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**An Approach for the Analysis of Regulatory Analytes
in High Level Radioactive Waste
Stored at Hanford, Richland, Washington
(PNNL-11942)**

**Pacific Northwest
National Laboratory**

Operated by Battelle for the
U.S. Department of Energy

**An Approach for the Analysis of
Regulatory Analytes in High Level
Radioactive Waste Stored at Hanford,
Richland, Washington**

K.D. Wiemers
M. Miller
M.E. Lerchen

December 1998

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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Abbreviations and Acronyms

ALARA	as low as reasonably achievable
CC	critical concentration
CFR	<i>Code of Federal Regulations</i>
CICN	cyanogen chloride
CV	coefficient of variation
DOE-RL	U.S. Department of Energy, Richland Operations Office
DQO	Data Quality Objectives
DST	double-shell tank
ECD	electron capture detector
Ecology	Washington State Department of Ecology
EDTA	ethylenediamine tetraacetic acid
EN	ethylenediamine
EPA	U.S. Environmental Protection Agency
EQL	estimated quantitation limits
FR	<i>Federal Register</i>
GC	gas chromatography
HCN	hydrogen cyanide
HASQARD	<i>Hanford Analytical Services Quality Assurance Requirements Documents</i>
HWMA	<i>Hazardous Waste Management Act of 1976</i>
ICP	inductively coupled plasma
LAW	low-activity waste
MDL	method detection limit
MS	mass spectrometry
NaOH	sodium hydroxide
NRC	U.S. Nuclear Regulatory Commission
PAH	polynuclear aromatic hydrocarbons
PCB	polychlorinated biphenyl
PRT	Practical Reporting Time
QA/QC	quality assurance/quality control
RCRA	<i>Resource Conservation and Recovery Act of 1976</i>
RPD	relative percent difference
RSD	relative standard deviation
SOP	standard operating procedures
SST	single-shell tank
SVOA	semivolatile organic analysis
VOA	volatile organic analysis
WAC	<i>Washington Administrative Code</i>

1.0 Introduction

The Hanford Site has 177 underground storage tanks that contain 54 million gallons of high-level radioactive waste. The U.S. Department of Energy (DOE), Washington State Department of Ecology (Ecology), and the U.S. Environmental Protection Agency (EPA) have entered into the Hanford Federal Facility Agreement and Consent Order (Tri-Party Agreement or TPA) under the *Resource Conservation and Recovery Act of 1976* (RCRA) and the *Washington Hazardous Waste Management Act of 1976* (HWMA). Under the RCRA and HWMA, the tank waste is designated as listed, characteristic, and criteria waste. Characterization data are needed for the tank waste to ensure compliant treatment, storage, and disposal of the waste, including requirements for meeting land disposal restrictions, delisting, and risk assessment. The DOE and Ecology through the Regulatory Data Quality Objectives (DQO) process have defined and documented (Regulatory DQO, Wiemers et al. 1998) characterization needs for the Hanford Site single-shell tank (SST) and double-shell tank (DST) waste.

The characterization identified in the Regulatory DQO will require the use of regulator approved methods (Wiemers et al. 1998). The U.S. Environmental Protection Agency (EPA) methods have not been demonstrated with Hanford high-level radioactive waste. Due to the radioactivity and complex sample matrix it is likely that the methods will need to be modified (DOE-RL 1994, DOE-EM 1997). Specific limitations may include sample size, holding times, and storage requirements. Ecology and DOE have agreed to an approach for providing the technical basis required for selection and validation of modified methods. A description of the approach and guidelines for implementation of the approach are provided in this document. Section 2.0 addresses options for method selection. The method modification process is outlined in Section 3.0. Suggested methods and target performance criteria are identified in Sections 4.0 and 5.0, respectively. The sample holding time and storage condition study is described in Section 6.0. Generic quality assurance/quality control requirements are provided in Section 7.0.

2.0 Methods Selection Options Under SW-846

2.1 Regulatory Requirement

Perform waste characterization using SW-846 methods or other regulator approved methods (generically referred to as SW-846 methods hereafter).

2.2 Problem

SW-846 and other regulator approved methods are not written for radioactive waste. Validated modified or alternative equivalent testing or analytical methods may be needed.

2.3 Background

The analysis for regulated hazardous constituents known or potentially in the tank waste presents a series of technical problems that must be resolved to provide defensible analytical data. The regulations require that SW-846 or other approved analytical methods be used to characterize waste. The SW-846 methods were not written for radioactive waste matrices where special handling is required to prevent worker exposure to radiation. In addition, the tank waste components may create matrix or interference problems not addressed in SW-846 methods.

Under the Regulatory DQO, SW-846 methods were assigned to individual compounds of interest either because the method is specific to that compound or because the compound could possibly be analyzed by that method. This approach is intended to provide an evaluation of the viability and validation of test methods for the Regulatory DQO's requested analyte list as well as to provide data for optimizing the requested method set. It is anticipated that method assignment and implementation will be further optimized and otherwise refined through the development and acceptance of the test plans and associated documentation in the overall Regulatory DQO implementation.

The nature of the waste matrices and special handling considerations dictate that some method modifications or alternative equivalent testing or analytical methods may be needed. The major issues are

- difficulty in collecting specified sample volume due to handling, limited storage areas in the hot cells, and transportation
- matrix effects due to waste with high-salt concentration and/or high non-regulated organic concentrations or other matrix effects
- method sensitivity (both detection limits and quantitation limits) that are affected by the sample volumes dictated for handling radioactive samples and affected by high-salt concentrations
- meeting appropriate QA/QC requirements and acceptance criteria while maintaining safe work environment
- sample holding times that extend beyond SW-846 criteria
- sample storage conditions unique to radioactive waste with a high-salt concentration that do not meet SW-846 requirements
- radiation protection regulations and the results from as low as reasonably achievable (ALARA) process (refer to Appendix A).

In 1994, DOE-RL published a report addressing many of these issues (DOE-RL 1994). The U.S. Nuclear Regulatory Commission (NRC) and the EPA also issued a joint policy statement on the analysis of mixed wastes in 1997 (*62 Federal Register* [FR] 224). In both cases, the need to modify methods and approaches was recognized to protect worker health and safety. In 1997, the EPA Office of Solid Wastes and Emergency Response issued the third update of SW-846, which added guidance on the use of modified EPA methods to provide technically defensible data in the analysis of unusual samples (EPA 1997). The activities discussed in the following sections are consistent with the recommendations of these guidelines.

Two options are available to resolve differences between SW-846 methods and their respective adaptation to specific sample matrices.

Option 1, Development of New Analytical Methods: Develop new or propose alternate equivalent testing or analytical methods using different extraction and analysis techniques that are not part of SW-846 and that work under Hanford tank waste conditions. Obtain Ecology approval per *Washington Administrative Code* (WAC) 173-303-110 by submitting a petition per WAC 173-303-910(2), followed by public review of the petition and comment resolution.

The following tasks are typically required:

- An alternative method is either selected from non-SW-846, technical iteration, or developed using as much existing off-the-shelf equipment as possible.
- New extraction techniques may be part of a new method.
- Standards and samples are analyzed in parallel with an established methodology, so a comparison of data can be performed.
- After the new method is validated, performance standards and actual samples are analyzed to establish baseline data and to establish statistical criteria for QC parameters.
- New methods which are successful in one laboratory could be tested in multiple laboratories with multiple operators. A statistical plan to allow comparison of the methods across laboratories could be developed to evaluate the ruggedness of the method.
- With appropriate support documentation, the new method can be proposed to a regulatory agency for approval. The approval process usually involves public review of the petition and comment resolutions. If needed, additional data may be required.

Option 2, Modify Existing SW-846 Methods: Use existing SW-846 methods with a performance-based approach. The performance basis is to meet target estimated quantitation limits (EQLs), accuracy/bias and precision requirements in SW-846, and provide supporting documentation. This will allow regulators to assess whether modifications are substantial. If the modifications are not substantial, a petition and public review may not be required, but validation is still required to meet SW-846 requirements.

