

- Identification of analyst

- Identification of instrument used (manufacturer, model number, serial number, location)

- Summary calibration data, including identification of calibration materials, dates of calibration and calibration checks, and calibration range(s); for GC/MS analyses, include DFTPP spectra and quantitation report

- Reconstructed ion chromatograms for each sample analyzed by GC/MS

- Mass spectra of detected target compounds for each sample analyzed by GC/MS

- Chromatograms for each sample analyzed by GC/ECD and/or GC/FID

- Raw data quantitation reports for each sample

- Description of all QC samples associated with each sample (e.g., reference materials, field blanks, rinsate blanks, method blanks, duplicate or replicate samples, spiked samples, laboratory control samples) and results of all QC analyses. QC reports should include quantitation of all target analytes in each blank, recovery assessments for all spiked samples, and replicate sample summaries. Laboratories should report all surrogate and matrix spike recovery data for each sample; the range of recoveries should be included in any reports using these data.

- Analyte concentrations with reporting units identified (as ppm or ppb wet weight, to two significant figures unless otherwise justified). **Note:** Reported data should not be recovery- or blank-corrected.

- Lipid content (as percent wet weight)

- Specification of all tentatively identified compounds (if requested) and any quantitation data.

- Data qualifications (including qualification codes and their definitions, if applicable, and a summary of data limitations).

To ensure completeness and consistency of reported data, standard forms should be developed and used by each laboratory for recording and reporting data from each analytical method. Standard data forms used in the EPA Contract Laboratory Program (U.S. EPA, 1991b, 1991c) may serve as useful examples for analytical laboratories.

All analytical data should be reviewed thoroughly by the analytical laboratory supervisor and, ideally, by a qualified chemist who is independent of the laboratory. In some cases, the analytical laboratory supervisor may conduct the full data review, with a more limited QA review provided by an independent chemist. The purpose of the data review is to evaluate the data relative to data quality specifications (e.g., detection and quantitation limits, precision, accuracy) and other performance criteria established in the Work/QA Project Plan. In many instances, it may be necessary to qualify reported data values; qualifiers should always be defined clearly in the data report. Recent guidance on the documentation and evaluation of trace metals data collected for Clean Water Act compliance monitoring (U.S. EPA, 1995h) provides additional useful information on data review procedures.

8.4.2   Summary Reports

Summaries of study data should be prepared for each target species at each sampling site. Specific recommendations for reporting data for screening and intensive studies are given in Section 9.2.