This option examines existing SW-846 analytical methods and establishes which test method conditions need to be modified to address the sample matrix and safety issues. The modifications allow Hanford tank waste to be analyzed using SW-846 analytical approaches and techniques modified for the tank matrices and radioactivity levels. Because this approach retains many of the same steps of established methods, the validation process is much less extensive than the approach required to establish new methods, discussed in Option 1. Fewer modifications should also require less review and technical discussion than new methods.

2.4 Preferred Option

DOE and Ecology have selected Option 2, "Modify Existing SW-846 Methods," for the initial tank waste evaluation. After comparing the projected EQLs of the modified SW-846 methods to the EQLs in SW-846 for waste, it was determined that for most of the Regulatory DQO high priority analytes, the EQLs are likely to be achievable with minor method modifications. Therefore, the SW-846 methods with target EQLs and quality control are the recommended goal.

3.0 Method Modification Process Outline

An approach agreed to by Ecology and DOE to provide a technical basis for modification of an existing SW-846 method or selection of alternative equivalent testing or analytical methods consistent with the SW-846 for tank waste is outlined below. The method validation will consist of three activities: (1) verify the ability of the performing laboratory(ies) to meet the SW-846 minimum detection limit (MDL) for the required method(s), (2) establish the estimated quantitation limits (EQL) and quality control (QC) using liquid and sludge tank waste samples, and (3) conduct the Holding Time and Storage Conditions study. A logic flowchart for the approach is provided in Figure 1.

1. Performing laboratory(ies) prepares a detailed test plan for MDL, EQL, and QC measurements. The plan will be reviewed and approved by DOE and Ecology.
2. Performing laboratory(ies) demonstrates the ability to achieve the MDL for the required SW-846 methods in accordance with Hanford Analytical Services Quality Assurance Requirements Documents (HASQARD) (DOE 1997). The MDLs are to be met for both liquid and solid standards.
3. If MDLs are met, the performing laboratory(ies) demonstrates the ability to achieve target EQLs and QC in both a liquid and a solid (sludge) tank waste matrix. The waste samples are to be supernate tank waste with a high concentration of organic constituents relative to other tank waste and solid (sludge) phase high-level tank waste. Target EQLs and QC for solids are to be in the range given for the SW-846 method low-concentration soil and high-concentration soil and sludges, or equivalent. Target EQLs and QC for liquid waste matrices have not been agreed to by Ecology and DOE and will be addressed during review/approval of the test plan. For single analytes with no EQLs listed in a specific SW-846 method, no special target EQL is required provided the analytes with EQL criteria for that method meet the target EQL criteria for that method as specified in SW-846.
4. Performing laboratory(ies) reports results including information as detailed under WAC 173-303-910, Petitions, and the HASQARD (DOE 1997, Volume 4, Section 5). Changes (substitutions, deviations) relative to the standard SW-846 procedure and the reason for the changes are to be documented and included in the report. Limiting the information reported is not desirable because it will be required in the event a petition is necessary and will not otherwise be available.
5. DOE and Ecology review results with performing laboratory(ies).

Figure 1. Implementation Logic for Methods Validation and Holding Time and Storage Conditions Study in Support of the Regulatory Data Quality Objectives.

(a) Document regulatory agency approval of method(s) per WAC 173-303-110 and WAC 173-303-910, as applicable.

6. If MDL, EQL, and QC results are acceptable, performing laboratory(ies) prepares a detailed test plan for Holding Time and Storage Conditions study. The study is to be conducted based on the method described by Maskarinec and Bayne (1996). DOE and Ecology will review and approve the test plan.
7. Performing laboratory(ies) conducts Holding Time and Storage Conditions study on both liquid and solid (sludge) tank waste matrices. The waste samples are to be supernate from tank waste with a high concentration of organic constituents relative to other tank waste and solid (sludge) phase from a high-level tank waste. The waste samples are to be from the same source tank(s) as used for the EQL and QC demonstration (Step 3), unless otherwise agreed to in writing by DOE and Ecology.
8. Performing laboratory(ies) prepares technical report summarizing the Holding Time and Storage Conditions study results. DOE and Ecology review report.

The validation steps are to be conducted in accordance with WAC 173-303-110 and consistent with the Hanford Analytical Services Quality Assurance Requirements (HASQARD) (DOE 1997, Volume 4, Section 5).

This approach will result in the information necessary to select and validate methods to support the Regulatory DQO for the performing laboratory(ies) per EPA protocol. The approach incorporates a number of checkpoints for the purpose of review by DOE and Ecology. DOE and Ecology will use these results in refining the selected methods, high priority analyte list, and identification of additional tank waste to characterize. As available, data needs identified during the treatment facility permitting process and activities associated with the Land Disposal Restriction Requirements and Delisting will also be used as input to the refinement process.

4.0 Suggested Methods

The Regulatory DQO high priority analytes and suggested target methods are identified in Table 1 and Table 2 for organic and inorganic constituents, respectively. Any SW-846 preparation and analysis method may be used that allows the analyst to fulfill the target EQLs accuracy and precision requirements. The EQL accuracy and precision requirements are defined in Section 5.0 and Section 7.0, respectively. A summary of the methods and the number of high priority analytes that may be analyzed by each method is provided in Table 3.

The suggested methods (Tables 1 and 2) are identified as "SW-846" and "modified." The method number listed under the heading "SW-846" is based on the actual analyte list in the SW-846 methods. Numbers under the heading "modified" are those methods recommended based on the following logic:

- Analytes that do not have SW-846 methods are assigned an SW-846 method, if in the opinion of the chemist, the analyte may be detected in a similar manner as those already listed in the method.
- Consolidation of the analytes into a small number of methods will decrease sample volume and handling, time to process, and cost. Therefore, in some cases, the preferred SW-846 method is substituted by an alternate SW-846 method which might be modified for the analyte of interest. For example, cyclohexanone is listed in method 8315. Many ketones are analyzed by method 8270C, therefore method 8270C is recommended.

Table 1. Priority Regulated Organic Compounds for Characterization in Support of the Regulatory Data Quality Objective (125 Compounds).
(Page 1 of 3)

CAS #	Constituent	SW-846 Method	Modified Method
100-00-5	p-Nitrochlorobenzene		8270C
100-25-4	1,4-Dinitrobenzene	8270C	
100-41-4	Ethyl benzene	8260B	
100-42-5	Styrene	8260B	
10061-01-5	cis-1,3-Dichloropropene	8260B	
10061-02-6	trans-1,3-Dichloropropene	8260B	
106-35-4	3-Heptanone		8260B
106-42-3	p-Xylene	8260B	
106-46-7	1,4-Dichlorobenzene	8270C	
106-93-4	Ethylene dibromide	8260B	
106-97-8	Butane		8260B
106-99-0	1,3-Butadiene		8260B
107-02-8	Acrolein	8260B	
107-05-1	3-Chloropropene	8260B	
107-06-2	1,2-Dichloroethane	8260B	
107-12-0	Propionitrile	8260B	
107-13-1	Acrylonitrile	8260B	
107-87-9	2-Pentanone	8260B	
108-10-1	4-Methyl-2-pentanone	8260B	
108-38-3	m-Xylene	8260B	
108-87-2	Methylcyclohexane		8260B
108-88-3	Toluene	8260B	
108-90-7	Chlorobenzene	8260B	
108-94-1	Cyclohexanone	8260B	
108-95-2	Phenol	8270C	
109-66-0	n-Pentane		8260B
109-99-9	Tetrahydrofuran		8270C
110-12-3	5-Methyl-2-hexanone		8260B
110-43-0	2-Heptanone		8260B
110-54-3	n-Hexane	8260B	
110-82-7	Cyclohexane		8260B
110-83-8	Cyclohexene		8260B
110-86-1	Pyridine	8270C	
111-65-9	n-Octane		8260B
111-84-2	n-Nonane		8260B
118-74-1	Hexachlorobenzene	8081A	
120-82-1	1,2,4-Trichlorobenzene	8270C	
121-44-8	Triethylamine		8260B
122-39-4	N,N-Diphenylamine	8270C	
123-19-3	4-Heptanone		8260B
123-38-6	n-Propionaldehyde	8260B	
123-86-4	Acetic acid n-butyl ester		8260B
123-91-1	1,4-Dioxane	8260B	
126-73-8	Tributyl phosphate		8270C
126-98-7	2-Methyl-2-propenenitrile	8260B	
127-18-4	1,1,2,2-Tetrachloroethene	8260B	

Table 1. Priority Regulated Organic Compounds for Characterization in Support of the Regulatory Data Quality Objective (125 Compounds).
(Page 2 of 3)

CAS #	Constituent	SW-846 Method	Modified Method
128-37-0	2,6-Bis(tert-butyl)-4-methylphenol		8270C
1321-64-8	Pentachloronaphthalene		8270C
1335-87-1	Hexachloronaphthalene		8270C
1335-88-2	Tetrachloronaphthalene		8270C
1336-36-3	Polychlorinated biphenyls (PCBs)	8082	
141-78-6	Acetic acid ethyl ester	8260B	
142-82-5	n-Heptane		8260B
144-62-7	Oxalic acid		(9056)
2234-13-1	Octachloronaphthalene	8081A	
287-92-3	Cyclopentane		8270C
309-00-2	Aldrin	8081A	
319-84-6	alpha-BHC	8081A	
319-85-7	beta-BHC	8081A	
3825-26-1	Ammonium perfluorooctanoate		8330
4170-30-3	2-Butenaldehyde (2-Butenal)	8260B	
465-73-6	Isodrin	8081A	
50-32-8	Benzo(a)pyrene	8270C	
53-70-3	Dibenz[a,h]anthracene	8270C	
541-73-1	1,3-Dichlorobenzene	8270C	
56-23-5	Carbon tetrachloride	8260B	
563-80-4	3-Methyl-2-butanone		8260B
57-14-7	1,1-Dimethylhydrazine		8270C
58-89-9	gamma-BHC (Lindane)	8081A	
591-78-6	2-Hexanone	8260B	
60-34-4	Methylhydrazine		8270C
60-57-1	Dieldrin	8081A	
62-75-9	N-Nitroso-N,N-dimethylamine	8270C	
624-83-9	Methyl isocyanate		8330
627-13-4	Nitric acid, propyl ester		8270C
64-17-5	Ethyl alcohol	8260B	
64-18-6	Formic acid		(9056)
64-19-7	Acetic acid		(9056)
67-56-1	Methyl alcohol (Methanol)	8260B	
67-63-0	2-Propyl alcohol (Isopropanol; Propan-2-ol)	8260B	
67-64-1	2-Propanone (Acetone)	8260B	
67-66-3	Chloroform	8260B	
684-16-2	Hexafluoroacetone		8260B
71-23-8	n-Propyl alcohol (1-propanol)	8260B	
71-36-3	n-Butyl alcohol	8260B	
71-43-2	Benzene	8260B	
71-55-6	1,1,1-Trichloroethane	8260B	
72-20-8	Endrin	8081A	
74-83-9	Bromomethane	8260B	
74-87-3	Chloromethane	8260B	

Table 1. Priority Regulated Organic Compounds for Characterization in Support of the Regulatory Data Quality Objective (125 Compounds).
(Page 3 of 3)

CAS #	Constituent	SW-846 Method	Modified Method
75-00-3	Chloroethane	8260B	
75-01-4	1-Chloroethene	8260B	
75-05-8	Acetonitrile	8260B	
75-09-2	Dichloromethane (Methylene Chloride)	8260B	
75-15-0	Carbon disulfide	8260B	
75-21-8	Oxirane	8260B	
75-34-3	1,1-Dichloroethane	8260B	
75-35-4	1,1-Dichloroethene	8260B	
75-43-4	Dichlorofluoromethane		8260B
75-45-6	Chlorodifluoromethane		8260B
75-65-0	2-Methyl-2-propanol	8260B	
75-69-4	Trichlorofluoromethane	8260B	
75-71-8	Dichlorodifluoromethane	8260B	
76-13-1	1,2,2-Trichloro-1,1,2-trifluoroethane	8260B	
76-14-2	1,2-Dichloro-1,1,2,2-tetrafluoroethane	8260B	
76-44-8	Heptachlor	8081A	
78-87-5	1,2-Dichloropropane	8260B	
78-92-2	1-Methylpropyl alcohol(2-butanol)		8260B
78-93-3	2-Butanone	8260B	
79-00-5	1,1,2-Trichloroethane	8260B	
79-01-6	1,1,2-Trichloroethylene	8260B	
79-10-7	2-Propenoic acid		8270C
79-34-5	1,1,2,2-Tetrachloroethane	8260B	
8001-35-2	Toxaphene	8081A	
82-68-8	Pentachloronitrobenzene (PCNB)	8270C	
87-68-3	Hexachlorobutadiene	8270C	
87-86-5	Pentachlorophenol		8270C
88-85-7	2-sec-Butyl-4,6-dinitrophenol (Dinoseb)	8151A	
88-89-1	Picric acid		8330
92-52-4	1,1'-Biphenyl		8270C
95-47-6	o-Xylene	8260B	
95-50-1	1,2-Dichlorobenzene	8270C	
96-22-0	3-Pentanone		8260B
98-86-2	Acetophenone	8270C	
98-95-3	Nitrobenzene	8270C	

CAS# = chemical abstract service number.

Table 2. Inorganic Constituents of Potential Regulatory Concern.

CAS#	Cation	Constituent
7440-22-4	Ag	Silver
7429-90-5	Al	Aluminum
7440-38-2	As	Arsenic
7440-42-8	B	Boron
7440-39-3	Ba	Barium
7440-41-7	Be	Beryllium
7440-69-9	Bi	Bismuth
7440-70-2	Ca	Calcium
7440-43-9	Cd	Cadmium
7440-48-4	Co	Cobalt
18540-29-9	Cr	Chromium
7440-50-8	Cu	Copper
7439-89-6	Fe	Iron
7439-97-6	Hg	Mercury
7440-09-7	K	Potassium
7439-93-2	Li	Lithium
7439-95-4	Mg	Magnesium
7439-96-5	Mn	Manganese
7439-98-7	Mo	Molybdenum
7440-23-5	Na	Sodium
7440-02-0	Ni	Nickel
7723-14-0	P	Phosphorus
7439-92-1	Pb	Lead
7440-16-6	Rh	Rhodium
63705-05-5	S	Total Sulfur
7440-36-0	Sb	Antimony
7782-49-2	Se	Selenium
7440-21-3	Si	Silicon
7440-31-5	Sn	Tin
7440-25-7	Ta	Tantalum
7440-28-0	Tl	Thallium
7440-61-1	U	Uranium
7440-62-2	V	Vanadium
7440-33-7	W	Tungsten
7440-65-5	Y	Yttrium
7440-66-6	Zn	Zinc
7440-67-7	Zr	Zirconium
7664-41-7	NH ₄ /NH ₃	Ammonia/Ammonium

CAS#	Anion	Constituent
24959-67-9	Br	Bromide
16887-00-6	Cl	Chloride
57-12-5	CN	Cyanide
16984-48-8	F	Fluoride
7553-56-2	I	Iodine
14797-65-0	NO ₂	Nitrite
7697-37-2	NO ₃	Nitrate
14280-30-9	OH	Hydroxide
14265-44-2	PO ₄	Phosphate
14808-79-8	SO ₄	Sulfate

CAS# = Chemical Abstract Service number.

Table 3. Summary of Suggested Methods and Total Number of High Priority Analytes to Which the Method May Be Applied

Suggested Methods for High Priority Regulated Organic Analytes	Total Number of Analytes	Number of Higher Toxicity Compounds ⁽¹⁾
8081A, Organochlorine Pesticides by Gas Chromatography (GC)/Electron Capture Detector (ECD)	11	11
8082, Polychlorinated Biphenyls (PCBs) by GC/ECD	1 (All Aroclors)	1
8151, Chlorinated Herbicides by GC	1	1
8260B, Volatile Organic Analysis (VOA) by GC/Mass Spectrometry (MS)	77	7
8270C, Semivolatile Organic Analysis (SVOA) by GC/MS	31	9
8330, Nitroaromatics and Nitramines by HPLC ⁽²⁾	3	3
Suggested Methods for High Priority Regulated Inorganic Analytes	Total Number of Analytes ⁽³⁾	Number of Higher Toxicity Compounds
310.1, Hydroxide, Alkalinity by Titration ⁽⁴⁾	1 (5)	1
345.1, Iodide, Titration ⁽⁴⁾	1 (1)	10
350.3, Ammonia by Selective Ion Electrode with Double Standard Addition ⁽⁴⁾	1	0
6010B, Metals by Inductively Coupled Plasma (ICP) or 6020 ICP/MS	33 (92)	8
7470/7471A, Mercury by Cold Vapor Atomic Absorption	1 (1)	0
9010B, Cyanide by Dissolution of Complexed Cyanides, Microdistillation, Spectrophotometric ⁽⁵⁾	1 (4)	0
9056, Anions by Ion Chromatography	3 (44)	3

⁽¹⁾High toxicity compound rankings are documented and described in the Regulatory Data Quality Objectives (Wiemers et al. 1998).

⁽²⁾Modifications may vary for each listed analyte.

⁽³⁾Number in parenthesis "(1)" represent the number of contaminants covered by a particular method. For inorganic methods such as ICP 33 cations are analyzed representing ions from 92 compounds.

⁽⁴⁾EPA methods for *Chemical Analysis of Water and Wastes* (EPA 1995).

⁽⁵⁾ The cyanide method has been routinely performed on tank waste. The SW-846 method 9010B has been modified by the initial dissolution of complexed stable cyanides followed by microdistillation. The SW-846 method does not discuss how to deal with extremely complexed cyanides as this is not typically seen in soil and water and uses a larger distillation apparatus. The cyanide method includes a procedure for the dissolution of the insoluble $\text{Na}_{(2-x)}\text{Cs}_{(x)}\text{NiFe}(\text{CN})_6$ (nickel ferrocyanide) compounds found in some Hanford Site waste. If insoluble cyanide compounds are known, through process knowledge, to be absent in the samples, this method is not necessary and the Determination of Cyanide by EDTA/EN Dissolution Followed by Microdistillation and Spectrophotometric Analysis (HAS 1997b) should be used.

- Where two SW-846 methods are recommended for a single analyte, the multi-analyte method that would give the most reliable identification was selected. For example, if a gas chromatography (GC) method with flame ionization detector method and a GC/mass spectrometry (MS) method were both listed for the same analyte, the GC/MS method is selected because GC/MS methods confirm the identification of the analyte provided a standard is analyzed for calibration.
- For some analytes such as ammonia, EPA-approved methods for Chemical Analysis of Water and Wastes (EPA 1995) are suggested.

5.0 Method Detection Limit and Target Estimated Quantitation Limits

5.1 Requirement

To meet EQLs as specified in SW-846 methods.

5.2 Problem

- How to reach the SW-846 EQL in tank waste matrices while meeting ALARA, 10 CFR 835, and while addressing matrix problems such as high-salt concentrations.

5.3 Background

Two commonly used terms for defining sensitivity requirements are method detection limit (MDL) and estimated quantitation limit (EQL). These items describe two different properties of an analytical method and cannot be used interchangeably. The definitions of these terms from Chapter 1 of SW-846 are listed below. The equations for calculating the MDL and EQL are in Chapter 1 of SW-846.

Method Detection Limit—The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix type containing the analyte.

Estimated Quantitation Limit—The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL analyte concentration is selected as the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs in SW-846 are provided for guidance and may not always be achievable.

Before performing the analysis on tank waste samples, the laboratory(ies) must demonstrate its ability to meet water and soil MDLs that are listed in the SW-846 method as required by HASQARD. Each laboratory performs water MDL determinations using spiked water or analyte-free sand for each method at preset intervals that are based on HASQARD criteria as part of the QA/QC system in the laboratory. EPA has not established regular intervals for determining MDLs, however, industry practice is at least once per year. EPA indicates that an MDL should be established before analyzing the waste by the method in question.

The EQL is affected by:

- sample matrix,
- sample volume/mass used,
- final concentrate volume or final digested volume from sample preparation,
- amount introduced into the instrument for quantitation, and
- use of dry or wet weight for reporting solids data.

Each EPA method in SW-846 lists target EQLs in water, soil, or waste matrices. Water EQLs are lower than those in soil or waste. For various waste types, the methods list EQL multipliers relative to water or soil. The SW-846 methods stress that the EQL will differ by matrix and should be evaluated by matrix.

The high-salt concentrations, radionuclide concentrations, corrosive (basic) matrices of the tank wastes, and ALARA requirements may make it difficult to reach the EQLs published in SW-846 for waste. For example, in EPA method 8270C for the analysis of semivolatile organic analysis (SVOA) in soils and sediments containing low concentrations of organics, the EQLs range from 660 to 3,300 $\mu\text{g/kg}$ depending on the compound. For soils and sludges containing high levels of organic material (e.g., paraffin-hydrocarbon containing slurries) method 8270C recommends applying a factor of 7.5 to the soil/sediment EQLs. For non-water miscible waste, the same SW-846 method recommends that a factor of 75 be applied to the soil/sediment EQL, producing EQLs ranging from 49,500 to 247,500 $\mu\text{g/kg}$.

Consultation (Stromatt et al. 1993) with two laboratories that have experience in analyses of tank wastes indicates that the factor applied based on typical tank waste is likely to be 10 to 100 times the soil/sediment EQL in the methods. This is in the range of a factor of 75 in method 8270C. This logic is consistent for other methods. Given the large uncertainties related to analysis of the regulated organic analytes in the tank waste matrix, target EQLs in the range of those specified in SW-846 will be used as a basis for assessing the acceptability of the method's performance.

5.4 Method Validation Target Performance Acceptance Criteria

The EQLs from the SW-846 methods based on soil/sediment and respective factors for wastes will be used as target EQLs. For the analytes that have SW-846 EQL criteria, the goal is that the measured EQLs meet the SW-846 criteria. For single analytes with no EQLs listed in a specific SW-846 method, no special target EQL is required provided the analytes with EQL criteria for that method meet the target criteria for that method as specified in SW-846.

The following were agreed upon by DOE and Ecology in the Regulatory DQO discussions:

- The laboratory(ies) performing the sample analyses must perform the MDL and EQL determinations.
- The MDLs will be determined using spiked distilled deionized water or purified sand for solid matrix per requirements in SW-846 and HASQARD.
- EQL determinations must include the same preparation and analyses methods used for the actual analyses.
- Preliminary EQLs may be obtained using waste simulants. Determination of actual EQLs will be based on analysis of the use of liquid and solid tank wastes. EQLs will be reported for both liquid and solid (sludge) waste phases.
- If the target waste EQLs in the SW-846 method cannot be met, the participating laboratory(ies) will document the technical basis for the deviation. The DOE and Ecology chemists will be notified and Ecology, DOE, and laboratory staff will determine the next step in the process.
- After information is obtained from the treatment facility permit activities, the EQLs will be compared to the concentration levels associated with the treatment facility permit. Differences will be discussed among DOE and Ecology and an agreed upon approach will be established and documented as necessary.

6.0 Sample Holding Time and Storage Conditions Study

The holding time and storage conditions requirements for samples must be considered together because they are the technical components of sample handling that determine the overall fate and integrity of the field samples after collection. The technical aspects of each component are presented below. The recommended approach for studies addressing holding time and storage conditions follows the issue descriptions. The information that will be provided to support the approach integrates both the time and condition variables so that the maximum amount of information will be collected per waste sample volume.

6.1 Holding Time Issue

6.1.1 Requirements

Holding times as specified in SW-846 for aqueous and solid samples.

6.1.2 Problems

- Time required for sampling, transport, handling of highly radioactive tank waste samples in the laboratory, and analysis exceeds SW-846 holding times.
- The usefulness of archived samples is limited by SW-846 holding time requirements.

- Lack of data demonstrating how differences in holding times affect the compound's integrity in Hanford tank waste.

6.1.3 Background

Holding time limits have been established by regulatory agencies because of potential analyte loss by physical processes from the sample container, biodegradation, and chemical change after sampling. These factors are common to storage conditions and are further discussed in Section 6.2.3.

The sample holding time requirements for volatile organic analysis (VOAs), semi-volatile organic analysis (SVOAs), polychlorinated biphenyls (PCBs), pesticides, herbicides, mercury, hexavalent chromium, and select anions as specified in SW-846 are difficult to meet for Hanford tank wastes. The logistics of collecting samples from the tanks, transport to the laboratory, and processing the sample casks in the hot cells frequently takes more time than the holding times allowed by SW-846. Examples of holding times in the methods are 14 days for VOAs, and 7 days for extraction of SVOAs/PCBs/pesticides.

6.2 Storage Conditions Issue

6.2.1 Requirements

Meet storage requirements as specified in SW-846.

6.2.2 Problems

- Lower temperatures may irreversibly alter the physical form of the sample (salt precipitation).
- Storage temperature during transport and work in hot cells is difficult to control.
- Lack of data demonstrating how differences in storage conditions affect the compound's integrity in Hanford tank waste.

6.2.3 Background

Storage condition requirements guidance was published by regulatory agencies in an effort to diminish the extent of chemical and biological processes that degrade target analytes. A number of factors may affect the quality of the sample analyzed. Storage conditions that may affect sample data quality include:

- temperature,
- use of preservatives,
- exposure to oxidants (e.g., air),
- exposure to light, and
- sample container headspace and materials of construction.

A discussion of the SW-846 holding time and storage condition requirements and current sample handling practices and a description of potential impacts due to differences between requirements and practices is provided below. These parameters are subsequently addressed in the holding time and storage conditions study (Section 6.4).

Temperature

Cool temperatures and preservatives are used to slow down biological processes of analyte degradation and some types of chemical change. This is especially important for trace levels of organics and inorganics in dilute aqueous solution.¹

In general, the regulatory requirement for sample storage is 4°C or below for organic samples and anions, and room temperature (~21 to 27°C) for metals. At this time, the transport cask for radioactive samples is exposed to ambient temperature which can range from approximately -23 to +66°C. These temperatures are estimates based on typical weather conditions plus increases due to solar heating of plastic tents to cover sampling areas. The casks are used during transport and storage at the sample site. Original samples and sub-samples aliquoted after compositing and before extraction are held in plastic or glass bottles at room temperature (~21 to 27°C). Organic extraction removes a majority of radionuclides from the organic material so that after extraction, the solutions containing the organic analytes of interest can be stored in glass vials at 4°C.

Methods for many of the anions of interest also require storage at 4°C followed by analysis as soon as possible. These anions include cyanide, chloride, nitrate, nitrite, sulfate, sulfide, bromine, fluoride, iodide, ammonium, hydroxide, and phosphate. Inorganic anions are not intentionally cooled after sample preparation as the extracted samples remain highly salt saturated and cooling may cause precipitation of the samples. Past experience has indicated that warming of a cooled (4°C) tank waste sample will not always result in all the precipitate returning to solution.

For implementation of the holding time and storage conditions study, the sample casks will be maintained within the range of normal temperatures for the time of year when the samples are collected (from seasonal weather records). The ambient temperature outdoors will be noted at the time of collection and daily temperature highs while casks are outside will be reported. The temperature of the hot cell during compositing/extrusion will be reported.

Exposure to oxidants

The sampling process frequently allows oxygen to contact the sample potentially in sufficient quantity to oxidize analytes. For nonvolatile species, the use of preservatives establishes a sample environment where these imposed conditions do not impact the oxidation state of the analytes. The oxidative nature of the tank matrices minimizes the concern about the possibility of changing the reduction and oxidation potential of the sample due to exposure to air. No preservatives will be used during implementation of the holding time and storage conditions study.

¹ Biological processes are likely of little concern with Hanford tank waste samples because of their radioactive constituents and high alkalinity. The planning basis for the holding time and storage conditions study does not address biological processes or the use of preservatives.

Exposure to light

Control of exposure to light stops photolytically catalyzed reactions in some classes of organic compounds (polycyclic aromatic hydrocarbons [PAHs], in particular). The samples are collected in bottles or core barrels and can be stored in the dark minimizing photolytic reactions.

Sample container materials and handling

The physical loss of analytes occurs from the thermal expansion and contraction of the sample material caused by temperature fluctuations. These expansion and contraction cycles can result in loss of gas-phase constituents due to the volatilization of gas into the headspace of the sample containers. The extent of this problem depends on:

- pressure tightness of the sample containers,
- amount of headspace in the containers,
- vapor pressure of the target analyte(s),
- range of temperature change,
- phase of the sample (liquid, slurry, solid),
- storage time before preparation,
- potential loss during extrusion or transfer of sample from grab sample, and
- high ventilation rate in hot cell and higher temperature.

Volatile analytes are particularly vulnerable to loss in sample handling, extrusion, and compositing. Industry practice for collection of water samples requires collection in a container such as a bailer for groundwater and the sample is poured into the bottles for storage. Loss of volatiles is generally accepted using this approach. For liquid samples from the tank, a weighted plastic bottle is lowered into the tank and stoppered. The sample can then be poured into the VOA vials.

Industry practice for soil coring acknowledges loss due to removal of material. In industry either soil samples are collected or in situ soil gas is monitored. In situ analysis within the waste is not possible, therefore, coring of the waste must be done.

Two options for removal of samples from cores are used for soil sampling. Either the core is capped or sealed with plastic and tape, shipped to the laboratory, and the laboratory removes the sample for volatiles from the end of the core. The laboratory typically does this with a small diameter clean cork borer and places the soil in a wide-mouth jar with minimal headspace or places the material directly in a VOA vial for analysis. The other option is that the core is opened (e.g., split spoon) or extruded in the field and aliquots of soil placed in glass containers without headspace. A similar situation occurs in the collection of cores in the tanks. As the cores are extruded, the volatile sample must be selectively removed before compositing. Because compositing requires stirring, the waste used for volatile analysis must be removed before mixing.

Generally, sample handling techniques during collection of tank waste are similar to typical environmental sample collection methods. Some losses, particularly of volatiles, are unavoidable and accepted as such in method guidance.

6.3 Target Maximum Holding Times

The initial target maximum sample holding time under ambient temperature conditions for all samples collected from the source tanks for compliance purposes are listed in Table 4. The initial target maximum holding times in Table 4 are based on current Hanford Site practices and are based on the assumption that the methods listed in Table 3 will be implemented.

Table 4. Initial Target Maximum Tank Waste Sample Holding Times.

Constituent	Initial Target Maximum Holding Time (days)				Current RCRA Holding Time (days)	
	Grab		Core		Aqueous	Solid
	Aqueous	Solid	Aqueous	Solid		
Volatile organics (collection to analysis)	22	22	25	25	14	14
Semivolatile organics/polychlorinated biphenyls/ pesticides/herbicides						
a. collection until extraction	22	34	16	34	7	7
b. extraction to analysis	40	40	40	40	40	40
Mercury	45	45	45	45	28	28
Metals, including total Cr ⁽¹⁾	180	180	180	180	180	180
Ammonia	45	45	45	45	28 if preserved	NS
Iodide	45	45	45	45	ASAP	NS
Cyanide	45	45	45	45	14 if preserved	--
Sulfide	45	45	45	45	7	NS
Hydroxide	45	45	45	45	14	NS
Picric	45	45	45	45	NS	NS
Anions	45	45	45	45	ASAP	ASAP
Cr ⁺⁶	Analyze total Cr				24 hr	1 month to extraction, 4 days after extraction

⁽¹⁾The EPA currently requires a 24-hour holding time for reliable hexavalent chromium measurement in aqueous samples. DOE acknowledges that the 24-hour holding time for sample preparation cannot be met. There will be no effort to measure hexavalent chromium as a discrete analyte in this characterization activity. This analyte participates in very complex oxidation-reduction reactions as part of the trivalent-hexavalent chromium redox pair. For the Regulatory DQO (Wiemers et al. 1998), total chromium will be measured by inductively coupled plasma (ICP). Assumptions regarding the oxidation state of chromium in the waste are the responsibility of the data user.

ASAP = as soon as possible. NS = not specified.

The maximum holding times reflect the best achievable schedule for both core and grab samples and consider the following:

- Transfer of samples from tank to cask.
- Transport of cask to laboratory (consider impact of space at the lab to receive casks).
- Loading samples into hot cell from cask.

- Time related to sample processing including:
 - Homogenization, compositing, and sub-sampling of core segments for SVOA, inorganic, and radioactive parameters as appropriate.
 - Sample load out and hot cell cleanup between samples.
- Sample preparation for metals, select anions, SVOA, and pesticide/herbicide analysis (including cleanup).
- Sample analysis (and re-analysis if needed).

Appendix B provides the detailed time assessment of each step of the sample collection and analysis process for collection of grab and core samples and shows how the times presented in Table 4 were derived.

6.4 Holding Time and Storage Conditions Study

Controlled, laboratory-scale tests will be used to evaluate the loss of constituent classes by testing solid and liquid tank waste spiked with representative target analytes. These tests will establish the baseline from which the impact of the proposed maximum holding times and storage conditions can be assessed. Data from this study may also be used to infer impacts due to current archive practices and may allow the use of archive samples for analysis of regulated compounds under conditions agreed to mutually by DOE and Ecology.²

The holding time and storage conditions study will be based on the work of Maskarinec and Bayne (Maskarinec and Bayne 1996), Bayne et al. (1994), and West et al. (1996). The study uses empirical data coupled with mathematical models and statistics to determine how long a sample can be held with reasonable assurance that the measured concentration can be used to predict the original concentration. This study will be performed for each of the constituent groups whose maximum holding time exceeds the RCRA requirement. The following text summarizes the general approach. It is anticipated that refinements of the proposed approach will be addressed in test plans to be prepared by the participating laboratories and approved by DOE and Ecology.

Test samples

The holding time and storage conditions study will be performed on both a liquid waste sample and a solid waste sample. It is preferable that waste from the same tanks used in the methods validation step (refer to Section 3.0) be used in the holding time and storage conditions study. Use of the same waste matrix provides added confidence in successful implementation of the analytical methods.

Test matrix

For each sample matrix, solid waste and liquid waste, four sets of samples will be prepared for each analytical method:

²DOE has agreed to begin analysis of archive samples for selected regulated compounds before completion of the holding time and storage conditions study. Any data collected from archive samples will be flagged to indicate that SW-846 holding times and storage conditions were not satisfied.

1. One set of three spiked samples of waste will be analyzed immediately after spiking (control sample) to verify homogeneity of the spike and to establish the initial concentration.
2. One set of three spiked samples of waste will be maintained at 4°C and analyzed periodically (at least once) and at the end of the specified holding times listed as the RCRA holding times in Table 4 to evaluate results at RCRA requirements.
3. One set of three spiked samples will be held at ambient temperature and analyzed periodically (at least once) and at the end of the DOE proposed maximum holding time in Table 4 to evaluate proposed holding times. Ambient temperatures will be reported.
4. One set of three spiked samples will be maintained under conditions similar to the maximum field ambient conditions (at highest estimated storage temperature) for samples in casks. These field simulation samples will be analyzed periodically (at least once) and at the proposed maximum holding time in Table 4.

The first set is time zero and is the control against which all other results are compared. The second set will demonstrate the best available recovery under the maximum allowable RCRA holding time for samples. The data from the third and fourth sets will demonstrate the impact to the DOE holding time under the warmest ambient storage conditions. This will assist in understanding the data from tanks sampled and analyzed at different times of the year. Data from periodic analyses will lead to understanding trends in analyte behavior under the various storage conditions. Extended holding times may be proposed to address the use of archive samples.

Sample handling

This approach assumes that the tank waste samples will be spiked in a manner described in Maskarinec and Bayne (1996). The reader is referred to the paper for details of spiking and analysis. Samples must be prepared for VOAs, SVOAs, pesticides and herbicides, PCBs, metals, and anions. The liquid tank waste for VOA analysis will be placed in a Tedlar bag, spiked with standards in methanol, mixed, aliquoted to 40 mL VOA vials, and analyzed by purge and trap GC/MS. Using the Tedlar bag to mix spiked waste promotes uniform concentrations between VOA vials without loss of volatiles. The SVOAs, pesticides and herbicides, PCBs, metals, and anions in liquids will be spiked with the appropriate analyte in a water soluble matrix (either water or methanol), mixed and aliquoted to separate sample containers. Glass containers with Teflon lids will be used for organics and polyethylene bottles will be used for metals and anions. No preservative will be used.

Solids for VOA analysis will be spiked into VOA vials to which solid is added with organic standards on the day the holding time and storage conditions study begins. These sealed containers will be mixed by vortex. Samples will be analyzed by purge and trap GC/MS. The aliquots of sample for volatiles will be collected before compositing. After spiking and mixing the waste, three samples will be taken from the waste to verify that the spike is properly mixed with the waste.

Salt formation can occur after samples have cooled to room temperature. Cooling may occur during transport and storage in the cask, during holding and preparation for analysis, and during aging which will occur in the holding time and storage conditions study. The performing laboratory's test plan must provide sufficient detail to describe how the precipitated solids will be managed. A consistent approach must be presented to prevent problems in the interpretation of the data in the future.

Target analyte spikes

The target analytes spiked to the samples for each analytical method will be representative of the range of vapor pressures of the high priority analytes listed in Table 1. Where possible, they will also be representative of the chemical compound classes (alcohols, halocarbons, aromatics, PAHs, PCBs, etc.).

The span in volatility will establish the relationship between vapor pressure of the analytes and the variety of holding times, storage conditions, and container types. The range of chemical classes will be important to determine if there is preferential adsorption of the compounds to the solid phase materials in the wastes. This is important in understanding the impact of the holding times and storage conditions on the adsorption of the analytes to the solid phase materials and other physical and chemical behaviors that may impact how representative tank waste data are in comparison to tank waste inventories.

Data Interpretation

A critical concentration (CC) will be determined on the first day of the holding time and storage conditions study. The CC is the concentration below which there is a 5% chance that a measured concentration will be observed (due to measurement error). As the concentration decreases with time, the measured concentration for an individual sample will be below the CC. The CC is based on calculating the lower 95% confidence limit of the initial measurement immediately after addition of the analyte to the matrix. This means that one will measure a concentration at or above the CC 95% of the time, provided one could measure the analyte immediately upon preparation of the spiked sample. The Practical Reporting Time (PRT) is defined as the day when there is a probability of 15% (an increase of 10%) that the measured analyte will be below the CC. An alternate definition is that the PRT is the time that one has an 85% or better chance of finding a concentration that is equal to or above the CC.

The PRTs are calculated using the following procedure: (1) an approximating model representing concentration versus time is fitted to the data by the method of least squares; (2) the one-sided 95% prediction limit for time zero is located for the approximating model (this limit is the CC); (3) a horizontal line is drawn from the CC until it intersects with the one-sided 85% prediction limit; and (4) a vertical line is drawn from this intersection (i.e., of the CC and the one-sided 85% limit) to the time axis. This final intersection with the time axis is the PRT.

The PRT depends on the mathematical model used to approximate the degradation of an analyte concentration and the precision (standard deviation) of the analytical measurement variation. For a given analyte, large measurement variations will give longer PRTs than those for smaller measurement variations. This result occurs because it is more difficult to detect changes in the initial concentration with larger measurement variation. The chance that a measured analyte is below CC will increase as an environmental sample is held longer past the PRT. The rate of this probability increase reflects the consequences of missing the PRT.

The PRTs depend on approximating models. Five approximating models were evaluated in the published holding time study. These models represent five different kinetic reaction models (see Figure 5 of Maskarinec and Bayne [1996]).

- Zero-order
- First-order
- Log-term
- Inverse-term
- Cubic-spline.

Seventy-three percent of the experimental cases tested by Maskarinec and Bayne fit the zero- and first-order models. Eighteen percent of the experimental cases tested fit the log- and inverse-term and 9% fit the cubic-spline model.

Assuming that the zero- or first-order model applies, a simple study will be conducted. Triplicate measurements are run at the initial and 'ending' time and a minimum of one additional interim time. In this case the ending times are the proposed maximum holding times in Table 4. From this experiment the slope and measurement standard deviation can be estimated. The PRT will be estimated from the polynomial equation in Maskarinec and Bayne (1996). If the PRT is longer than the proposed holding time in Table 4, then proposed holding time is sufficient. A more detailed test using the log, inverse, and cubic models will be performed and or adjustments, alternative sample collection, preparation, and analysis methods may need to be considered if the PRT is shorter than the maximum holding times.

Reporting

Status reports on the holding time and storage conditions study will be provided from DOE to Ecology on a regular, pre-agreed schedule. This schedule will be established at the time of test plan review. DOE and Ecology will determine if the holding time and storage conditions study results indicate that constituent concentration can be predicted under tested conditions. If prediction of the compound's concentration is not validated by the holding time and storage conditions study, DOE and Ecology will determine if it is possible to improve estimation of the compound's concentration by making reasonable changes in the sample collection, transportation, and storage processes. If potentially beneficial changes can be identified, the revised process conditions will be tested using similar methodology. If a better, more cost-effective testing scenario can be identified, it will be used.

7.0 Quality Control Procedures and Appropriate Criteria

7.1 Requirement

Bias and accuracy as defined in SW-846.

7.2 Problem

Matrix interference in the waste material.

7.3 Option

Use bias and accuracy as specified in SW-846 and use data validation processes to flag problematic data.

7.4 Criteria

Matrix spikes and surrogates as defined in SW-846 will be used to assess bias. Bias is sometimes called accuracy. SW-846, Chapter 1, defines bias as:

Bias: *The deviation due to matrix effects of the measured value from a known spiked amount. Bias can be assessed by comparing a measured value to an accepted reference value in a sample of known concentration or by determining the recovery of a known amount of contaminant spiked into a sample (matrix spike).*

The matrix spike compound recovery listed in the appropriate SW-846 methods will be used as the initial advisory limits. For analytes with no specified bias in the SW-846 methods, no additional criteria will be used. Spike recoveries for organics vary by analyte and by method. Spike recoveries for metals and anions are 75 to 125% for most methods. For non-SW-846 analytes such as ammonia and hydroxide, the typical accuracy specified for the metals methods of 75 to 125% will be used.

Precision: *The agreement among a set of replicate measurements without assumption of knowledge of the true value. Precision is estimated by means of duplicate/replicate analyses. These samples should contain concentrations of analyte above the MDL, and may involve the use of matrix spikes "duplicates or sample duplicates". The most commonly used estimates of precision are the relative standard deviation (RSD) or the coefficient of variation (CV), and the relative percent difference (RPD) when only two samples are available.*

Duplicates and matrix spike duplicates are used to assess precision. The SW-846, Chapter 1, definition will be used for precision. The RPD between two sample duplicates is used or the RSD is used if three or more samples from the same location are evaluated.

The precision for organic methods varies depending on the analyte and method and is specified in each method. For inorganic methods, the RPD is typically specified as $\pm 20\%$. For methods such as hydroxide or ammonia that are not part of SW-846, the precision limits as specified in SW-846 of $\pm 20\%$ RPD will be used. This precision specification is based on current industry practice that has adapted SW-846 criteria for common non-SW-846 anions.

The precision is defined in SW-846 Chapter 1 and is evaluated for three or more samples from the same location (e.g., triplicates), RSD, or coefficient of variance. For organic analyses that have triplicate or more results, the standard deviation will be calculated and used in any tables that provide an estimate of precision (e.g., SW-846 method, 8270C, Table 7). When triplicate samples are available, the RSD will be used to assess the data for the uncertainty. For those methods that do not have specified RSD or tables such as those presented in 8270C, Table 7, the RPD will be calculated from the two samples with the greatest difference and will be compared to SW-846 criteria.

7.5 Applying Bias and Precision to Hanford Tank Samples

The matrix spikes and duplicates must be taken through sample preparation and analysis as appropriate. For example, no preparation is needed for the titration for hydroxide, but sample preparation is appropriate for organic SVOAs. The following additional QA/QC criteria are required:

- Conformance with both SW-846 and HASQARD requirements for analytes listed in the SW-846 methods.
- For analytes that are not listed in SW-846 methods, but are analyzed by SW-846 methods, the accuracy and precision will be measured and reported per SW-846 method.
- Use matrix spikes that are held at similar temperatures and times as tank waste samples.
- Continue use of laboratory control samples processed alongside the tank waste samples to verify laboratory method control.
- Use data validation approaches and data flags to clearly show where volume/mass limitations restrict the use of matrix spikes, matrix spikes duplicates, laboratory duplicates, and re-analysis (if needed).
- Data obtained for Hanford tank samples will be reviewed periodically to establish new recovery control limits for a given matrix (i.e., solids and liquids), as needed.

8.0 Conclusion

Radiation levels, salt concentration, and the oxidizing nature of the waste dictates modifications to the SW-846 methods. Modified methods will be used to meet target EQLs and QC currently in SW-846. Method modifications will be validated per SW-846 and HASQARD and will be documented consistent with WAC 173-303-910. The affect of modifications to holding times and storage conditions will be evaluated using techniques developed by Maskarinec and Bayne (1996). After validating the methods and performing the holding time study on a minimum of two Phase 1 candidate feed souce tank wastes, DOE and Ecology will assess:

- whether different methods are needed,
- whether holding time/storage conditions should be altered,
- whether the high priority analyte list should be refined, and
- which additional tank waste needs to be characterized.

9.0 References

10 CFR 835. "Department of Energy, Occupational Radiation Protection." *Code of Federal Regulations*, as amended.

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Appendix A

Regulations for Radiation Protection for Workers and As Low As Reasonably Achievable

A1.0 As Low As Reasonably Achievable

A1.1 Requirement

Follow the as low as reasonably achievable (ALARA) principles of 10 *code of Federal Regulations* (CFR) 835, "Department of Energy, Occupational Radiation Protection," when handling waste.

A1.2 Problem

The maximum volume/mass of a sample that can be safely handled under ALARA may be less than allowed by the US Environmental Protection Agency (EPA) methods.

A1.3 Background

This section outlines the basics of the regulatory requirements and ALARA process, its affect on the volume/mass of sample used, and the handling of samples.

The following is the applicable regulatory requirements for radioactive waste:

10 CFR 835.202 Occupational exposure limits for general employees.

(a) The occupational exposure to general employees resulting from DOE activities, other than planned special exposures under Sec. 835.204 and emergency exposure situations under Sec. 835.1302, shall be controlled so the following annual limits are not exceeded:

- (1) A total effective dose equivalent of 5 rems (0.05 sievert);
- (2) The sum of the deep dose equivalent for external exposures and the committed dose equivalent to any organ or tissue other than the lens of the eye of 50 rems (0.5 sievert);
- (3) A lens of the eye dose equivalent of 15 rems (0.15 sievert); and
- (4) A shallow dose equivalent of 50 rems (0.5 sievert) to the skin or to any extremity.

(b) All occupational exposure received during the current year shall be included when demonstrating compliance with Sec. 835.202 (a).

(c) Exposures from background, therapeutic and diagnostic medical radiation, and voluntary participation in medical research programs shall not be included in dose records or in the assessment of compliance with the occupational exposure limits.

ALARA is defined as:

The "approach" to radiation protection to manage and control exposures (both individual and collective) to the work force and to the general public to levels as low as is reasonable, taking in to account social, technical, economic, practical, and public policy considerations. "ALARA is not a dose limit but a process" which has the objective of

attaining (and maintaining, if achieved) doses as far below the applicable limits of 10 CFR 835 as is reasonably achievable (HNF-PRO-1629).

ALARA is implemented by evaluation and measurement of the dose to the worker, evaluating what could be done to decrease the dose below regulatory controls, and determining whether it is practical, cost effective, and efficient to implement these controls. In the analytical laboratory, samples such as tank waste are received that cannot be handled without proper shielding. Hot cells and gloveboxes as appropriate are used to provide necessary shielding. Whether the sample will be handled in a hot cell, glovebox, hood, or at the laboratory bench is based on the allowed worker dose, the sample handling logistics, and the technical requirements.

Many of the current SW-846 methods typically use volumes of 1 L and sample masses of 30 g. These volumes and masses may exceed the allowable sample sizes determined by regulations and ALARA. The glassware and equipment needed for analysis may or may not fit inside the openings of the hot cell/glovebox. Manipulation of intricate glassware may not be possible with manipulators.

Typically laboratories manage ALARA in one of two ways:

1. Calculating every sample individually requires monitoring each aliquot of each sample separately. There are many (10 to 20) aliquots per sample. When calculating the maximum allowed volume/mass for each sample, the variance of particles in the matrix may not be accounted for. Calculating each sample may allow usage of either too large a volume or too small depending on the area of the survey of the sample. This means that each time an analyst held a sample, qualified health physics technicians are required to be present to perform the calculations. This doubles the number of staff and does not provide effective radiological control. Sample through-put drops significantly using this approach.
2. The laboratory establishes administrative control levels that are based on numerical dose constraints established at a level below the regulatory limits to control and reduce individual and collective doses. Conformance with control levels is monitored through use of dosimeters and procedural controls. For each method and potentially radioactive sample matrix, the laboratory establishes a sample volume that will not exceed the administrative controls for radioactivity. The volume/mass is evaluated using the ALARA process. For a given matrix, such as tank waste, the volumes/masses are preset based on these initial calculations and if the actual dose readings exceed criteria, the analyst must notify health physics management for a special assessment. Sample volumes for analysis are calculated for each matrix type and method, under specific handling conditions and not for each individual tank sample. Calculating each individual tank sample does not take into account the variance by particle of the waste matrix and is very inefficient for the laboratory. Changing the volume/mass for each sample aliquot increases the risk that an analyst exceeds radiological exposure criteria.

A1.4 Selected Approach

Worker exposure regulations will be met and ALARA will be done by the participating laboratory(ies) with the goal of achieving the target estimated quantitation limits (EQLs) and quality control (QC) criteria. The ALARA implementation will be documented in the test plan and available for US Department of Energy and Washington State Department of Ecology review. Performance criteria for the EQLs and QC will be specified and the laboratory(ies) will adjust analysis parameters to achieve target EQLs and QC criterion. Failure to meet the target EQLs and QC must be technically justified and documented by the participating laboratory(ies).

A2.0 References

10 CFR 835. "Department of Energy, Occupational Radiation Protection." *Code of Federal Regulations*, as amended.

HNF-PRO-1629. *ALARA Administrative Control Levels*. Rev. 0. Fluor Daniel Hanford, Richland, Washington.

Appendix B

Support Information for Holding Times

Tables B.1 and B.2 provide detailed time assessment of each step of the sample collection and analysis process for collection of grab and core samples. Tables B.1 and B.2 show how the times in Table 4 were derived. The times presented in Table B.1 and Table B.2 are based on the radiological handling and transportation from the tanks to the laboratories and are for information only and are not to be used to assess the data.

Table B.1. Holding Times for Grab Samples from Tank Waste for Volatiles and Semivolatiles. (Page 1 of 2)

Process Step	VOA ⁽¹⁾ (24 hr days) (assumes three 120 ml bottles: one bottle from each of three levels in tank, ambient storage conditions, assumes NO compositing for volatiles)			SVOA ⁽²⁾ (24 hr days) (assumes nine 120 ml bottles: three bottles from each of three levels in tank, ambient storage conditions, assumes compositing)		
	Original Input	Normal/Standard Operations	Maximum Required Time	Original Input	Normal/Standard Operations	Maximum Required Time
a. Transfer of samples from tank to bottle and bottle to cask, transport of cask to laboratory	2	2	3	3	3	4 (6.2)
b. Laboratory receipt of cask (consider impact of laboratory to receive case, and limited number of clean casks). Allow for time to sit in laboratory before loading into hot cell	1	1	2	3	2	3 (4.4)
c. Load samples into hot cell from cask, remove sample (VOAs extracted at this step)	2	1	2	3	1	2
Clean up after extraction		1	2			
Ship to low-level laboratory for analysis ⁽³⁾		1	1			
d. Time from step c to analysis of VOA ⁽³⁾	3	2	4	not applicable		
Total volatile holding time from collection to analysis	8	8	14 (22) days counting weekends	not applicable		
e. Time to composite, homogenize, separate solids from liquids for extraction (assume done in hot cell)				3	2	3
Load samples out of hot cell					1	1
f. Time to extract ⁽⁴⁾				3	3	6

Table B.1. Holding Times for Grab Samples from Tank Waste for Volatiles and Semivolatiles. (Page 2 of 2)

Process Step	VOA ⁽¹⁾ (24 hr days) (assumes three 120 ml bottles: one bottle from each of three levels in tank, ambient storage conditions, assumes NO compositing for volatiles)			SVOA ⁽²⁾ (24 hr days) (assumes nine 120 ml bottles: three bottles from each of three levels in tank, ambient storage conditions, assumes compositing)		
	Original Input	Normal/Standard Operations	Maximum Required Time	Original Input	Normal/Standard Operations	Maximum Required Time
Clean up samples after extraction						
Ship to low-level lab for analysis ⁽³⁾					1	1
Total SVOA (pesticide/PCB/herbicide/GC/MS) holding time from collection to beginning of extraction				15	14	22 (34) days with weekends

⁽¹⁾VOA = volatile organic analysis, SVOA = semivolatile organics analysis.

⁽²⁾For planning holding times only, SVOA includes 8270 type extraction, for 8082 and 8081.

⁽³⁾Extracts would be shipped to low-level laboratory for analysis after extraction.

⁽⁴⁾The time to analyze and extract may be altered by mutual agreement from DOE and Ecology after evaluation of the final steps for analysis. The current times are based on current SW-846 VOA and SVOA, pesticide, and PCB procedures.

Table B.2. Holding Times for Core Samples from Tank Waste for Volatiles and Semivolatiles.

Process Step	VOA ⁽¹⁾ (24 hr days) (assumes three 120 ml bottles: one bottle from each of three levels in tank, ambient storage conditions, assumes NO compositing for volatiles)			SVOA ⁽²⁾ (24 hr days) (assumes nine 120 ml bottles: three bottles from each of three levels in tank, ambient storage conditions, assumes compositing)		
	Original Input	Normal/Standard Operations	Maximum Required Time	Original Input	Normal/Standard Operations	Maximum Required Time
a. obtain core and transport to laboratory	2	3	4	2	3	4
b. Laboratory receipt of core. Allow for time to sit in laboratory before loading into hot cell.	3	2	3	3	2	3
c. Load samples into hot cell from cask, remove sample, extrude one segment for volatiles at three different levels in tank	2	2	3	2	2	3
Clean up after extraction		1	1	not applicable		
d. Time from step c to analysis of VOA ⁽³⁾	3	3	5	not applicable		
Total volatile holding time from collection to analysis	6	11	16 (25) days counting weekends	not applicable		
e. Time to extrude, composite, homogenize, separate solids from liquids for extraction (assume done in hot cell)	not applicable			4	2	4
Load samples out of hot cell					1	1
f. Time to extract ⁽³⁾	not applicable			3	2	4
Clean up samples after extraction					1	2 (3.1)
Total SVOA (pesticide/PCB/herbicide/GC/MS) holding time from collection to beginning of extraction	not applicable			14	13	21 (34) days with weekends

⁽¹⁾VOA = volatile organic analysis, SVOA = semivolatile organics analysis.

⁽²⁾For planning holding times only, SVOA includes 8270 type extraction, for 8082 and 8081.

⁽³⁾The time to analyze and extract may be altered by mutual agreement from DOE and Ecology after evaluation of the final steps for analysis. The current times are based on current SW-846 VOA and SVOA, pesticide, and PCB procedures.

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